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Singlet Energy Transfer in *p*-Terphenyl Crystal Doped with Tetracene

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The transfer of singlet energy in *p*-terphenyl crystal was measured as a function of the dopant (tetracene) concentration and the temperature. The simple hopping model yields a value of 3×10^{-14} s. This value is believed to be correct within a factor of 5. In the low temperature phase of the crystal, the energy transfer is temperature dependent with an activation energy of 66 cm^{-1} in undeuterated *p*-terphenyl and 90 cm^{-1} in perdeuterated *p*-terphenyl. It seems probable that in the low temperature phase the freedom of the conformational change of the molecule plays an important role in the energy migration.

p-Terphenyl is known as one of the fastest scintillators. Its short fluorescence lifetime (5 ns in the crystalline state) and the consequent excellent pulse pair separation makes the measurement of very high count-rates possible. The energy migration in *p*-terphenyl crystal is interesting because the molecule has some freedom of conformational change. There is some evidence that the three benzene rings of the free molecule are not coplanar in the electronic ground state, whereas the molecule tends to be planar in its electronic excited states.1) Thus it is possible that the migration of the electronic excitation energy is accompanied by some molecular deformation. The energy migration in *p*-terphenyl crystal, however, has not been well investigated, seemingly just because the short lifetime makes the detailed investigation difficult.

Long range migration of excitation energy in organic crystals has been commonly studied with either of the two experimental approaches. One is based on the observation of sensitized luminescence from doped crystals, wherein guest molecules act as emission centers. The intensity2) or the lifetime3–5) of the host and the guest emission is measured as a function of the guest concentration. A bimolecular reaction between a singlet exciton which migrates over the host lattice and a guest molecule is thought to give rise to the guest emission. The other involves the analysis of the bimolecular annihilation of two singlet excitons.6–9 This approach is superior to the former in the sense that doping is not necessary and the possible complications therefrom need not be considered. However, the precise knowledge of the initial concentration and the temporal behavior of the excitons which is needed limits the application of this method to materials with relatively long lifetimes.

In the present work the singlet energy migration in *p*-terphenyl crystal doped with tetracene was investigated with the steady state excitation. This system is ideal in that the solubility of tetracene in *p*-terphenyl crystal is very high. This makes the segregation of microcrystals of the dopant improbable, which is the major difficulty when data for a wide range of dopant concentration is needed. It also means that the distortion of the host lattice caused by the doping will be minimal. Another advantage of the system is the small overlap of the absorption and the emission spectra of *p*-terphenyl crystal. This feature makes the reabsorption of the fluorescence unimportant. It is to be noted also that the host and the guest fluorescence are well separated. The correction for the overlap of the respective fluorescence and for the absorption are accordingly unimportant and hence the quantitative determination of the relative intensity is possible.

Experimental

p-Terphenyl (GR grade, Tokyo Kasei Co.) was purified by column chromatography with activated alumina and by zone melting. The trace amount of tetracene in the starting material was removed by refluxing with maleic anhydried. Perdeuterated *p*-terphenyl (Merck Sharp and Dohme) was purified by chromatography and by zone melting. After extensive zone melting the crystal gave the same fluorescence spectrum as that of the undeuterated compound. The tetracence (Eastman) used as dopant was sublimed *in vacuo*. "Pure" *p*-terphenyl showed no detectable sensitized fluorescence and had a triplet lifetime of ≈100 ms. A weighed amount of tetracence was added to the "pure" *p*-terphenyl to give a sample with a dopant concentration of 10^{-2} mol/mol. Doped crystals of various concentrations were made by successively diluting this highly doped sample with the "pure" *p*-terphenyl. This procedure may be justified because the solubility of tetracene in *p*-terphenyl is practically unlimited, as described below. Crystals with tetracene concentration of 10^{-7} mol/mol prepared with this procedure exhibit faint sensitized fluorescence, whereas the "pure" sample showed no detectable guest fluorescence. This observation eventually showed that the concentration of tetracence in the "pure" sample was less than 10^{-7} mol/mol.

Melting point of doped crystals were measured in a stirred silicone oil bath and were observed visually.

Emission spectra were measured with a fluorescence spectrophotometer (Hitachi, MPF 2A). Temperature was controlled either by flowing cold nitrogen gas in a quartz cryostat or by thermal conduction using liquid nitrogen. The fluorescence lifetime was measured with the single photon counting technique with an air gap spark (pulse width 6 ns) as the excitation light source.

Results

Melting points for the samples with tetracene concentration up to 30 mol% were measured (Fig. 1). The fluorescence spectra of *p*-terphenyl crystal and of tetracene doped in *p*-terphenyl crystal are shown in Fig. 2. Also shown in the figure are the absorption spectrum of *p*-terphenyl and the excitation spectrum of the fluorescence of tetracene doped in *p*-terphenyl monitored at 530 nm. Figure 3 shows the concentration dependence of the ratio I_G/I_H, the intensity of the guest fluorescence observed at 570 nm

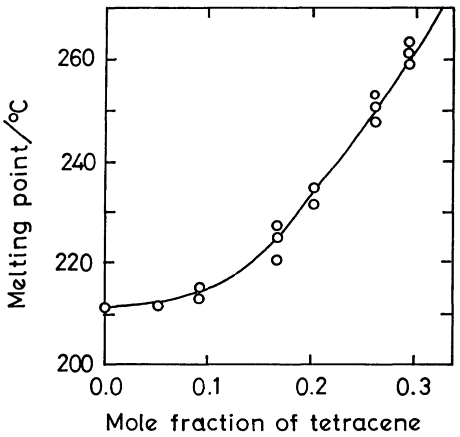

Fig. 1. Melting point of *p*-terphenyl doped with tetracene. The melting point goes up with the concentration of tetracene, indicating that *p*-terphenyl forms a solid solution in this concentration range.

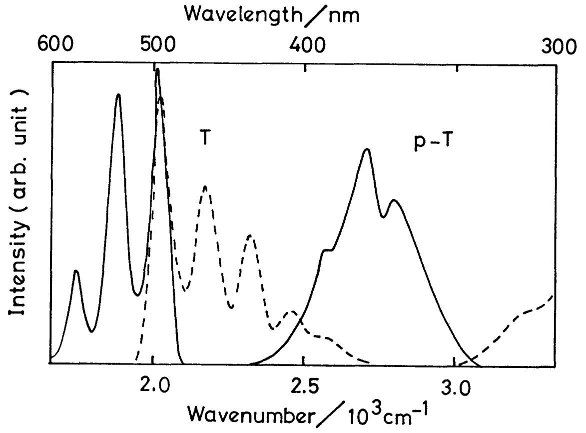

Fig. 2. Full lines (——) show the fluorescence spectra of *p*-terphenyl crystal (*p*-T) and of tetracene (T) doped in *p*-terphenyl. Dashed lines (----) show the absorption spectrum of *p*-terphenyl crystal and the excitation spectrum of the fluorescence of tetracene (as doped in *p*-terphenyl) monitored at 530 nm. The radiative transfer is not important in the system *p*-terphenyl doped with tetracene. The reabsorption of the fluorescence of *p*-terphenyl by *p*-terphenyl itself is also small.

over that of the host fluorescence observed at 370 nm, each corrected for the spectrometer sensitivity and expressed in a unit proportional to photons/s. The result is best fitted by

$$I_G/I_H = Ac_G{}^n, \qquad (1)$$

with

$$A = 5.6\times10^5,\ n = 0.91\pm0.1,$$

for 300 K and

$$A = 9.4\times10^3,\ n = 0.81\pm0.1,$$

for 77 K; c_G is the mole fraction of the guest. The above wavelengths were chosen in order to minimize the effect of reabsorption. Figure 4 shows an effect of the reabsorption. It shows the emission spectra of the guest at different temperatures, excited at 460 nm (direct excitation of tetracene). The intensity of 570 nm peak relative to that at 530 nm is constant, whereas the relative intensity at 500 nm decreases with rising temperature. This is caused by the reabsorption of emitted fluorescence by tetracene itself. Reabsorption is significant at higher temperatures. Figure 5(a) shows the temperature dependence of I_H for an "pure" sample. Figure 5(b) shows the variation of I_H and I_G with temperature for a sample with the guest concentration of 10^{-5} mol/mol. The temperature dependence of I_G/I_H is shown in Fig. 6. Activation energies of 66 cm^{-1} for undeuterated *p*-terphenyl (*p*-T-h_{14}) and 90 cm^{-1} for perdeuterated *p*-terphenyl (*p*-T-d_{14}) were obtained from the slope of the straight parts of the figures corresponding to temperatures lower than 200 K.

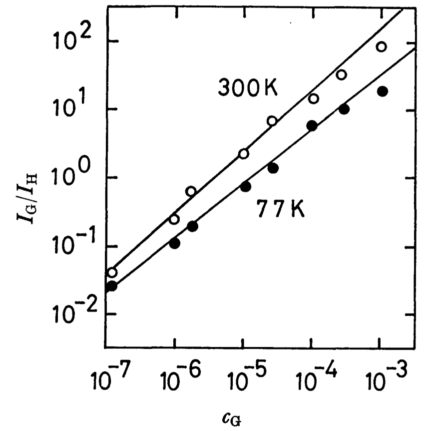

Fig. 3. The relative intensity of the guest fluorescence (I_G) over the host fluorescence (I_H) as a function of the mole fraction of tetracene (c_G).
The intensities are coreected for the detector sensitivity.
○; 300 K, ●; 77 K.

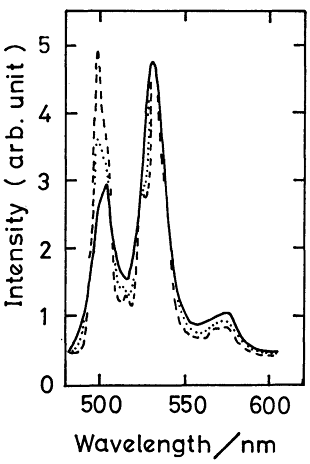

Fig. 4. Fluorescence spectra of tetracene doped in *p*-terphenyl (not corrected) showing the effect of reabsorption at different temperatures. The fluorescence was excited with 460 nm light (direct excitation of the guest).
---- 77 K, ······ 135 K, —— 300 K. $c_G = 1\times10^{-3}$ mol/mol. The intensity of the guest fluorescence (I_G) throughout this work was monitored at 530 nm.

Discussion

Solubility. *p*-Terphenyl exhibits a higher melt-

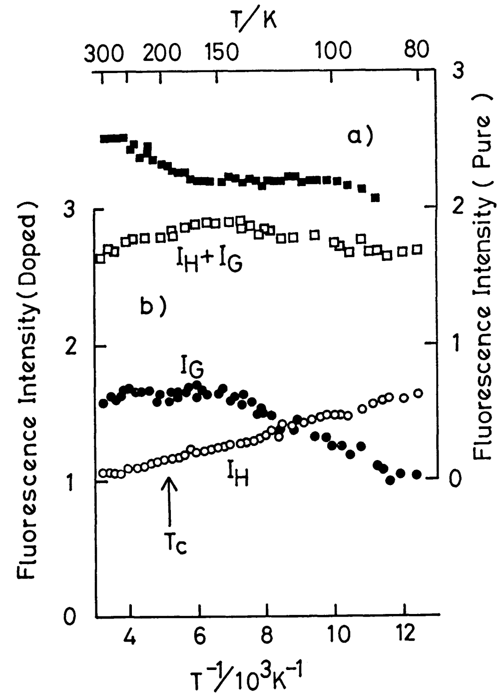

Fig. 5. (a) Temperature dependence of the fluorescence intensity (right ordinate) of an undoped *p*-terphenyl crystal. It is seen that the fluorescence quantum yield is constant within 15%. (b) Temperature dependence of the host (I_H) and the guest (I_G) fluorescence intensity of a doped crystal (left ordinate). Note that the sum (I_H+I_G) is nearly independent of temperature, showing that the radiationless decay is not important. T_c denotes the phase transition temperature.

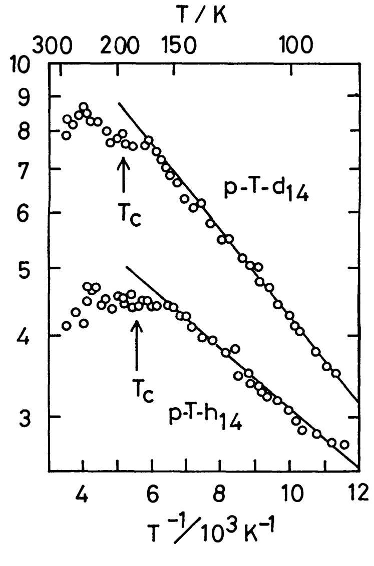

Fig. 6. Temperature dependence of the relative fluorescence intensity (I_G/I_H). Activation energies are 66 cm^{-1} for *p*-T-h_{14} and 90 cm^{-1} for *p*-T-d_{14}. T_c denotes the phase transition temperature.

ing point when it is doped with tetracene (Fig. 1). During zone refining it was noticed that the distribution coefficient k (concentration in the solid phase/concentration in the liquid phase) is larger than unity; tetracene accumulated at the top of the zone refining tube. These facts indicate that the solubility of tetracene in *p*-terphenyl crystal is very high. In this respect this system is basically different from the classical system of tetracene in anthracene, in which the solubility of tetracene is reported to be $\approx 10^{-5}$ mol/mol.[10] *p*-Terphenyl crystallizes in monoclinic form and tetracene has a triclinic lattice, so they are not isomorphic. Accordingly, they can not form a solid solution for the entire concentration range. However, the similar size and shape of the molecules of the two compounds seem to make possible the formation of the solid solution in a rather wide concentration range.

Kinetics. If a *p*-terphenyl crystal (host, hereafter with subscript H) doped with tetracene (guest, hereafter with subscript G) is illuminated with light of intensity I, the rate equations for the concentrations of the host and the guest singlet excited states are[2]

$$dS_H/dt = \alpha I - k_H S_H - k_{HG} S_H, \qquad (2)$$

and

$$dS_G/dt = k_{HG} S_H - k_G S_G, \qquad (3)$$

where α is the absorption coefficient, k_H and k_G are the monomolecular decay constants, and k_{HG} is the rate constant of the energy transfer. In the steady state condition

$$dS_H/dt = dS_G/dt = 0,$$

and the ratio of the fluorescence intensity I_G/I_H is given by

$$I_G/I_H = k_G{}^* S_G/k_H{}^* S_H = k_G k_{HG}/k_H{}^* k_G = \eta_G k_{HG}/\eta_H k_H, \qquad (4)$$

where k^*'s are the radiative rate constants and η's are the fluorescence quantum yields.

The observed concentration dependence of I_G/I_H (Fig. 3) comes from the concentration dependence of k_{HG}, if η_G is constant. This is likely for the low concentration range of concern (10^{-7} to 10^{-3} mol/mol), where the trap-trap interaction must be negligible. If it is assumed that k_{HG} is proportional to the guest concentration, *i.e.*, $k_{HG}=c_G/t_h$, where t_h is the hopping time of the exciton,

$$I_G/I_H = \eta_G c_G/t_h \eta_H k_H. \qquad (5)$$

From the fact that I_G/I_H is unity at the concentration of 5×10^{-6} mol/mol and the observed fluorescence decay time of 5.3 ns ($=1/k_H$) the hopping time, t_h, of an exciton on a lattice site is obtained to be 3×10^{-14} s (300 K) or 6×10^{-14} s (77 K), with an assumption $\eta_G/\eta_H=1$. It is possible that, with this assumption, we underestimate t_h by a factor of 3—5. The hopping time is shorter than that in anthracene, which is in accord with the result by Belitz, who measured the effect of doping on the fluorescence lifetime by using the phase method.[10] The spectral overlap of the host fluorescence and the guest absorption, which is the key factor in determining the host-guest energy transfer efficiency, is larger in anthracene–tetracene mixed crystal than in *p*-terphenyl–tetracene system. In the above analysis we have assumed that the last step of the energy migration, namely the transfer of the excitation energy to the guest molecule, is diffusion-limited. If it is not diffusion-limited, the result in Fig. 3 implies that t_h is even smaller than that given above.

The hyperlinear concentration dependence, *i.e.*, $n<1$ in Eq. 1, has been observed in several materials.[11–14] The deviation is small, but definitely present. It introduces an uncertainty of a factor of 2 in determining the value of k_{HG}. The attempt to explain it by a simple diffusion theory or by random walk consideration has not been successful so far.[15] In this work we analyze the result in terms of the simple hopping model, although the fact $n<1$ is not compatible with the assumption $k_{\mathrm{HG}}=c_{\mathrm{G}}/t_{\mathrm{h}}$, at least in principle. The understanding of this feature awaits further investigation. It is interesting that Auweter *et al.* have found that the time dependent part of k_{HG} in naphthalene crystal is important for low dopant (anthracene) concentrations and that it is not simply proportional to the guest concentration.[9] It is to be noted that the hyperlinear dependence has been observed only for singlet energy transfer, but not for triplet.

Temperature Dependence of the Energy Transfer. The temperature dependence is quite different from that for anthracene and for naphthalene. In anthracene crystal the rate constant for the bimolecular annihilation, γ_{ss}, has been found to be proportional to $T^{-1/2}$; this has been explained in terms of the scattering of excitons by phonons.[16] In naphthalene, γ_{ss} is almost temperature independent.[9] Figure 4 shows that the fluorescence quantum yield of tetracene in *p*-terphenyl lattice, when corrected for the reabsorption, is independent of temperature. It is shown in Fig. 5(b) that I_{G} and I_{H} change with temperature, whereas the sum, $I_{\mathrm{H}}+I_{\mathrm{G}}$, shows only a slight variation in the temperature range 85—300 K. This shows that the quantum yield of the total fluorescence from the mixed crystal does not change within this temperature range and indicates that the effect of the traps for singlet excitons that may act as quenchers is not significant. Thus it seems reasonable to assume that the observed temperature dependence of $I_{\mathrm{G}}/I_{\mathrm{H}}$ (Fig. 6) corresponds to that of k_{HG}. We may thus conclude that the energy transfer in *p*-terphenyl crystal is almost temperature independent in the temperature range 300—160 K (*p*-T-h_{14}) or 300—170 K (*p*-T-d_{14}) and that at lower temperatures the temperature dependence changes to that with an activation energy.

p-Terphenyl undergoes a phase transition around 190 K.[17–20] In the high temperature phase the molecules are planar. However, the amplitude of the rotational vibration of the central benzene ring about the molecular long axis is large and is better analyzed with the model in which the rotational vibration has a double well potential.[21] The sign of the resulting tilt of the central ring is random and no long range order is present. Below the transition temperature, however, the tilt of the central ring occurs in an ordered fashion, similar to the spins in antiferromagnetic materials. It has been observed that the order parameter grows as the temperature goes down. Hence the transition is thought to be of the order-disorder type.[22,23] It is proposed that a *p*-terphenyl molecule in its electronic ground state is non-planar, whereas in the excited state it is planar. This is based on the observation that the absorption spectrum of the compound in the solution lacks any vibrational structure, whereas its fluorescence spectrum is clearly structured.[1] It is also known that the absorption spectrum becomes more structured when the molecule in a viscous solution is excited to higher excited states.[24] In view of this conformational change accompanying the electronic excitation, the following mechanism of the energy transfer seems to be probable. A *p*-terphenyl molecule in a crystal takes the planar conformation when it is excited. Energy transfer to a neighboring molecule takes place equienergetically only when the latter takes the planar conformation. In this simplified model the energy barrier for the rotation of the central ring is expected to manifest itself in the temperature dependence of the energy transfer. When the four hydrogen atoms attached to the central benzene ring are replaced by four deuterium atoms, the moment of inertia about the molecular long axis increases by some 20% and the zero point energy becomes correspondingly lower. Accordingly, the activation energy ΔE is expected to be larger in *p*-T-d_{14} compared to *p*-T-h_{14} (Fig. 7), which is consistent with our observation. One could argue that the temperature dependence is caused by the presence of traps for excitons and the observed activation energies correspond to the trap depth. This possibility is denied by estimating the number of traps. Let us assume that the fraction x of the molecular sites is occupied by traps (impurities or displaced molecules), the depth of which is ΔE. The fraction $1-x$ is thus occupied by normal host molecules. An exciton migrates with occasional trapping. Detrapping is possible because ΔE (66 cm^{-1} or 90 cm^{-1}) is comparable to, or smaller than, kT for the temperature range investigated. The average hopping time of an exciton will be

$$t_{\mathrm{h}} = (1-x)t_{\mathrm{h}}{}^{0} + xt_{\mathrm{h}}{}^{0}\exp(-\Delta E/kT), \tag{6}$$

where $t_{\mathrm{h}}{}^{0}$ is the hopping time between two normal

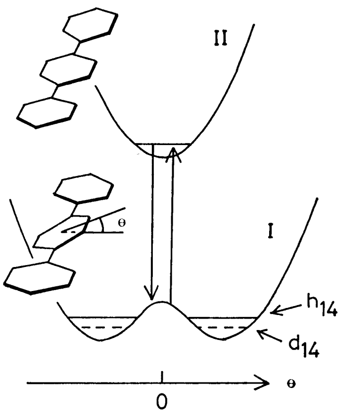

Fig. 7. A model for the intermolecular energy transfer in *p*-terphenyl crystal. In the electronic ground state (I) the molecule has a double well potential as regards the rotation of the central ring around the molecular long axis (θ). A molecule in the excited state (II) transfers its energy to a neighboring molecule equienergetically when the latter takes the planar conformation. The difference in the librational zero point energy of *p*-T-h_{14} and of *p*-T-d_{14} may account for the difference in the activation energies.

molecules. The observed temperature dependence of I_G/I_H could not be fitted with this model with x smaller than 0.8. This obviously contradicts the idea that a very low concentration of unidentified impurity is affecting the results. The fact that the temperature below which the plot log (I_G/I_H) *vs.* $1/T$ is linear corresponds roughly, although not exactly, to the transition temperature also seems to support our view that the temperature dependence, as well as the effect of deuterium substitution, is not determined by impurities, but is intrinsic.

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