# Exciton Phosphorescence of p-Terphenyl Crystal at 300 K

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Exciton phosphorescence from pure p-terphenyl crystals was observed at 300 K. The 0—0 band of the phosphorescence spectrum was found at $20.4 \times 10^3$ cm$^{-1}$. The vibrational progression of $1.46 \times 10^3$ cm$^{-1}$ is present. The maximum exciton lifetime observed was 200 ms. The excitation spectrum of the exciton phosphorescence differs considerably from that observed in glassy solution, but is poorly structured as well. The absorption coefficient near the origin is small. The absence of sensitized delayed fluorescence from doped tetracene suggests that the triplet energy transfer to this guest is not diffusion limited.

## Introduction

Phosphorescence of organic molecules originates from their metastable triplet states. Phosphorescence is easily observed with frozen glassy solutions because radiationless processes are suppressed in rigid matrices and the quantum yield of the phosphorescence is accordingly high. In the crystalline state the triplet state can migrate through the crystal lattice. Radiative decay, namely phosphorescence, of this exciton state competes with the following processes.

1) The migration of excitons leads to an efficient energy transfer to impurity molecules or lattice defects. Typically an exciton surveys $10^7$ molecules before it dies away either radiatively or nonradiatively [1]. These imperfections may emit impurity phosphorescence or defect phosphorescence, or may act as quenching centers, if they do not radiate the transferred energy.

2) The collision and annihilation of two migrating triplet excitons gives rise to delayed fluorescence (DF). This process is proportional to the square of the triplet concentration and constitutes a very efficient decay route when the triplet concentration is high.

These processes reduce the quantum yield of the radiative decay and make the observation of the phosphorescence difficult. Most observations of the phosphorescence of crystalline materials have accordingly been limited to crystals of heterocyclic compounds or ketones where the radiative decay from $n\,\pi^*$ triplet states is relatively fast [2]. Compounds such as 1,4-dibromonaphthalene also emit phosphorescence at room temperature because the presence of heavy atoms in these molecules enhances the spin-orbit coupling which mixes singlet and triplet states [3]. The radiative transition between the singlet ground state and the triplet states in aromatic hydrocarbons is an example of stricly forbidden transitions. Its transition probability is some eight orders of magnitude smaller than that of allowed singlet to singlet transitions [4]. To date the phosphorescence from free excitons in hydrocarbon crystals is reported only for anthracene [5], naphthalene [6] and pyrene [7].

We report here the observation of exciton phosphorescence of pure p-terphenyl crystals at 300 K. The exciton state of this compound is interesting because there is the possibility that the p-terphenyl molecule has different conformations in different electronic states and this could be reflected in the behavior of the excitons.

## Experimental

p-Terphenyl (GR grade, Tokyo Kasei Co.) was purified by zone melting. A small amount of maleic anhybride was added to the starting material to eliminate trace amounts of tetracene which was present as impurity. The middle portion of the zone refined material was transferred to a new tube and further zone refined. The lifetime of the triplet exciton $\tau_T$ was monitored by measuring the decay time of the delayed fluorescence $\tau_{DF}$. The apparatus used is shown in Figure 1. The photon flux in the excitation light was measured using a Rhodamine B quantum counter [8]. All measurements were made at room temperature except otherwise stated.

Fig. 2. The delayed emission spectrum from a p-terphenyl crystal at 300 K. It consists of two components with different decay times. DF denotes the vibrational structure of the delayed fluorescence. Structure indicated by P is assigned to the phosphorescence.

The lifetime of the triplet exciton became longer as the zone refining was repeated. A maximum lifetime of 200 ms was attained. Judged from the absence of sensitized (prompt) fluorescence the possible concentration of tetracene is below $10^{-7}$ mol/mol [9]. The triplet lifetime of p-terphenyl crystals was relatively insensitive to oxygen or UV irradiation once the crystals were grown, although it was greatly reduced if the material was exposed to oxygen during the purification process. During a measurement over several days in air only a slight decrease of $\tau_T$ was detectable.

### Results

The spectrum of the delayed emission is shown in Figure 2. It consists of two components with different decay times. The ratio of the intensity of the emission the wavelength of which is shorter than 450 nm ($I_{BLUE}$) and that of the emission the wavelength of which is longer than 490 nm ($I_{GREEN}$), $I_{GREEN}/I_{BLUE}$, was different for each sample and larger for samples of smaller $\tau_{DF}$ ($\tau_{BLUE}$). The excitation spectrum of the green emission is shown in Figure 3. The intensity of the green emission was found to be proportional to the excitation intensity over two decades for excitation wavelengths longer than 390 nm, i. e., beyond the onset of the strong singlet absorption (Figure 4). Figure 5 shows that the decay time of the green emission is twice as long as that of the blue emission. We verified that the
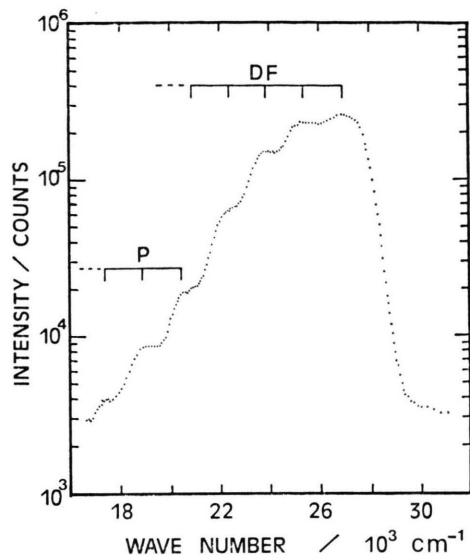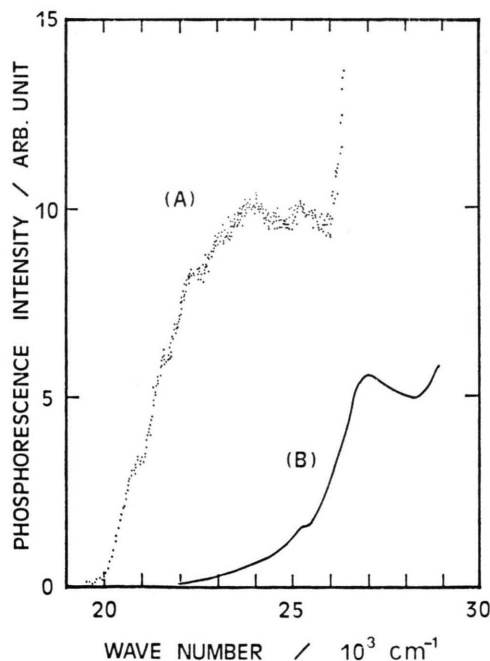


Fig. 3. (A) Excitation spectrum of the green emission from a p-terphenyl crystal at 300 K. (B) Excitation spectrum of the phosphorescence of p-terphenyl in rigid organic matrix at 77 K.
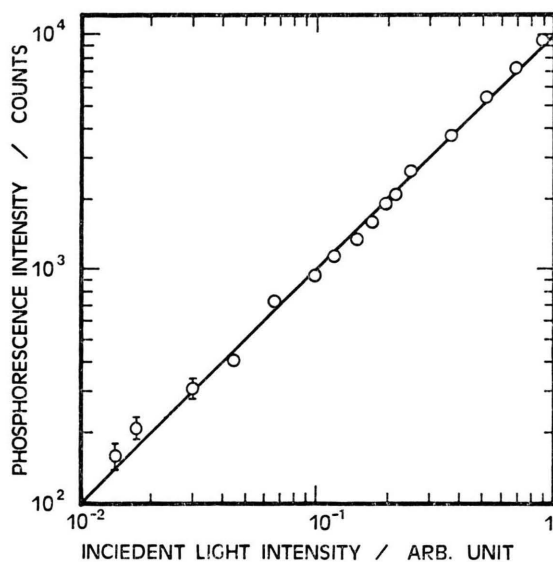
Fig. 4. The intensity of the green emission as a function of the intensity of the excitation light (400 ∼ 500 nm). A linear relationship holds over two orders of magnitude, indicating that the emission is not delayed fluorescence, but phosphorescence.



Fig. 5. The decay of the green and the blue emission. The relationship $\tau_{\text{GREEN}} = 2\,\tau_{\text{BLUE}}$ was found for all samples with triplet lifetimes ranging from 200 ms to 7 ms. This relationship clearly shows that a common state is responsible for both emissions.

relationship

$$2\,\tau_{\text{BLUE}} = \tau_{\text{GREEN}}$$

held for all samples tested which had triplet lifetimes ranging from 200 ms to 7 ms, although the green emission from crystals with short lifetimes was very weak. Some of these samples were intentionally doped with rather high concentrations of tetracene (up to $10^{-3}$ mol/mol).

Decay times of the delayed emission for a pure crystal as well as samples doped with anthracene, perylene or tetracene are summarized in Table 1. Crystals containing anthracene or perylene as guests showed spectra which indicate that both host and guest molecules are emitting delayed fluorescence.
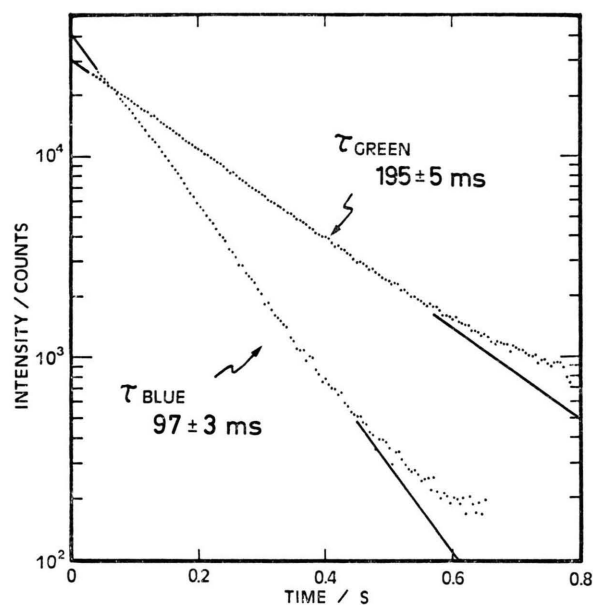
## Discussion

### 1. Decay Kinetics

When a p-terphenyl crystal is excited to its optically allowed state by light of intensity $I$, the rate equations for singlet and triplet excitons are [1]

$$dn_{\text{S}}/dt = \sigma_{\text{S}}\,I - k_{\text{S}}\,n_{\text{S}} - k_{\text{ISC}}\,n_{\text{S}} + (f/2)\,\gamma\,n_{\text{T}}^2 \qquad (1)$$

and

$$dn_{\text{T}}/dt = k_{\text{ISC}}\,n_{\text{S}} - k_{\text{T}}\,n_{\text{T}} - (1/2)\,\gamma\,n_{\text{T}}^2 , \qquad (2)$$

where $\sigma_{\text{S}}$ is the absorption coefficient, $k_{\text{S}}$ and $k_{\text{T}}$ are the monomolecular decay rate constants of singlet

Table 1. The lifetimes of delayed emissions in doped and undoped p-Terphenyl crystals.

| Guest | $E(T_1)$/cm$^{-1}$ | $\Delta E$/cm$^{-1}$ [c] | $\tau_{\text{BLUE}}$ /ms | $\tau_{\text{GREEN}}$/ms [d] |
|---|---|---|---|---|
| — | 20400 [a] | — | 65 | 140 |
| — | 20400 | — | 100 | 200 |
| Anthracene | 14700 [b] | 5700 | 6 | 7 |
| Perylene | 12600 [b] | 7800 | 7 | 8 |
| Tetracene | 10200 [b] | 10200 | 6 | 12 |
| Tetracene | 10200 | 10200 | 3.5 | 7 |

[a] This work.

[b] G. Porter and M. Windsor, Proc. Roy. Soc. London, **245 A**, 238 (1958).

[c] The difference of the triplet energy of the host (p-terphenyl) and that of the guest.

[d] For anthracene or perylene as guest the long-lived emission which has the wavelengths corresponding to the fluorescence of the respective compound was monitored.

and triplet excitons, respectively, $k_{ISC}$ is the intersystem crossing rate constant and $\gamma$ is the rate constant for the triplet-triplet bimolecular annihilation. The factor $f$ stands for the fraction of annihilated triplet pairs that yield singlet excitons. The intensity of the delayed fluorescence, $I_{DF}$, is expressed as

$$I_{DF} = \varphi_F (f/2) \gamma \, n_T^2 , \qquad (3)$$

where $\varphi_F$ is the fluorescence quantum yield. The intensity of the phosphorescence is given by

$$I_P = k_P^* \, n_T , \qquad (4)$$

where $k_P^*$ is the radiative rate constant of the process $T_1 \rightarrow S_0$. If the concentration of triplet excitons is not very large (e. g., long after the excitation is shut off)

$$I_{DF} \propto n_T^2 \propto \exp(-2 \, k_T \, t) \qquad (5)$$

and

$$I_P \propto \exp(-k_T \, t), \qquad (6)$$

hence the decay time of the delayed fluorescence, $\tau_{DF} = 1/2 \, k_T$, is one half that of the decay time of the phosphorescence, $\tau_P = 1/k_T$. Figure 5 indicates that the green emission ($\lambda \geq 490$ nm) is the phosphorescence originating from the triplet state that is responsible for the delayed fluorescence (blue emission). We suggest that the observed luminescence is due to free triplet excitons. If we assume instead that the observed fluorescence arises via annihilation of free and trapped excitons we must consider that the lifetime of the free excitons manifests itself in the lifetime of the delayed fluorescence. (Trapped excitons are thought to be longer lived, because the collisional deactivation by imperfections is absent for the trapped excitons.) Then the green emission has to be assigned to the phosphorescence from trapped excitons. As the relationship $\tau_{GREEN} = 2 \, \tau_{BLUE}$ always helds irrespective of the quality of the crystals investigated, we do not think that $\tau_{GREEN}$ is the lifetime of trapped excitons, which must be specific for the nature of the traps. The fact that the sensitized delayed fluorescence emitted by anthracene or perylene as guest had the same decay time as that of the host delayed fluorescence (Table 1), whereas the green emission of "pure" crystals decayed with $2 \, \tau_{DF}$ seems to preclude the possibility that the green emission is either (1) impurity phosphorescence or (2) delayed fluorescence arising from heterofusion with some unidentified impurity.

## 2. Relative Intensity of Phosphorescence vs. Delayed Fluorescence

In the time-averaged emission spectrum the intensity of the phosphorescence relative to that of the delayed fluorescence was found to be larger for crystals with smaller $\tau_T$. In the steady state $I_P$ and $I_{DF}$ are expressed as

$$I_P = k_T [k_{ISC}/(k_S + k_{ISC})] \alpha \, I \, \tau_T \qquad (7)$$

and

$$I_{DF} = (f/2)\gamma [k_{ISC}/(k_S + k_{ISC})]^2 \, \alpha^2 \, I^2 \, \tau_T^2 \qquad (8)$$

by solving the Eqs. (1) and (2) for the steady state. Thus we obtain the ratio

$$I_P/I_{DF} \propto (1/\tau_T) \exp(\Delta/\tau_T) \qquad (9)$$

where $\Delta$ is the dead time of the phosphoroscope. (9) is consistent with the above observation.

## 3. Phosphorescence Spectrum and Excitation Spectrum of Phosphorescence

The spectrum of the exciton phosphorescence shown in Fig. 2 has a similar vibrational structure as that in the phosphorescence spectrum of p-terphenyl in a rigid matrix [10]. Comparing spectra of several samples with various lifetimes, which accordingly differ in the ratio of delayed fluorescence and phosphorescence intensity, we assigned the peak at $20.4 \times 10^3$ cm$^{-1}$ to the $0-0$ band of the $T_1 \leftarrow S_0$ transition. This compares with $20\,490$ cm$^{-1}$ reported for the ragid matrix spectrum [10]. A vibrational progression of $1.46 \times 10^3$ cm$^{-1}$ is present.

The excitation spectrum of the phosphorescence, on the other hand, differs considerably from that in the rigid matrix [10], as seen in Figure 3. The spectrum has the onset at $20.0 \times 10^3$ cm$^{-1}$ and is poorly structured. Above $26 \times 10^3$ cm$^{-1}$ the spectrum shows a steep rise, which seems to be due to the tail of the strong $S_1 \leftarrow S_0$ absorption. A very weak structure with $700 \sim 800$ cm$^{-1}$ separation is seen, but the possibility that this structure is due to an error in the correction of the excitation intensity can not be excluded. The absorption coefficient near the origin is small. This is in contrast to the spectra of anthracene, naphthalene or perylene, where the $0-0$ band is sharp and has a large intensity. It is interesting to note that trans-stilbene, which may have also a freedom of conformational change in the electronically excited states shows a similar behavior [11].

*4. Sensitized Delayed Fluorescence. Is Delayed Fluorescence Always Very Sensitive to Minute Amounts of Impurities?*

It is generally accepted that delayed fluorescence is very sensitive to small amounts of impurities when the impurity molecules have lower triplet energies than the host. Table 1 shows that tetracene is an exception in this respect. There is no indication that tetracene emits sensitized delayed fluorescence even if the concentration of tetracene is as high as $10^{-3}$ mol/mol. It has been found that tetracene forms a solid solution with p-terphenyl and the solubility of tetracene in p-terphenyl is practically unlimited in the concentration range studied [9]. The sensitized delayed fluorescence from anthracene or perylene was not strong either. These findings seem to indicate either of the following two possibilities.

1) The assumption often made that the transfer of triplet energy to guest molecules is limited by diffusion of the excitons is not correct. The energy transfer between host and guest has specific rate constants (i. e., reaction limited).

2) The energy transfer is diffusion limited, but the annihilation of a trapped exciton with an exciton migrating over the host lattice (heterofusion) gives rise only to excited host, but not guest, molecules in the case of tetracene in p-terphenyl.

The second assumption contradicts the result obtained in the pyrene in naphthalene system [12] and, moreover, does not explain the observation made on the present system. Tetracene emits sensitized fluorescence efficiently when it is included in the p-terphenyl lattice. The transfer of singlet energy seems to be diffusion limited [9]. Accordingly it is difficult to understand why the singlet excitation created just next to the impurity tetracene molecule is not transferred to it. Baessler et al. observed a decay of the sensitized delayed fluorescence from doped crystals and concluded that the transfer time (i. e., the reciprocal of the transfer rate constant) of the triplet energy between host and guest, $\tau_{DA}$, is governed by an energy gap law similar to that found in intramolecular radiationless transitions, namely

$$\tau_{DA} = \tau_{DA}^0 \exp\left(\Delta E/E_0\right) \tag{10}$$

with $E_0 = 0.115 \pm 0.01$ eV, where $\Delta E$ is the energy difference of the triplet state of host and guest [13]. p-Terphenyl seems to be another candidate which illustrates this rule. The triplet level of p-terphenyl is situated relatively high (Table 1). In the tetracene in p-terphenyl system $\Delta E$ is 1.35 eV. This energy gap is far larger than the largest gap (0.83 eV) investigated by Baessler et al. If one puts this value into Eq. (10), one obtains $\tau_{DA}/\tau_{DA}^0 \sim 1.2 \times 10^7$, which implies that the transfer of triplet energy occurs with $\sim 10^{-7}$ of the diffusion controlled rate. This may account for the above observation, although a quantitative investigation remains to be made.

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