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Fluorescence Spectra and Energy Migration Behavior of *o*-Terphenyl Single Crystal and Glassy Solid

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Fluorescence spectra of very pure *o*-terphenyl single crystal and glassy solid were observed and their origins were assigned to intramolecular excimer states. For the anthracene-doped *o*-terphenyl solids, the concentration dependence and/or time evolution behavior of the fluorescence spectra showed that the energy transfer really occurs even in the glassy solid and its rate is of nearly the same order of magnitude as in the crystal.

INTRODUCTION

When solids lose their structural long-range order and become amorphous, some properties may significantly change. Such a correlation between structure and property of solids has recently been a challenging subject in the field of solid state physics or chemistry. Although the fundamental ways of approach to the analysis of disordered systems have been explored rather systematically and applied to various inorganic solids,[1] few have been attempted and known for the organic disordered solids.

In this report, we will describe the results of observations of the fluorescence spectra and energy migration behavior of *o*-terphenyl solids and compare these phenomena in the glassy state with those in the crystalline state. *o*-Terphenyl has been known to form either a stable glassy or crystalline state in some temperature region below 240 K depending on the quenching speed from its melt. This may be due to its molecular structural characteristic, that is, the non-coplanarity of the molecule due to the steric hindrance between two phenyl rings substituted at *ortho*-sites.[3]

The electron drift mobilities in the crystalline and glassy state of *o*-terphenyl solids have been observed and their anomalous temperature dependences have also been tentatively analyzed.[4]

EXPERIMENTAL

Samples: Commercial *o*-terphenyl, or 1,2-diphenyl benzene, (Tokyo Kasei, 98% GCgrade) was purified firstly by repeated recrystallizations from ethyl acetate and/or *n*-heptane solutions and further by column chromatography on basic alumina and vacuum sublimation. Finally it was passed through about 1200 zones in a specially designed zone-refining system.[5] Synthesized anthracene was also purified by the usual zone-refining method.

Pure or anthracene doped *o*-terphenyl polycrystalline solid was put into a cylindrical quartz tubecell (5 mm in diameter) and sealed off with 0.5 atm He gas after proper evacuation. After melting the sample, while leaving a small seed crystal at the bottom of the cell, a single crystal was grown by the Bridgman technique. The glassy solid was prepared by rapid quenching of the molten solid by liquid N_2.

Fluorescence measurement: Stationary fluorescence and its time-resolved spectra were observed for pure and anthracene-doped *o*-terphenyl solids. Transient time-response behaviors were also measured at several wavelengths. The excitation light used for these measurements was a second harmonics generated through a KDP crystal which was fed the output of a N_2-laser (NRG, Model 0.2-5-200) pumped dye (Rhodamin-6G)-laser (NRG, Model DL-0.03). Its specifications were 287 nm in wavelength, 7 ns in duration and 50 Hz in repetition rate. The emitted light in the right angle direction from a sample was focused at the inlet slit of a grating monochromator (OPTEC, GM-N300) and detected by a HTV-R955 photomultiplier. Photocurrents were properly averaged with a Boxcar Integrator (PAR, Model 162, 163 and 164) and recorded by a X-Y Recorder (Rikendenshi, Model D-72C). All measurements were carried out at 88 K in a heat-exchange type cryostat. No intensity correction was made for the spectra shown here.

RESULTS AND DISCUSSION

1. Pure *o*-terphenyl solids

Figure 1 shows the fluorescence spectra of an *o*-terphenyl single crystal and a glassy solid at 88 K. Both spectra are rather broad and have no distinct vibrational structures which are present in the emission spectra of ordinary aromatic hydrocarbons. Sangster and Irvine reported the fluorescence spectrum of *o*-terphenyl single crystal which is illustrated as *c* in Figure 2.[6] Their spectrum shifts to longer wavelength side compared with the present one (*a* in Figure 2). Since the present sample was purified more elaborately than the previous one, and its time-resolved fluorescence spectra (300–500 nm) showed no time dependent change within the time scale of 0 (8 ns) to 16 ns, curve *a* may be assigned to the intrinsic *o*-terphenyl fluorescence.

The broadness of the crystalline spectrum in Figure 1 may be ascribed to the intramolecular excimeric nature of this band based on the following reasons. Besides the fact that there is no vibrational structure, the peak wavelength of crystalline emission is almost the same as that in solution and their Stokes shifts are extraordinarily large.[7] The band shape of this spectrum was almost independent of the temperature (88–300 K), and it is very similar to the benzene excimer in the liquid state.[8]

On the other hand, the fluorescence spectrum in the glassy state in Figure 1 seems to be essentially the same as in the crystalline state except its broader band width, which may be caused by the structural disorder of the solid.

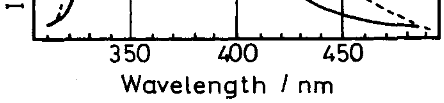

FIGURE 1 Fluorescence spectra of an *o*-terphenyl crystal (solid line) and a glassy solid (dashed line) at 88 K.

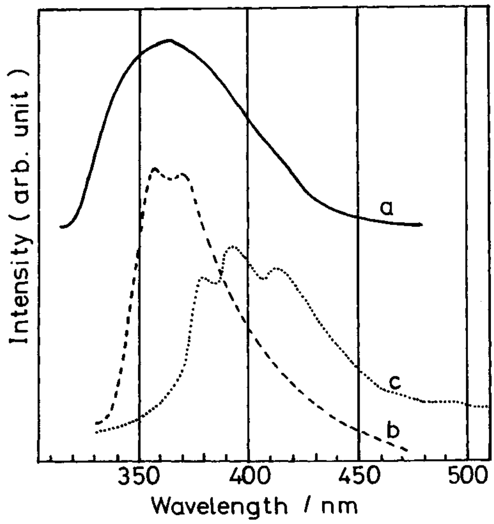

FIGURE 2 Fluorescence spectra of *o*-terphenyl at room temperature. (a) Present work, crystal (b) Present work, in cyclohexane solution (c) Sangster and Irvine, crystal.

2. Anthracene doped *o*-terphenyl solids

2.1 Crystalline state

The fluorescence spectra of *o*-terphenyl single crystals doped with anthracene in various concentrations are shown in Figure 3. Intensity ratios of both components, *o*-terphenyl and anthracene, were evaluated by subtracting the pure *o*-terphenyl component from each mixed crystal spectrum. These ratios were found to be roughly proportional to the anthracene concentrations.

The time-resolved spectra of sample *E* shown in Figure 4 clearly manifest the time evolution of two kinds of fluorescence bands, ~360 nm (*o*-terphenyl) and ≳400 nm (anthracene). The origin of the clock in this measurement was at the start point of the excitation light pulse. Moreover, the direct time response curve for the 460 nm band (anthracene) clearly shows the delay of a few nanoseconds at the onset point from the 360 nm band (*o*-terphenyl) as shown in Figure 5. The decaytime constant for the *o*-terphenyl (360 nm) curve was roughly estimated to be 8.9 ns and the risetime constant for anthracene (460 nm) band was about 8.4 ns. These time constants are just coincident with each other within experimental error. Although there still remains a deconvolution analysis to be done with respect to the finite excitation pulse width (7 ns) for a more elaborate

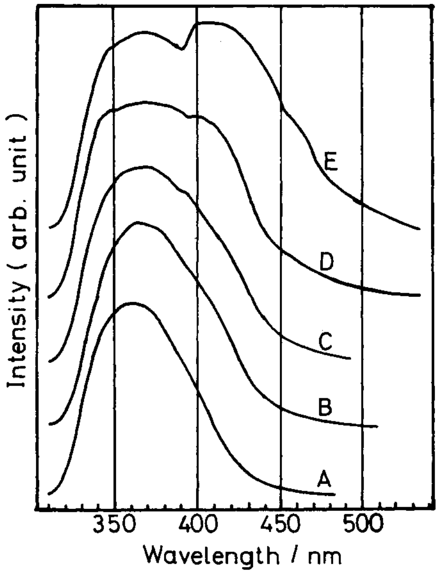

FIGURE 3 Fluorescence spectra of *o*-terphenyl crystals doped with anthracene at 88 K. A: pure, B: 3.0×10^{-5} mol/mol, C: 9.0×10^{-5} mol/mol, D: 9.4×10^{-4} mol/mol, E: 2.5×10^{-3} mol/mol.

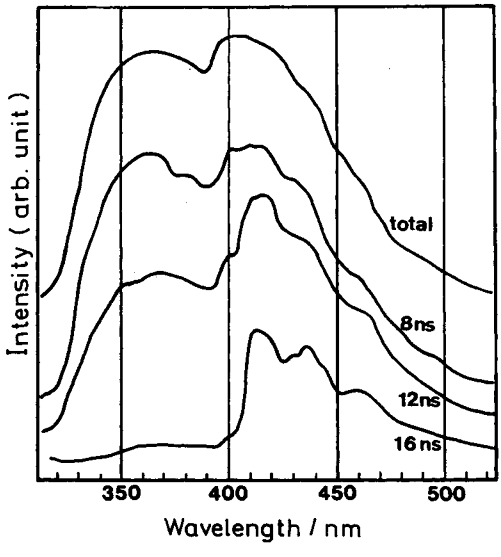

FIGURE 4 Time-resolved fluorescence spectra of a mixed crystal (2.5×10^{-3} mol/mol) at 88 K. Each sampling time after excitation is indicated and sampling gate duration was 75 ps except for the curve "total" (~50 ns gate).

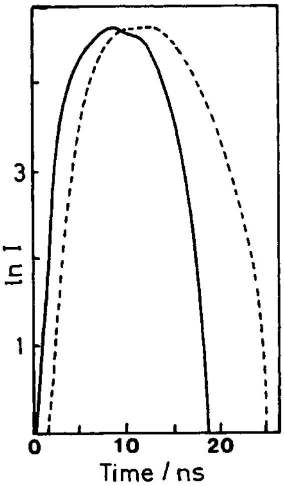

FIGURE 5 Time response curve of fluorescence intensity for 360 nm (solid line) and 460 nm (dashed line) emissions of the mixed crystal (E: 2.5 × 10^{-3} mol/mol) at 88 K.

discussion, all these observations described above indicate a Stern-Volmer type energy transfer in these *o*-terphenyl mixed crystals.

2.2 Glassy state

The fluorescence spectra of *o*-terphenyl glassy solids doped with anthracene in various concentrations are shown in Figure 6. The striking differences between the mixed glass and crystal spectra are the occurrence of distinct structures in the *o*-terphenyl bands and the clear appearance of molecular anthracene emission in the mixed glass spectra. It can be clearly seen from the time-resolved spectra in Figure 7 that these split bands come from the *o*-terphenyl component. One possible origin for this splitting may be a characteristic deformation of the *o*-terphenyl molecules around the doped anthracene. These locally rather ordered *o*-terphenyl molecules may form a few discrete emission levels. The time response curves for both emission components are shown in Figure 8. The same order of delay at the onset of anthracene emission as in the crystals can be recognized.

3. Kinetic analysis on energy migration

Overall energy evolution behavior in these systems, crystal and glass, is schematically illustrated in Figure 9. In the case of the glass, each level

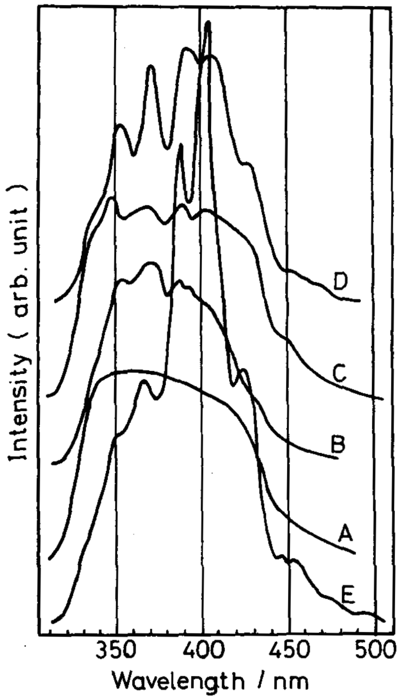

FIGURE 6 Fluorescence spectra of *o*-terphenyl glassy solids doped with anthracene at 88 K. A: pure, B: 3.0×10^{-5} mol/mol, C: 1.8×10^{-4} mol/mol, D: 9.4×10^{-4} mol/mol, E: 2.5×10^{-3} mol/mol.

may spread somewhat broadly and the rather discrete levels in the intramolecular excimer exciton band(E) speculated above are shown by dotted lines. The time dependence of the density, n_E, of intramolecular excimer exciton is,

$$dn_E/dt = \alpha I - (k_E + k_E')n_E - k_{EA}n_En_A \qquad (1)$$

where n_A is the density of anthracene and the definitions of other symbols are stated in the figure caption. Similarly, the density, n_{A^*}, of the excited anthracene molecules can be written as

$$dn_{A^*}/dt = k_{EA}n_An_E - k_An_{A^*} \qquad (2)$$

Under stationary condition, the fluorescence intensity I_E from the excimer state and I_A from the excited anthracene are expressed as the following using (1) and (2),

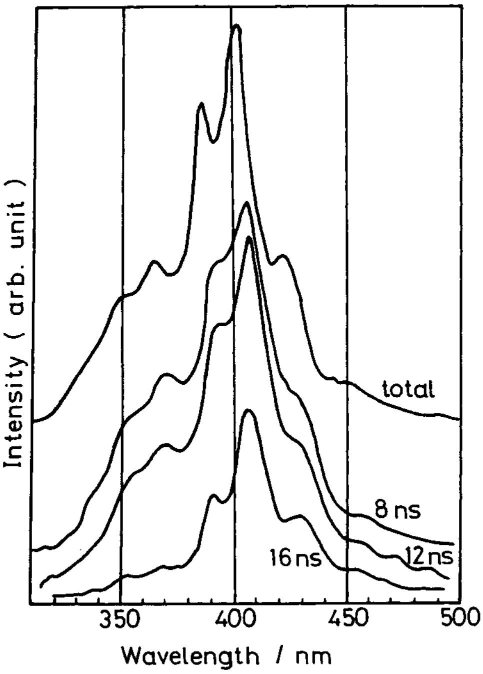

FIGURE 7 Time-resolved fluorescence spectra of a mixed glass (2.5 × 10^{-3} mol/mol) at 88 K. Each sampling time after excitation is indicated and the sampling gate duration was 75 ps except for the curve "total" (~50 ns gate).

$$I_E = k_E n_E = k_E \alpha I/(k_E + k_E' + k_{EA} n_A) \tag{3}$$

and

$$I_A = q_A k_A n_{A^*} = q_A k_{EA} n_A n_E = q_A k_{EA} n_A \alpha I/(k_E + k_E' + k_{EA} n_A) \tag{4}$$

where q_A is the fluorescence quantum yield of anthracene. Thus, the ratio of these intensities, (3) and (4), is,

$$I_A/I_E = q_A k_{EA} n_A/k_E = K n_A\,, \qquad K \equiv q_A k_{EA}/k_E \tag{5}$$

From the analysis of the spectra for mixed solids (Figures 3 and 6), we obtained the following K values; 2.46 × 10^2 for the crystalline state at 88 K and 2.50 × 10^2 for the glassy state at 88 K. Assuming q_A and k_E are nearly the same for both states, we may conclude that k_{EA}s, energy transfer rates from *o*-terphenyl to anthracene, for both states are of the same order of magnitude. Moreover, we observed the similar mixed crystal spectra at room temperature (293 K) and obtained 8.22 × 10^2 for K. Thus, by a

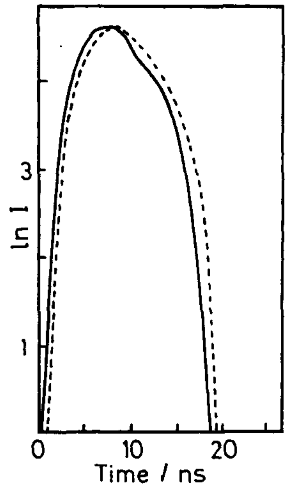

FIGURE 8 Time response curve of fluorescence intensity for 360 nm (solid line) and 400 nm (dashed line) emissions of the mixed glass (3.0 × 10^{-5} mol/mol) at 88 K.

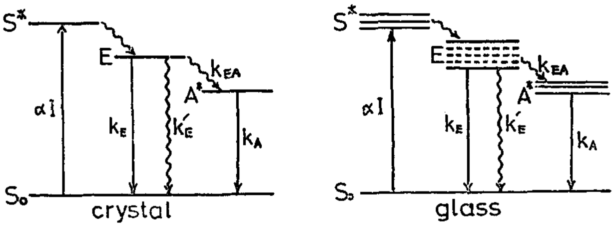

FIGURE 9 Schematic diagrams for the energy evolution behavior in *o*-terphenyl crystal and glass. α: absorption coefficient, I: excitation light intensity, k_E and k_E': radiative and non-radiative transition rates of the intramolecular excimer exciton state (E), respectively, k_{EA}: energy transfer rate from E to A, and k_A: radiative transition rate of excited anthracene.

similar assumption, we may say that k_{EA} at 293 K is 3.3 times larger than that at 88 K.

On the other hand, under transient condition, the fluorescence intensities $I_E(t)$ and $I_A(t)$ are obtained by solving eqs. (1) and (2) respectively

$$I_E(t) = k_E n_E(t) = k_E n_E(0) e^{-(k_E + k_E' + k_{EA} n_A)t}$$

and

$$I_A(t) = q_A k_A n_{A*}(t) = \frac{q_A k_A k_{EA} n_A n_{\mathrm{E}}(0)}{k_E + k_E' + k_{EA} n_A - k_A} \{e^{-k_A t} - e^{-(k_E + k_E' + k_{EA} n_A)t}\}.$$

From the decaytime of the host, *o*-terphenyl, and the risetime and decaytime of the guest, anthracene, we obtained the relations

$$k_E + k_E' + k_{EA}n_A = 1.1 \times 10^8 s^{-1}$$

and

$$k_A = 9.1 \times 10^7 s^{-1}$$

for the mixed crystal (2.5×10^{-3} mol/mol) at 88 K. Since we can evaluate the term ($k_E + k_E'$) to be $1.0 \times 10^8 s^{-1}$ making use of the pure *o*-terphenyl decaytime, we finally obtained k_{EA} for the *o*-terphenyl mixed crystal at 88 K

$$k_{EA} \simeq 4 \times 10^9 s^{-1}.$$

The reported k_{EA} for anthracene crystal and disordered thin film are $\sim 10^{13} s^{-1}$ and $10^{10} s^{-1}$,[9] respectively. Comparing these values with our present k_{EA}, we may say that the energy transfer rate in the *o*-terphenyl solid is remarkably small even in the crystalline state and it is rather close to the value in the disordered solids. The slow energy migration in this solid may be partly caused by the formation of intramolecular excimer state. Thus, the k_{EA} in the glassy state is not so much smaller than that in the crystalline state.

In summary, we could identify the intrinsic *o*-terphenyl fluorescence band and its origin. The energy transfer really occurs even in the glassy solid and its rate is of nearly the same order of magnitude ($\sim 10^9 s^{-1}$) as in the crystal.

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