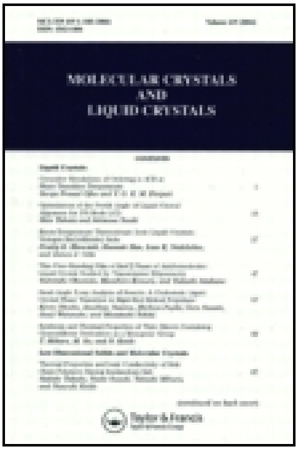

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Singlet and Triplet Energy Transfer in Tetracyanobenzene-Biphenyl Crystals

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Singlet and Triplet Energy Transfer in Tetracyanobenzene-Biphenyl Crystals

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Singlet and triplet excitonic energy migration in mixed-stack charge-transfer crystals of tetracyanobenzene-biphenyl (TCNB-B) doped with anthracene (10^{-4}–10^{-2} M/M) have been studied within temperature range 5–300 K by using optical, spectroscopic and kinetic techniques. It has been found, that the motion of excitons is thermally activated with the activation energies of 450 ± 60 and 550 ± 60 cm^{-1} for the singlet and triplet excitons, respectively. The later value differs from the activation energy in undoped TCNB-B crystals (where it is 360 ± 60 cm^{-1}) and suggests that doping with anthracene perturbs the host crystal lattice.

Keywords: Charge-transfer crystals; energy transfer; fluorescence; delayed fluorescence

PACS code: 33.50

1. INTRODUCTION

Excitation energy transport (exciton migration) is an inherent property of molecular crystals and has been studied in great detail for anthracene, naphthalene and other systems [1]. Our knowledge [2, 3] about energy transfer processes in mixed-stack charge-transfer (CT) crystals is however minor and still requires an experimental verification. There are two interesting aspects, the dimensionality of migration and possibility of self-trapping, which are related to a peculiar crystal structure and to a redistribution of the electronic charge in the excited states. Mixed-stack CT crystals are build of stacks of alternating donor and acceptor molecules, where the molecular planes are approximately parallel, thus indicating highly anisotropic, one-dimensional (1D) energy migration. Excitation of the lowest excited singlet

(S_1) or triplet (T_1) states of such crystals induces partial transfer of an electronic charge from a donor to an acceptor molecule and creation of a ionic pair within the host, non-ionic crystal lattice. This should result in attraction of donor and acceptor molecules leading to some relaxation of the lattice energy and finally, in self-trapping of the excitation at low temperatures.

In the present paper, we study the process of energy migration and exciton self-trapping in tetracyanobenzene-biphenyl (TCNB-B) crystals. TCNB-B crystals were already studied by EPR [4–9], zero field ODMR [10] and optical [9,11–14] techniques. From the previous studies we know, that both, S_1 and T_1 electronic states of TCNB-B have a high contribution of the CT electronic configuration, approaching full transfer of electron from the donor to the acceptor molecule for the S_1 state [2] and the CT character of 0.54 for the T_1 state [4]. The activation energy of mobility of singlet excitons was found to be 300 cm^{-1} [13] and that for triplet excitons-700 [4] and 250 ± 80 cm^{-1} [15] from the EPR studies and 360 ± 60 cm^{-1} [14] from the recent optical kinetic analysis. The previous studies indicated that the activation energy of excitonic migration in TCNB-B crystals is very sensitive to the crystal preparation procedure [4, 15]. To go deeper into this problem in the present work we study the energy migration in TCNB-B crystals doped with anthracene (A). A is an electron donor, which creates deep, TCNB-A, singlet and triplet traps acting as sensors for the energy transfer. The aim was to study activation energies and to estimate the hopping times for the singlet and triplet excitonic transfer.

2. EXPERIMENTAL

B and A were purified by zone-refining, TCNB was recrystallized from ethanol and next, vacuum sublimed. Crystals of TCNB-B with different concentrations of A were grown from acetone solution. The dopant concentration was estimated spectrophotometrically at room temperature, by dissolving the crystals in toluene and measuring the absorbance and fluorescence spectra. The procedure is similar to that already presented in ref. [16,17].

Spectroscopic studies within the 5–300 K temperature range were done with the experimental set-up described already in ref. [14,16,17]. Fluorescence, phosphorescence and delayed fluorescence spectra were measured by using a Parker-type disc-chopper phosphorimeter. Decays of fluorescence were measured by "time-correlated" single photon counting technique with a Coherent 700 dye laser pumped by a mode-locked Anthares 76-YAG laser and a Hamamatsu R28090-07 microchannel plate. Time resolution of this set-up is about 50 ps. Decays of delayed fluorescence were obtained by using 337 nm light pulses emitted by a home-made nitrogen laser which operated in synchronization with the phosphorimeter disc-chopper, cutting off an intense prompt fluorescence. Transients, over a period of 5 ms, were accumulated with the aid of a Stanford SR430 multichannel scaler. Delay time between a laser pulse and opening of the disc-chopper was about 80 μs.

3. RESULTS AND DISCUSSION

3.1. Singlet Energy Transfer

Fluorescence spectra at 5 K of TCNB-B crystals doped with different concentration of A are shown in Figure 1. The shape of the spectra clearly confirms the prediction that molecules of A replace the donor, B, and form CT complexes of TCNB-A in the host crystal lattice. The spectra of doped crystals (b–e) are composed of two, overlapping components, one corresponding to the host TCNB-B (a) and second, to the TCNB-A trap (f). The trap fluorescence spectrum has the onset at 17800 cm^{-1} and two maxima, at 17200 and 15700 cm^{-1} (see Fig. 1f). This spectrum is shifted to lower energy as compared with the corresponding fluorescence band of single TCNB-A crystals (onset at $\approx$ 19000 cm^{-1}, [18]) and as compared with the fluorescence band of TCNB-A trap in crystals of TCNB-naphthalene (onset at 18950 cm^{-1}, [19]) and TCNB-2,3dimethylnaphthalene (onset at 18400 cm^{-1}, [17]). With increasing dopant concentration a contribution of the host fluorescence (observed in the spectral range 18000–22500 cm^{-1}) is decreasing at the cost of increasing contribution of the sensitized guest (trap) fluorescence (observed below 17800 cm^{-1}).

In TCNB-B crystals doped with A, the intensity of the host fluorescence relative to that of the guest fluorescence decreases with increasing temperature above 100 K. Such a behavior reflects temperature dependence of the singlet energy transfer.

Decays of the host fluorescence (observed at 21700 cm^{-1}) are non-exponential at nearly all studied temperatures – see Figure 2. Only at lowest temperatures (5–60 K) and small dopant concentrations of the host fluorescence decays can be well approximated by the mono-exponential dependence, with the decay time of 100 ns. These decays become continuously shorter with increasing temperature above 60 K, as a consequence of the host → guest energy transfer. Decays of the guest fluorescence (observed at

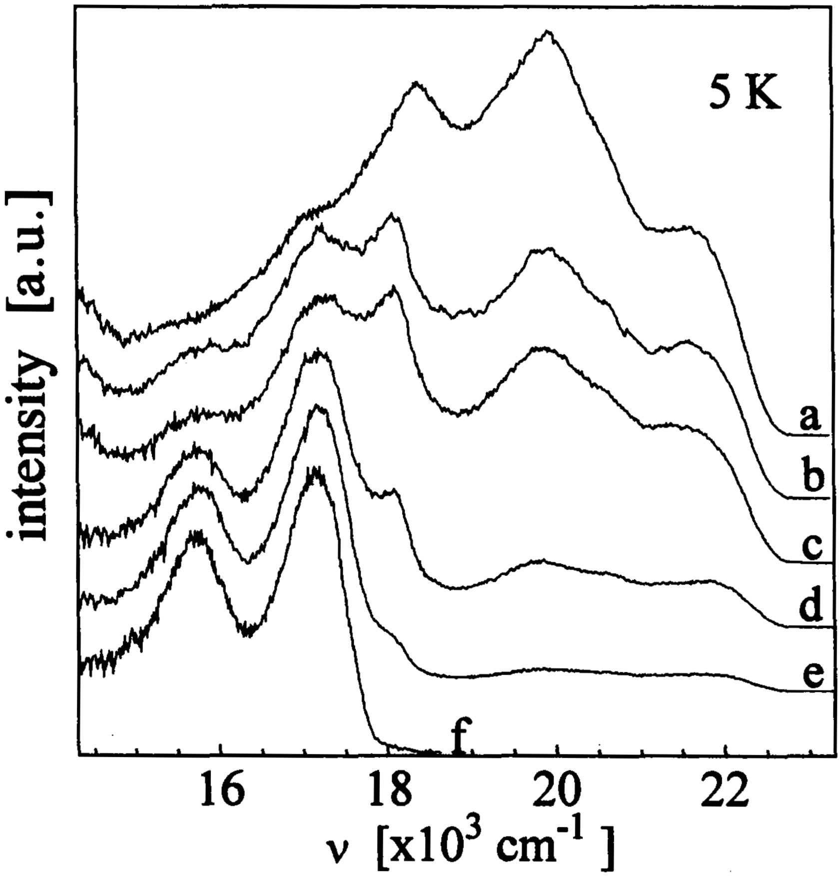

FIGURE 1 Fluorescence spectra at 5 K of undoped TCNB-B crystals (a) and TCNB-B crystals doped with: (b) 5.10^{-4}, (c) 10^{-3}, (d) 2.10^{-3} and (e) 5.10^{-3} M/M of A. Dopant, guest fluorescence spectrum (f) was obtained for a TCNB-B crystal doped with 5.10^{-3} M/M of A when this crystal was excited directly to its $S_1^{\mathrm{TCNB\text{-}A}}$ state by using 20000 cm^{-1} light.

17200 cm^{-1}) are also non-exponential, with well distinguished rise, extended over a 5 ns time range. Long time tails of the guest fluorescence decays are slightly longer as compared with the decays of the host fluorescence at the same temperature.

Singlet energy transfer can be studied by the kinetic analysis of the host fluorescence, as it was successfully done for some other CT crystals [16,17,19]. A time scale of the host fluorescence decay in TCNB-B crystals is approximately one order of magnitude longer than in majority of other CT crystals. Thus, imperfections of the lattice structure of TCNB-B crystals can contribute

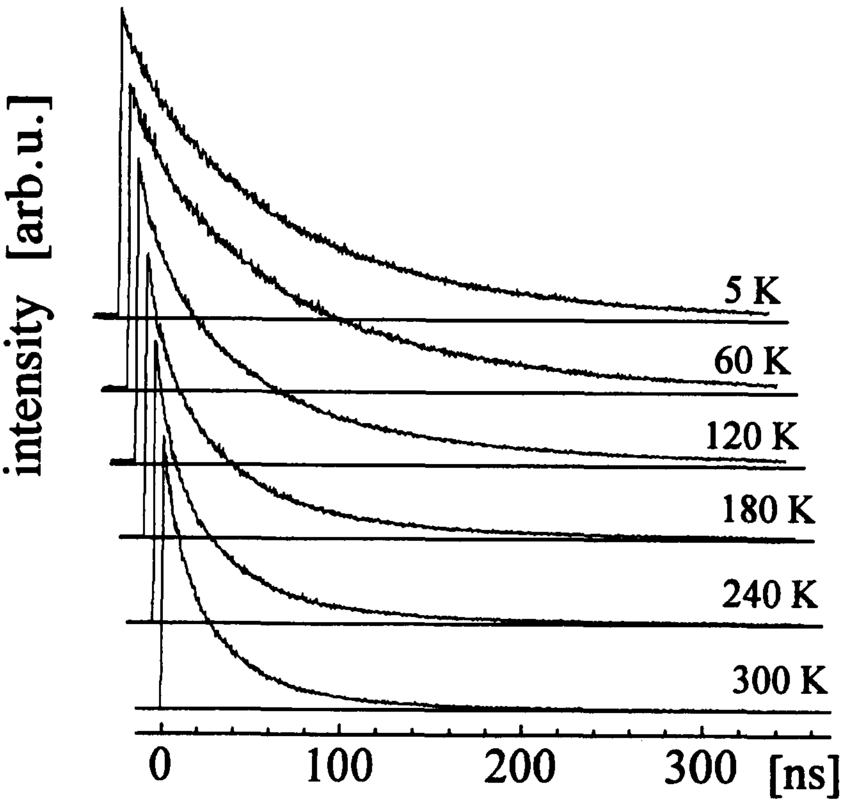

FIGURE 2 The host fluorescence decays of a TCNB-B crystal doped with 5.10^{-3} M/M of A at some temperatures. Observation at 21700 cm^{-1}.

more efficiently to the singlet energy migration and may lead to non-exponential fluorescence decays in undoped and doped TCNB-B crystals. To deal with the problem, in the present work we applied a general approach [19,17], which is to consider the experimental ratio of the time averages of the host-guest transfer rate constant, $\langle k_{HG} \rangle$, to the host decay rate constant, $\langle k_H \rangle$:

$$\langle k_{HG} \rangle / \langle k_H \rangle = \left(\int I^{\mathrm{undoped}}(t)\,dt - \int I^{\mathrm{doped}}(t)\,dt \right) / \int I^{\mathrm{doped}}(t)\,dt \qquad (1)$$

In the above equation, $I^{\mathrm{undoped}}(t)$ and $I^{\mathrm{doped}}(t)$ are the experimentally detected decays of the host fluorescence of undoped TCNB-B crystals and TCNB-B crystals doped with A, respectively. The dependence (1), as a function of temperature for the two different concentrations of A, is shown in Figure 3. A characteristic feature of this dependence is approximately constant value of the $\langle k_{HG} \rangle / \langle k_H \rangle$ at low temperatures and its increase at temperatures above 100 K. The decay of the host fluorescence of undoped TCNB-B crystals (given by $\langle k_H \rangle$) is only weakly dependent on temperature and therefore, the dependence (1) defines first of all a temperature behavior of the host-guest energy transfer rate constant ($\langle k_{HG} \rangle$). According to the polaron model [1, 20], a temperature dependence of the host-guest transfer rate is proportional to $T^{-1/2} \exp(-\Delta E/kT)$, where ΔE is the activation energy of the polaron motion. Using this formula, it was possible to plot the solid curves presented in Figure 3, which lead to the activation energy $\Delta E = (450 \pm 60)\ \mathrm{cm}^{-1}$.

In a simple diffusion, hopping model (in a cubic lattice) the energy transfer rate is $k_{HG} = 0.66 c_G/t_h$, where c_G is the dopant concentration and t_h, the singlet exciton hopping time. Using this last formula and $\langle k_H \rangle = 10^7\ \mathrm{s}^{-1}$ the hopping time at 300 K is:

$$t_h = (1.1 \pm 0.5) \cdot 10^{-10}\mathrm{s}.$$

Alternative way to study the singlet energy transfer in TCNB-B crystals seemed to be a kinetic analysis of the rise of the guest fluorescence. It appeared however, that the rise time of this emission is only weakly dependent on

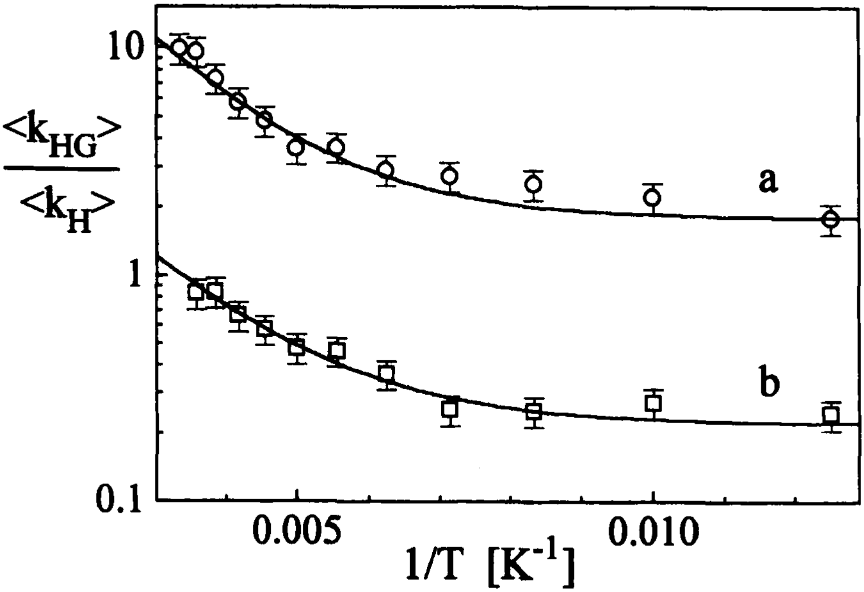

FIGURE 3 Temperature dependence of the ratio $\langle k_{HG} \rangle / \langle k_H \rangle$ for TCNB-B crystals doped with 10^{-2} (circles) and 2.10^{-3} M/M of A (squares).

temperature and much shorter than the decay time of the host fluorescence, being 4.6 and 3.6 ns at 80 and 300 K, respectively. The observed rise of the guest fluorescence should be therefore related to the long-range dipole-dipole energy transfer (within the Förster model) between the host-guest pairs, created already by a laser excitation, and not to the excitonic energy transfer.

3.2. Triplet Energy Transfer

Phosphorescence and delayed fluorescence spectra of TCNB-B crystals doped with some different concentrations of A at 5 K are shown in Figure 4. The main component of these spectra, which can be related to the TCNB-A dopant, has the high energy maximum at 17200 cm^{-1} (see Fig. 4e) and closely resembles the guest fluorescence band (see Fig. 1f). Such the spectral behavior indicates that the efficient channel of the host-guest triplet energy transfer is the intersystem crossing $T_1^{TCNB\text{-}B} \rightarrow S_1^{TCNB\text{-}A}$. Furthermore, the phosphorescence quantum yield of TCNB-A trap is very small. A weak intensity anthracene-like phosphorescence band, with the maximum at 14920 cm^{-1}, can be observed at 5 K (Fig. 4f) if the sample is excited directly to the lowest excited singlet state of the TCNB-A guest ($S_1^{TCNB\text{-}A}$). Under this condition, a ratio of the quantum yield of the guest fluorescence to that of the guest phosphorescence was estimated to be 0.0075. Temperature evolution of the long-lived emission spectrum of TCNB-B crystals doped with 2.10^{-3} M/M of A is shown in Figure 5. With increasing temperature, above 40 K, a contribution of the host phosphorescence (observed between 20500–18500 cm^{-1}) decreases and simultaneously, a contribution of the intensity of the delayed sensitized fluorescence (which originates from the guest $S_1^{TCNB\text{-}A}$ state) increases. With a further temperature increase, above 100 K, a dominating component of the long-lived spectra becomes a weak anthracene-like phosphorescence, originating from the $T_1^{TCNB\text{-}A}$ state. Finally, above 200 K, the intersystem crossing process, $T_1^{TCNB\text{-}A} \rightarrow S_1^{TCNB\text{-}A}$, is thermally activated and the guest, E-type delayed fluoresence dominates in the spectral range below 18000cm^{-1}. At low temperatures, the host, P-type delayed fluorescence can be observed in the spectral range 20500–22500 cm^{-1}, as shown in Figures 4 and 5. Intensity of this last emission depends non-linearly on the intensity of exciting light and its decay is complicated and dependent on temperature. Decays of delayed fluorescence of a TCNB-B crystal doped with 5.10^{-3} M/M of A for some temperatures are shown in Figure 6. Temporal behavior of the host, P-type delayed fluorescence depends on spatial separations between annihilating triplet pairs, migrating within the crystal lattice. Therefore, in the present

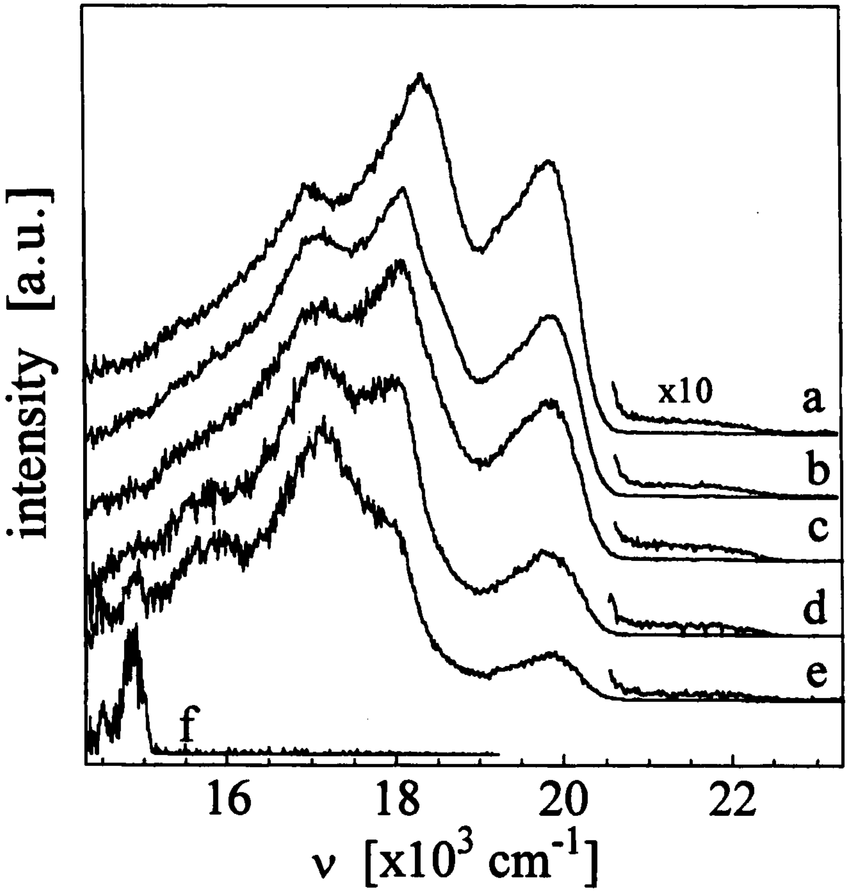

FIGURE 4 Long-lived emission spectra at 5 K of undoped TCNB-B crystals (a) and TCNB-B crystals doped with different concentrations of A (d–e). Concentrations of A are: 5.10^{-4} (b), 10^{-3} (c), 2.10^{-3} (d) and 5.10^{-3} M/M (e). Phosphorescence spectrum (f) was obtained for a TCNB-B crystal doped with 5.10^{-3} M/M of A when this crystal was excited by a 20000 cm^{-1} light. To visualize the presence of a weak (P-type) delayed fluorescence, the high energy part of the spectra (20500–23000 cm^{-1}) is also shown with the × 10 magnification.

contribution we analyze the decay shape of the host delayed fluorescence to extract an information about the migration of triplet excitons. It has been shown [14], that triplet excitons in undoped TCNB-B crystals are self-trapped below 30 K and they become mobile at higher temperatures. Between 60 and 100 K, decays of delayed fluorescence ($I_{DF}(t)$) are well approximated by the dependence predicted by the theoretical model [21], which assumes that excitons move by hopping between neighboring crystal

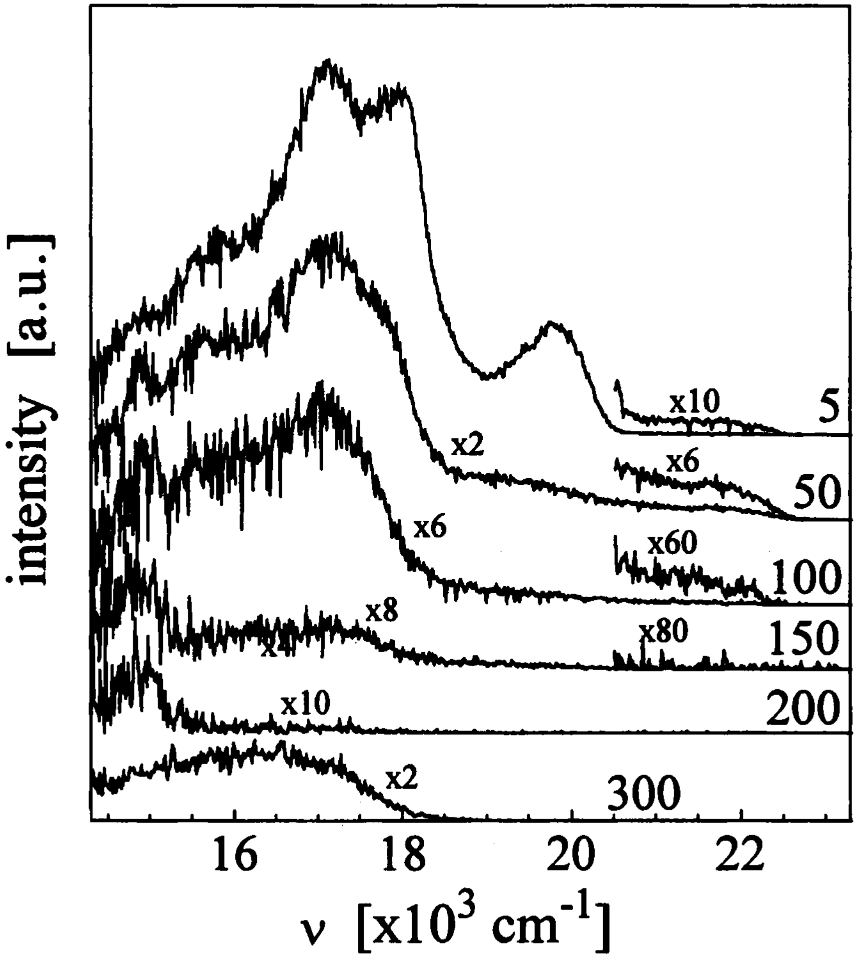

FIGURE 5 Long-lived emission spectra of TCNB-B crystals doped with 2.10^{-3} M/M of A at different temperatures, indicated at the right side of the spectra. Relative intensities of the spectra are given in respect to the intensity at 5 K.

sites along a 1D chain, caged by randomly distributed traps (or reflecting barriers). According to the model, the (long-time) decay formula is given by

$$I_{DF}(t) \propto t^{1/6} \cdot \exp(-b \cdot t^{1/3} - 2 \cdot \beta \cdot t) \qquad (2)$$

where: β is the inverse of the triplet lifetime and b is a fitting parameter. The best fits of the delayed fluorescence decay curves by the formula (2) are given by the solid lines in Figure 6. The parameter b in eq. (2) depends on a trap concentration c_G and on a probability W, that triplet exciton hops to neighboring site. W is the reverse of the exciton hopping time. The theoretical model [21] provides:

$$b = 3/2 \cdot (10 \cdot \pi^2 \cdot c_G{}^2 \cdot W)^{1/3} \tag{3}$$

It is important to notice, that a good fitting by the formula (2) can be obtained for undoped TCNB-B crystals as well [14]. Hence, the trap concentration in the eq. (2) is the sum of the concentration of anthracene and a concentration of contributing, remaining crystal impurities and defects. Under these circumstances, the hopping probability is given by

$$W = 8 \cdot (b^{3/2} - b_0{}^{3/2})^2 / (270 \cdot \pi^2 \cdot c_G{}^2),$$

where b_0 is the fitting parameter b for undoped TCNB-B crystals. The

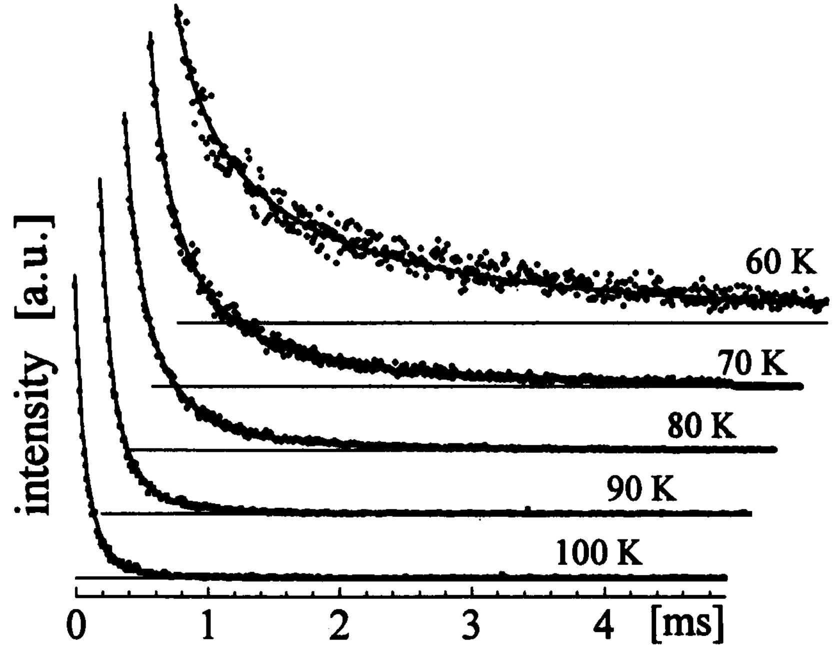

FIGURE 6 Decays of delayed fluorescence of a TCNB-B crystal doped with 5.10^{-3} M/M of A at temperatures between 60 and 100 K. Observation at 21700 cm^{-1}. The time 0 corresponds to a 80 μs delay after a laser pulse. The solid curves present the best fits to the theoretical formula (2), with the fitting parameter b: 27.3, 42.2, 59.2, 84.0 and 102.9 at 60, 70, 80, 90 and 100 K, respectively.

Arrhenius-type dependence of W, using experimentally determined fitting parameters b and b_0, is shown in Figure 7. The already mentioned temperature dependence of the polaron host-guest energy transfer rate allows to estimate the activation energy of the triplet exciton motion, (550 ± 60) cm^{-1}. It is remarkable to notice that this activation energy is considerably higher than the activation energy of the triplet exciton motion in pure, undoped TCNB-B crystals, where it is (360 ± 60) cm^{-1} [14]. (The last activation energy can be obtained from the temperature dependence of the fitting parameter b_0). Hence, doping with A induces some geometrical rearrangement of the host crystal lattice, which manifests in higher CT character of triplet excitons and deeper energy of their self-trapping. This conclusion is in some way unexpected as the crystal units of pure TCNB-B [22] and TCNB-A [23] crystals are not much different and one would predict a rather good, substitutional replacement of B by A. It is however in agreement with the results of the previous EPR studies [4,15] which pointed to a very high sensitivity of the activation energy of mobility of triplet excitons to a quality of TCNB-B crystals. Using the experimentally obtained parameter b_0 and the hopping probability W, we can estimate the concentration of defects in pure TCNB-B crystals. Defect concen-

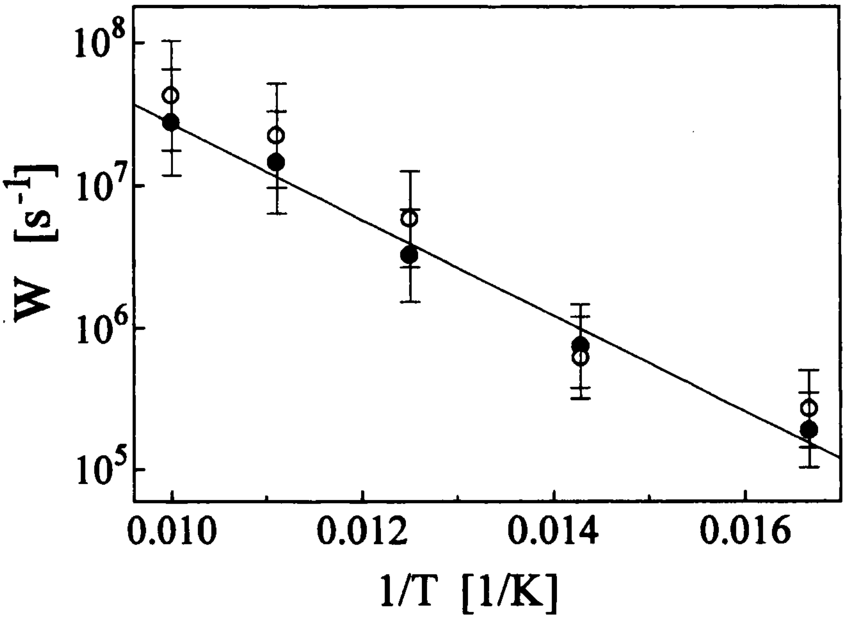

FIGURE 7 Triplet excition hopping probability W as a function of temperature (60–100 K range) for TCNB-B crystals doped with 5.10^{-3} (full circles) and 2.10^{-3} M/M of anthracene (open circles). Solid line corresponds to the activation energy $\Delta E = 550$ cm^{-1}.

tration was found to change from 10^{-2} at 60 K to 5×10^{-3} M/M at 100 K. The very high concentration of defects, without any doubt, can not be related to chemical impurities, as we use extensively purified materials. We can also exclude mistakes in the donor-acceptor alternation order, because their concentration in the host crystal is independent on temperature. Defects contributing to the exciton migration are probably analogous to X traps, well-known in one-component molecular crystals. In crystals under consideration a small change of the complex geometry may strongly influence the energy of CT state. We postulate that the lattice of TCNB-B crystals is in some way strained, thus easy creating a high concentration of defects, which can trap excitons. With increasing temperature some of these traps can be thermally overcome and therefore their effective concentration is decreasing. The same conclusion was proposed to explain kinetic behavior of the host fluorescence in TCNB-B crystals doped with TCNQ [13]. A high disposition of TCNB-B crystals to create defects was also suggested by the previous EPR studies [4, 15], which showed that the EPR line width is sensitive to a crystal quality.

4. CONCLUSIONS

The kinetic analysis of the prompt and delayed fluorescence in TCNB-B crystals doped with A confirms the previous observations that singlet and triplet excitons are self-trapped at low temperatures and mobile at higher temperatures. The activation energies of mobility were found to be (450 ± 60) and (550 ± 60) cm^{-1} for the singlet and triplet excitons, respectively. It comes clearly, that the activation energy of triplet excitons mobility is higher in A doped TCNB-B crystals as compared to that in undoped crystals, (360 ± 60) cm^{-1}, obtained by using the same experimental approach. The observation can be explained by some disturbance of the lattice in TCNB-B crystals doped with A as compared with the undoped one. Doping leads to higher CT character of triplet excitons. Optical studies alone cannot provide convincing arguments for the geometrical rearrangement of the lattice. A detailed X-ray crystal structure investigation at liquid helium temperatures of TCNB-B crystals, undoped and doped with A, are needed to elucidate this point.

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References

[1] V. M. Agranovich and M. D. Galanin, in: Electronic excitation energy transfer in condensed matter, eds. V. M. Agranovich and M. D. Galanin (North-Holland, Amsterdam, 1982).

[2] D. Haarer and M. R. Philpott, in: Spectroscopy and excitation dynamics of condensed molecular systems, eds. V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1982).

[3] J. Krzystek and J. U. von Schütz, *Advan. Chem. Phys.*, **86**, 167 (1993).

[4] H. Möhwald and E. Sackmann, *Chem. Phys. Lett.*, **21**, 43 (1973).

[5] H. Möhwald and E. Sackmann, *Z. Naturforsch.*, **A29**, 1216 (1974).

[6] C. Corvaja and L. Pasimeni, *Chem. Phys. Lett.*, **88**, 347 (1982).

[7] L. Pasimeni, G. Guella, C. Corvaja, D. A. Clemente and M. Vicentini, *Mol. Cryst. Liq. Cryst.*, **91**, 25 (1983).

[8] G. Agostini, C. Corvaja, G. Giacometti and L. Pasimeni, *Chem. Phys.*, **77**, 233 (1983).

[9] C. Corvaja, B. Kozankiewicz, L. Pasimeni and J. Prochorow, *Chem. Phys.*, **119**, 399 (1988).

[10] G. Agostini, D. Carbonera, G. Giacometti, A. L. Maniero and L. Pasimeni, *Chem. Phys. Lett.*, **167**, 78 (1990).

[11] M. Yagi, S. Nagakura and H. Aayashi, *Chem. Phys. Lett.*, **18**, 272 (1973).

[12] M. Yagi and S. Nagakura, *Chem. Phys. Lett.*, **21**, 119 (1973).

[13] G. Agostini, G. Giacometti, A. Toffoletti and L. Pasimeni, *Il Nuovo Cimento*, **12D**, 233 (1990).

[14] B. Kozankiewicz, *Chem. Phys. Lett.*, **217**, 91 (1994).

[15] J. Krzystek and J. U. von Schütz, *Material Science XIII*, 133 (1987).

[16] B. Kozankiewicz, J. Al-Abbas and J. Prochorow, *Chem. Phys. Lett.*, **235**, 456 (1995).

[17] B. Kozankiewicz, *J. Luminescence*, in press.

[18] W. Steudle, J. U. von Schütz and H. Möhwald, *Chem. Phys. Lett.*, **54**, 461 (1978).

[19] E. Betz, H. Port, W. Schrof and H. C. Wolf, *Chem. Phys.*, **128**, 73 (1988).

[20] T. Holstein, *Ann. Phys.*, **8**, 325, 343 (1959).

[21] A. I. Onipko and I. V. Zozulenko, *J. Luminescence*, **43**, 173 (1989).

[22] L. Pasimeni, G. Guella, C. Corvaja, D. A. Clemente and M. Vicentini, *Mol. Cryst. Liq. Cryst.*, **91**, 25 (1983).

[23] J. Lefebvre, G. Odou, M. Muller, A. Mierzejewski and T. Luty, *Acta Cryst.*, **B45**, 323 (1989).