Kinetics of Delayed Emission in Charge-Transfer Crystals. TCPA—HMB Crystal

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Fluorescence, phosphorescence and thermally activated delayed fluorescence of tetrachlorophthalic anhydride-hexamethylbenzene charge-transfer crystal have been studied, under photostationary and transient conditions, in a wide temperature range (1.7–300 K). The rate constants for various radiative and non-radiative processes have been determined within the framework of a photokinetic model, which is considered to be a typical one for those charge-transfer crystals which are characterized by very high charge-transfer character of the lowest triplet state (charge-transfer triplet excitons).

I. INTRODUCTION

The excited states of single crystals of weak charge-transfer (CT) complexes have been studied by optical and electron paramagnetic resonance (EPR) methods for more than the last decade (for a review see Ref. 1). However, optical properties and excitation energy migration processes in CT crystals where the lowest triplet state has pure or almost pure charge-transfer character are still poorly understood. Preliminary studies[2,3] have signalled that triplet excitons in this group of crystals had qualitatively different properties as compared to the majority of CT crystals which are characterized by local (mainly donor) character of triplet excitons.[4]

Our recent studies have included a number of CT single crystals with the lowest triplet state of very high CT character. These were: tetrachlorophthalic anhydride (TCPA)-hexamethylbenzene (HMB),[5,6] pyromellitic dianhydride (PMDA)-HMB,[7] tetracyanobenzene (TCNB)-

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HMB[8] and PMDA-phenanthrene.[9] It has been found that in all above-mentioned crystals, behaviour of triplet excitons is controlled, in moderate temperature ranges, by the process of their thermal activation to the singlet excitonic band. This seems to be directly connected to the well-known fact that the energy gap between the lowest CT singlet and CT triplet excitonic bands is in such crystals very small, thus leading to the observation of thermally activated, delayed fluorescence (E-type delayed fluorescence).[10]

Very small singlet-triplet (S_1–T_1) separation (usually not exceeding 500 cm^{-1}) seems to provide rather unique possibility for quantitative studies of photophysical properties, particularly of $S_1 \rightsquigarrow T_1$ and $T_1 \rightsquigarrow S_1$ intersystem crossing processes in CT complexes. Furthermore, such studies can be carried out in the wide temperature range between the two limits: (a) low temperature limit—when $T_1 \rightsquigarrow S_1$ process is inhibited, and (b) high temperature limit—when the triplet excitonic band is totally depopulated by the thermal activation to the S_1 excitonic band.

The main part of the present work deals with a kinetic model of emission and of triplet exciton migration appropriate for discussion of this group of CT crystals. This model is quantitatively discussed for TCPA-HMB crystal, for which detailed optical investigations have been carried out in the wide temperature range (1.7–300 K).

II. EXPERIMENTAL

TCPA (electron acceptor) and HMB (electron donor) were vacuum sublimed, zone refined separately and subsequently zone refined as a CT complex. Single crystals were grown by the "plate sublimation" method.[11]

Emission spectra were measured by a standard synchronous-choppers spectrophosphorometry technique.[12] For excitation to the lowest CT singlet state a mercury, HBO 200, lamp with a suitable filter combination (404 nm line), or xenon, XBO 101, lamp and monochromator were used. Emission was dispersed by a 0.25 m Jarrell-Ash monochromator and detected by photon counting (composed of an ORTEC 9302 amplifier-discriminator, 9315 photon-counter and 9320 sampling/control unit) with the aid of a cooled EMI 9659 photomultiplier.

The decay curves in the milisecond time regime were accumulated with the aid of an EMG NTA 1024 multichannel analyser (in multi-scalar mode). A "third chopper" method[13] was used for decay times

longer than 10 ms. Detection of nano- and microsecond decays was performed with the use of the time correlated single photon counting system which includes: a N_2 nanosecond flash lamp triggered at 10–50 kHz[14] (with 337 nm line isolated by appropriate filters), an RCA 1P28—start and Phillips XP 2020—main photomultipliers, a 0.25 m Jarrell-Ash monochromator, two Polon 1503 constant fraction discriminators, a Canberra 2044 time-amplitude converter and an EMG NTA 1024 multichannel analyser.

III. RESULTS

The emission of TCPA-HMB crystals observed at 1.7 K is composed of prompt fluorescence and of long-lived emission. Spectra of both emissions have a similar shape and spectral position (Figure 1). At this temperature an integral intensity of the prompt fluorescence is 4 times higher than that of long-lived emission (Figure 2) and their ratio does not depend on the wavelength of excitation (within the 310–420 nm range).

When the temperature is increased, the spectral characteristics of prompt and long-lived emission are changing. The results of tem-
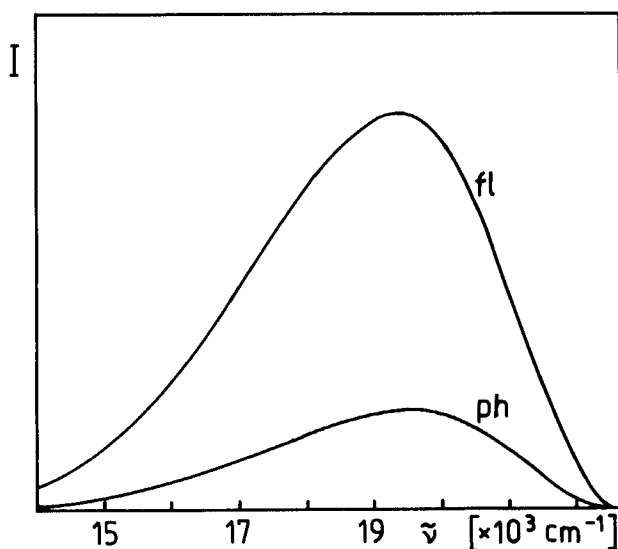

FIGURE 1   Fluorescence (fl) and phosphorescence (ph) spectra of TCPA-HMB crystal at 1.7 K.
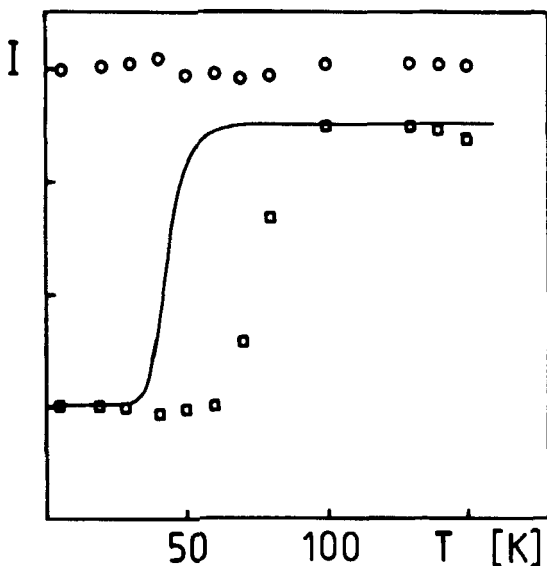
FIGURE 2   Temperature dependence of the integral intensities of fluorescence (○) and long-lived emission (□). Solid-line curve is a theoretical simulation [with the use of Eq. (16)] of the temperature dependence of long-lived emission intensity (see Sec. 4.3.).

perature studies of both emissions can be briefly summarized as follows:

3.1. Fluorescence

The fluorescence emission band, which is identified as the charge-transfer fluorescence of the TCPA-HMB complex, is broad and structureless in the whole temperature range (1.7–300K). Its maximum undergoes a small red shift with increasing temperature, amounting to ca. 200 cm^{-1} between 1.7 and 300 K. The fluorescence intensity is constant between 5 and 150 K (Figure 2) and then decreases slightly with increasing temperature.

The decay curve of fluorescence is not strictly exponential and is dependent on the wavelength of observation, with faster decay observed at the energetically higher part of the fluorescence band. The dominant component of the fluorescence decay is the long-lived one. Figure 3 illustrates the temperature dependence of the long-lived component of fluorescence decay between 1.7 and 150 K. It is seen that in this temperature range, the decay time of 23 ± 2 ns is nearly
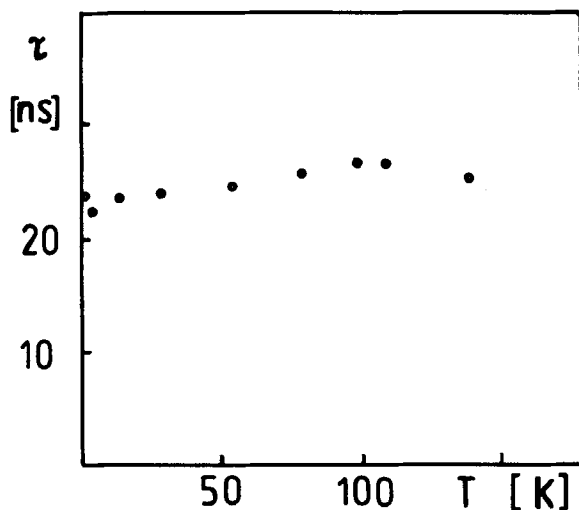
FIGURE 3   Temperature dependence of the decay times of fluorescence of a TCPA-HMB crystal (see text for details).

constant, whereas at higher temperatures it becomes only slightly shorter.

3.2. Phosphorescence and delayed fluorescence

A long-lived emission band, which undergoes a continuous shift to-ward lower energies in the temperature interval of 1.7–40K, (Figure 4) is assigned to the phosphorescence that results from shallow traps. An increase of temperature above 40 K leads to a shift of the long-lived emission band to higher energies. Our previous, detailed, studies of the time-resolved spectra of long-lived emission[5] have clearly dem-onstrated that this shift is apparent and is due to increasing intensity of delayed fluorescence with increasing temperature. Delayed fluo-rescence is a dominant long-lived emission for temperatures above 60 K and its spectral position is the same as that of the prompt fluorescence.

   A strictly linear dependence of the intensity of delayed fluorescence on the intensity of exciting light, at all investigated temperatures, proves that the delayed fluorescence is of E-type, in other words, it originates from the process of thermal activation of triplet excitons to the singlet excitonic band.

   Between 60–100 K an integral intensity of the long-lived emission band increases approximately 4 times, thus reaching about 90% of
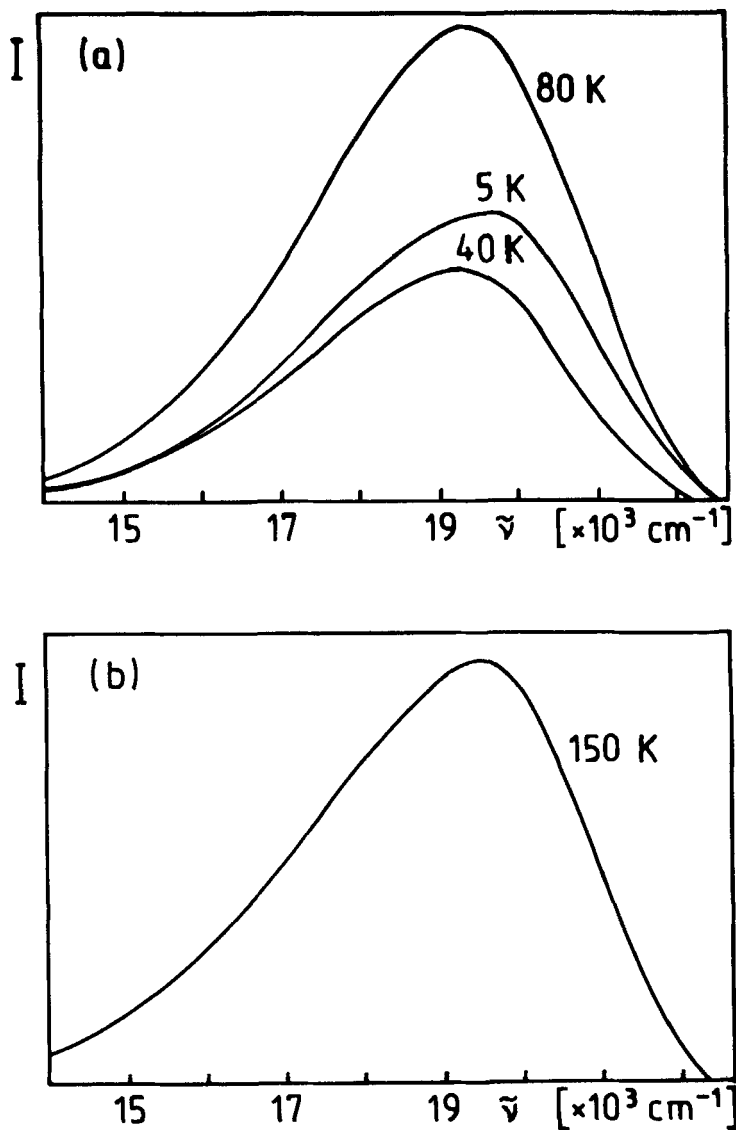
FIGURE 4   Long-lived emission spectra of a TCPA-HMB crystal at different tem-
peratures. Spectra were recorded with the delay time: 0.15 ms(a) and 10 μs (b), after
excitation.

the intensity of prompt fluorescence (Figure 2). Above 100 K it remains constant and at this temperature it is almost exclusively the intensity of the delayed fluorescence which contributes to the observed long-lived emission of TCPA-HMB crystals (though the phosphorescence from very deep traps can be observed even at 300 K[5]).

As it was demonstrated earlier,[5] a very characteristic feature of delayed fluorescence is a drastic decrease of its decay time with increasing temperature (Figure 5). At 100 K this decay time is 75 μs and only 10 μs at 150 K and still becoming shorter at higher temperatures (for comparison the decay time of phosphorescence at 1.7 K is 60 ± 5 ms). The temperature dependence of decay time of the delayed fluorescence is illustrated by the Arrhenius-type plot in Figure 6 and it leads to the activation energy for delayed fluorescence of $\Delta E = 400 \pm 30$ cm^{-1}.

IV. DISCUSSION

4.1. Summary of observations

The most important conclusion which comes out from our investigations of TCPA-HMB crystals is that the process of thermal activation of the triplet excitons to the singlet excitonic band is the main process that controls and governs migration of triplet excitons for temperatures higher than 60 K.

It is important to notice that the triplet-triplet annihilation process, usually very efficient in CT crystals with high local character of triplet excitons[4] is absent in TCPA-HMB crystals. This is probably connected with a short lifetime of triplet excitons at elevated temperatures, which reduces a migration range and by the same token results in the low probability of triplet-triplet annihilation events.

Since, at 1.7 K, the intensity ratio of phosphorescence to prompt fluorescence, does not depend on excitation wavelength, we may infer that the triplet excitons are created by the intersystem crossing process from the S_1 excitonic band.

Both, the integral intensity (Figure 2) and the decay time (Figure 3) of prompt fluorescence are constant in the temperature range of 1.7–150K. Hence, the overall depopulation rate constant of the singlet CT excitonic band, k_S, is temperature independent. If one takes into account that at temperatures above 100 K an integral intensity of delayed fluorescence amounts to ~90% of intensity of prompt fluorescence (Figure 2), which indicates that at least 40–50% of sin-
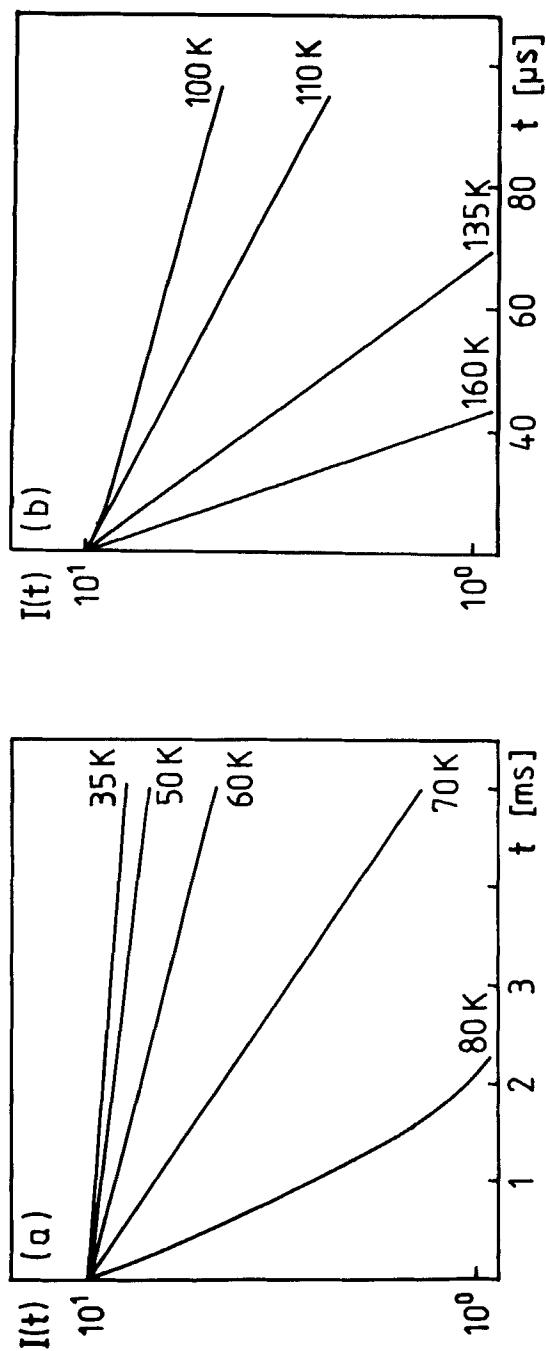
FIGURE 5   Decay curves of the long-lived emission of TCPA-HMB crystal in the 35–160 K temperature range.
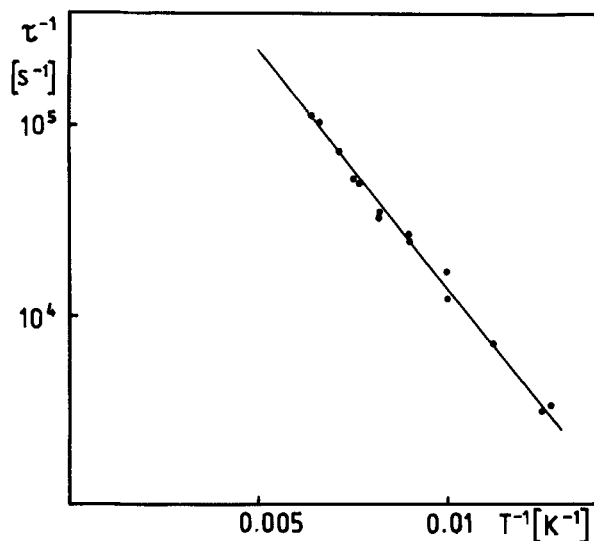
FIGURE 6   Inverse temperature dependence of the decay time (given as τ^{-1}) of thermally activated delayed fluorescence.

glet excitons concentration is being diminished by $S_1 \rightsquigarrow T_1$ intersystem crossing process, then one comes to the conclusion that the components of k_S, i.e. a sum of the rate constants for radiative and non-radiative transition ($k_S^r + k_S^{nr}$) from S_1 to S_0 and the rate constant k_{ST} of the $S_1 \rightsquigarrow T_1$ intersystem crossing must also be temperature independent.

In view of these facts it is evident that the intersystem crossing $S_1 \rightsquigarrow T_1$ process has no activation energy, contrary to the back $T_1 \rightsquigarrow S_1$ process which is thermally activated, with activation energy, as was found above, of 400 cm^{-1}. Therefore, the activation energy for delayed fluorescence should correspond to the energy difference ΔE_{ST} between S_1 and T_1 charge-transfer excitonic bands. Accordingly one could expect that phosphorescence and fluorescence emission bands should be spectrally separated (by ca. 400 cm^{-1}), which is not the case as both emission bands have the same spectral position at 1.7 K. One has to bear in mind, however, that in the CT electronic configuration a relative orientation of the donor-acceptor pair may differ in the singlet and in the triplet state, as it was postulated earlier on the basis of quantum mechanical arguments.[15,16] Thus, contrary to the activation energy, the energy of the electronic transition may also include differences of the destabilization energy of Franck-Con-

don ground-state configurations which are the final states for relevant electronic transitions. Hence the activation energy of delayed fluorescence does not have to correspond directly to the observed differences in fluorescence and phosphorescence emissions. Although this problem is a very interesting one, especially in connection with the crystalline phase of CT complexes, it would necessitate experimental evidence to be gathered in order to validate its importance.

4.2. The kinetic model

In discussion of the above-outlined results, the following kinetic scheme will be adopted (Figure 7):

i. Singlet excitons are created in a singlet excitonic band, S_1, by absorption of light of intensity I_a, upon $S_0 \rightsquigarrow S_1$ transition from the ground state with absorption coefficient σ_a.

ii. Singlet excitons decay from S_1 to the ground state S_0 either radiatively (fluorescence) with the rate constant k_S^r, or nonradiatively with the rate constant k_S^{nr}, they can also cross to the triplet excitonic band T_1 via nonradiative $S_1 \rightsquigarrow T_1$ intersystem crossing with the rate constant k_{ST}, thus creating triplet excitons.

iii. Triplet excitons decay from T_1 to the ground state S_0 either radiatively (phosphorescence) with the rate constant k_T^r, or nonradiatively with the rate constant k_T^{nr}.

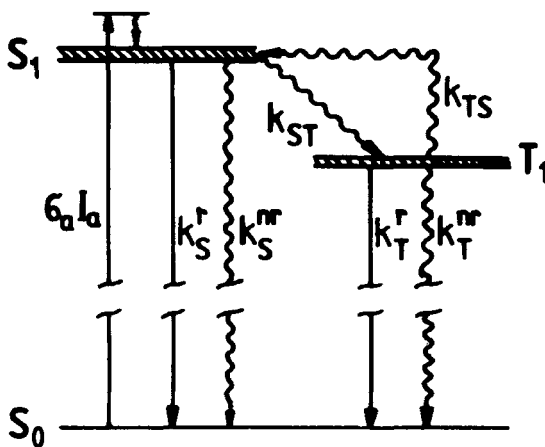iv. Triplet excitons are also thermally activated back to the singlet

FIGURE 7   Excitonic bands and various deactivation pathways for TCPA-HMB crystal (details in the text).

excitonic band S_1 with the temperature dependent rate constant $k_{TS} = k'_{TS} \cdot \exp(-\Delta E_{ST}/kT)$, where ΔE_{ST} is the energy gap between singlet and triplet excitonic bands.

v. Singlet excitons created in the way (iv) can undergo every one of deactivation processes described in (ii), when they undergo radiative decay a delayed fluorescence results.

For this photokinetic scheme one has the following coupled differential equations that describe time-dependence of the population of the singlet, $[S_1]$, and of the triplet, $[T_1]$, excitons:

$$\frac{d[S_1]}{dt} = \sigma_a I_a - k_S [S_1] + k_{TS} [T_1] \tag{1}$$

$$\frac{d[T_1]}{dt} = k_{ST} [S_1] - k_T [T_1] - k_{TS} [T_1] \tag{2}$$

where $k_S = k_S^r + k_S^{nr} + k_{ST}$ and $k_T = k_T^r + k_T^{nr}$. Under steady-state (photostationary) conditions the solutions of Eqs. (1) and (2), are

$$[S_1] = \frac{\sigma_a I_a}{k_S} \left(1 + \frac{\phi_T k_{TS}}{k_T + k_{TS}(1 - \phi_T)} \right) \tag{3}$$

$$[T_1] = \sigma_a I_a \frac{\phi_T}{k_T + k_{TS}(1 - \phi_T)} \tag{4}$$

where $\phi_T = k_{ST}/k_S$.
Also

$$I_{fl} \sim k_S^r [S_1]' \tag{5}$$

$$I_{ph} \sim k_T^r [T_1] \tag{6}$$

$$I_{dfl} \sim k_S^r [S_1]'' \tag{7}$$

where $[S_1]' = \sigma_a I_a/k_S$ describes this part of the population of the singlet excitonic band which is created by direct absorption of exciting light, and $[S_1]'' = (\sigma_a I_a/k_S) \cdot \{\phi_T k_{TS}/[k_T + k_{TS}(1 - \phi_T)]\}$ describes

the part of the population of the singlet excitonic band which is created by thermal activation of triplet excitons from the triplet excitonic band.

Description of the transient behavior depends on the time dependence of $I_a(t)$ and for instantaneous excitation, eqs. (1) and (2) yield the following solutions for the time dependence of exciton concentrations:[17]

$$[S_1](t) = A_1 \exp(-\lambda_1 t) + B_1 \exp(-\lambda_2 t) \tag{8}$$

$$[T_1](t) = A_2 \exp(-\lambda_1 t) + B_2 \exp(-\lambda_2 t) \tag{9}$$

In general, preexponential factors in Eqs. (8) and (9), as well as the rate parameters for exponential terms, λ_1 and λ_2, are functions of rate constants of various deactivation pathways of the photokinetic scheme (Figure 7) and of the system's boundary value conditions.[17] Below we will limit analysis of the transient behaviour to decay times only (i.e. λ_1 and λ_2 rate parameters). Then, adopting the well known definitions of λ_1 and λ_2 (for instance Eq. (59) in Ref. 17) and under conditions of our experiments (i.e. $k_S \gg k_T, k_{TS}$) one obtains the following approximate expressions for rate parameters:

$$\lambda_1 = k_S \tag{10}$$

$$\lambda_2 = k_T + (1 - \phi_T)k_{TS} \tag{11}$$

The results of transient measurements do not depend on steady-state measurements and both should provide consistent rate constants, which should verify the validity of the kinetic scheme.

4.3. Analysis of the kinetics

The complexity of the analysis can be greatly reduced when one considers the limiting cases. Thus, in the low temperature limit, i.e. when $k_{TS} \ll k_T$, one obtains:

i. the ratio of phosphorescence to fluorescence intensity [combining Eqs. (3)–(6)], as

$$\frac{I_{ph}}{I_{fl}} = \frac{k_T^r \cdot k_{ST}}{k_S^r \cdot k_T} \tag{12}$$

ii. the decay time of phosphorescence [from Eq. (11)], as

$$\lambda_2^{-1} = k_T^{-1} \qquad (13)$$

In the high temperature limit, when $k_{TS} \gg k_T$, one obtains:

i. the ratio of delayed fluorescence to fluorescence intensity [combining eqs. (3), (5) and (7)], as

$$\frac{I_{dfl}}{I_{fl}} = \frac{k_{ST}}{k_S - k_{ST}} \qquad (14)$$

ii. the rate constant of delayed fluorescence, [Eq. (11) in the limit $T \to \infty$], as

$$\lambda_2 = (1 - \phi_T)k'_{TS} \qquad (15)$$

All quantities defined by Eqs. (10) and (12)–(14) have been experimentally determined (and listed in Sec. 3). The decay constant λ_2, defined by Eq. (15), can easily be obtained from extrapolation of the Arrhenius plot in Figure 6 to infinitely high temperature ($1/T \to 0$), and its value is $(5.0 \pm 0.6) \cdot 10^6 \text{ s}^{-1}$.

Eqs. (10) and (12) through (15) can now be combined in order to yield some of the individual rate constants of the photokinetic scheme. After some simple algebraic manipulations one obtains:

$$k_S = (4.4 \pm 0.4) \cdot 10^7 \text{ s}^{-1},$$

$$k_T = (16.7 \pm 1.4) \text{ s}^{-1},$$

$$k_{ST} = (2.1 \pm 0.3) \cdot 10^7 \text{ s}^{-1}$$

$$k'_{TS} = (0.94 \pm 0.25) \cdot 10^7 \text{ s}^{-1}$$

and

$$\frac{k_S^r}{k_T^r} = (4.8 \pm 10) \cdot 10^6$$

These rate constants can now be used for theoretical simulations of temperature dependence of intensities of different emissions, which in turn can be compared with experimentally observed intensity changes,

thus verifying the validity of estimations of the rate constants as well as the proposed kinetic model. From Eqs. (6) and (7) the sum of intensities of long-lived emissions (phosphorescence + delayed fluorescence) is given as:

$$(I_{ph} + I_{dfl}) \approx \frac{1}{k_T + k_{TS}(1 - \phi_T)} \left(\frac{k_T^r}{k_S^r} k_S + k_{TS} \right) \qquad (16)$$

A plot of $(I_{ph} + I_{dfl})$ vs. T (normalized at 5K) calculated according to Eq. (16) is shown as a solid-line curve in Figure 2. It is seen that Eq. (16) follows qualitatively the experimental temperature dependence of $(I_{ph} + I_{dfl})$ in the whole temperature range. However, it fits experimental results accurately only in the low (<40 K) and in the high (>100 K) temperature range.

In view of apparent discrepancy between Eq. (16) and experimental observations, in the moderate temperature range (40 − 100 K), it is obvious that the proposed kinetic model underestimates the role of trapping processes at low and moderate temperatures. As was mentioned earlier (c.f. Sec. 3.2), delayed fluorescence becomes a dominant long-lived emission above 60 K, still, however, phosphorescence emission resulting from deep traps can be observed even at room temperature.[5] Trapping of triplet excitons on shallow and deep traps may be a crucial factor diminishing the intensity of delayed fluorescence at any given temperature. This may be especially important for deep traps due to unfavorable energetics for thermal activation of trapped excitons, at low and moderate temperatures, and to presumable non-radiative decay of trapped excitons (low energy gap to the ground state).

Although, formally, trapping processes could be easily introduced into the kinetic scheme, any quantitative treatment of such kinetics would be very difficult, as no data exist concerning either concentrations and distribution of the traps, or rate constants for transfer of triplet excitons to traps and for their radiative and non-radiative decays. This must ultimately be done in order that there is to emerge a complete picture of excitation energy migration in CT crystals. At the present stage, however, we will confine ourselves to conclusions that the proposed kinetic scheme is qualitatively correct and that the rate constants estimated within its framework reliably reflect kinetics of migration of triplet excitation energy in TCPA-HMB crystal.

To our best knowledge the experiment described above is the first single case where both, the rate constant for $S_1 \rightsquigarrow T_1$ intersystem crossing, k_{ST}, and the rate constants for backward $T_1 \rightsquigarrow S_1$ intersystem

crossing, k'_{TS}, have been simultaneously obtained. In the following we discuss these rate constants in more details.

4.4. The rate constants for intersystem crossing

In the framework of quantum mechanical theory of radiationless transitions,[18] the rate constants for $S_1 \rightsquigarrow T_1$ intersystem crossing transition, k_{ST}, and for the reverse $T_1 \rightsquigarrow S_1$ transition, k_{TS}, can be expressed in terms of level densities of corresponding states (under assumption that for both transitions, final states form a continuum). Thus

$$k_{ST} = \frac{2\pi}{\hbar} Z_S^{-1} \int \rho_S(\epsilon_S) d\epsilon_S \exp(-\beta\epsilon_S) \int \rho_T(\epsilon_T) d\epsilon_T \, |V_{\epsilon_S,\epsilon_T}|^2.$$

$$\cdot \, \delta(\Delta E_{ST} + \epsilon_S - \epsilon_T) \quad (17)$$

$$k_{TS} = \frac{2\pi}{\hbar} Z_T^{-1} \int \rho_T(\epsilon_T) d\epsilon_T \exp(-\beta\epsilon_T) \int \rho_S(\epsilon_S) d\epsilon_S \, |V_{\epsilon_T,\epsilon_S}|^2$$

$$\cdot \, \delta(-\Delta E_{ST} - \epsilon_S + \epsilon_T) \quad (18)$$

where $\beta = (kT)^{-1}$, ΔE_{ST} is the singlet-triplet energy separation, $\rho_S(\epsilon_S)$ and $\rho_T(\epsilon_T)$ are the densities of vibrational-phonon-spin levels at energies measured from the electronic origin within the singlet and triplet manifold, respectively. $V_{\epsilon_S,\epsilon_T}$ and $V_{\epsilon_T,\epsilon_S}$ are relevant coupling elements. The partition functions are $Z_S = \int \rho_S(E)\exp(-\beta E) \, dE$, and $Z_T = \int \rho_T(E)\exp(-\beta E) \, dE$, respectively.

After integration of Eq. (17) and (18) over $d\epsilon_T$ and some algebraic manipulations, a following relation is obtained:

$$\frac{k_{TS}}{k_{ST}} = \frac{Z_S}{Z_T} \exp(-\beta\Delta E_{ST}) \quad (19)$$

which is just a reflection of the requirement of microscopic reversibility of the intersystem crossing. With $k_{TS} = k'_{TS} \exp(-\beta\Delta E_{ST})$ (c.f. Sec. 4.2.) we immediately obtain

$$\frac{k'_{TS}}{k_{ST}} = \frac{Z_S}{Z_T} \quad (20)$$

With the rate constants determined in this work (c.f. Sec. 4.3.) this ratio is $k'_{TS}/k_{ST} = 0.45 \pm 0.16$. The condition $Z_S/Z_T < 1$ may be fulfilled only when the density of levels $\rho_T(E) > \rho_S(E)$. Due to spin degeneracy of the triplet state one would expect that $\rho_T(E) \approx 3\rho_S(E)$ and this should assure a ratio $(k'_{TS}/k_{ST}) \approx 0.33$. However, in a crystal, a competition between spin-lattice relaxation and relaxation of triplet spin-sublevels must be taken into account. If the rate of spin-lattice relaxation is slow as compared to the decay rates of the triplet then a selective population of triplet spin-sublevels may be achieved and the effective density of levels may tend to $\rho_T(E) \approx \rho_S(E)$. Such a selective population of triplet spin-sublevels, which would demonstrate itself as an effect of spin polarization, has been in fact found, at low temperatures, for a number of CT crystals.[19-22] However, for moderate and higher temperatures the spin-lattice relaxation rate is usually much faster than the decay rate of the triplet, thus thermally equalizing a population of the triplet spin-sublevels. Hence, the above-found ratio of k'_{TS}/k_{ST} seems to be consistent with our observation that thermally activated delayed fluorescence becomes important in the temperature range of 40–60K and above.

We should also mention that another possibility which may lead to the relation $Z_S/Z_T < 1$ would be assured by the change of frequencies of relevant vibrational modes between the singlet and the triplet state. However, no data pertinent to this problem exist and it would require separate studies.

Acknowledgment

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