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# Spectral Dependence of Fluorescence Lifetime as a Monitor for Purity of Fluoranthene Crystal

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**Abstract**—Fluorescence lifetime was successfully used as a monitor for the purity of solid fluoranthene purified by several different methods; i.e., sublimation in vacuo, zone refining, a newly developed chemical process, and the chemical process followed by zone refining. The spectral response of the lifetime was found to be an appropriate criterion for purity. The chemical process followed by zone refining was found to be an excellent method for purification of fluoranthene. Furthermore, studies were made on the effect of such impurities as anthracene, carbazole, fluorene, and naphthacene on the lifetime and its spectral dependence.

## 1. Introduction

Considerable efforts have been made over the past decade concerning the study of optical and electrical properties of molecular crystals. Large deviations in the reported values of their intrinsic properties may mainly, or at least partly, be due to the variation in the purity of the crystals. Therefore, the determination of their purities is very important in obtaining the intrinsic properties. Only few researches, however, have hitherto been made on this problem. Recently, the triplet lifetime of anthracene obtained from the decay time of delayed fluorescence was used as a monitor to check the purity at several stages of zone refining.(1) The present authors reported that the spectral response of fluorescence lifetime could successfully be applied to the assignment of fluorescence bands of benzo[*g*, *h*, *i*]perylene-perylene mixed crystals.(2)

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In this study, we present data to show that the singlet lifetime and its spectral dependence can be used as a criterion for the purity of a fluoranthene crystal.

## 2. Experimental

Commercially available fluoranthene (Tokyo Kasei, reagent grade) was purified by the following methods; sublimation in vacuo under $10^{-5}$ Torr, zone refining,† and the chemical processes.‡

The lifetime was determined from an analysis of the fluorescence decay curves of fluoranthene crystals excited by an AVCO–EVERETT nitrogen gas laser. The details of the measurement were described in a previous paper.(2) The spectral measurement was made by a JASCO CT–50 grating monochromator attached with an RCA 1P28 photomultiplier. A reabsorption effect was carefully eliminated by arranging a light source (a 100 W Hg lamp), a sample, and the monochromator at the most appropriate geometry.

## 3. Results and Discussion

The samples designated by *S*, *Z*, *M*, and *MZ* are the solid fluoranthene purified by sublimation, zone refining, the chemical process, and the chemical process followed by zone refining, respectively. *U* is the original sample itself. The numerical values in the parentheses after the symbol, *Z*, show the travelling rate, the number of zone passes, and the distance from the top (high-purity zone) of the zone refining tube.

Figures 1 and 2 show the spectral dependence of the fluorescence lifetime measured with various samples at room temperature (296 °K) and at liquid nitrogen temperature (77 °K), respectively.

The fluoranthene samples purified by the above-mentioned methods have fluorescence spectra at room temperature (296 °K) similar to each other, except *Z* (3.1 mm/day, 100 passes, 25 cm) which exhibits a different type of fluorescence spectrum because of

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† The zone length was kept approximately equal to the inside diameter of the tube, ~1 cm. The interzone spacing was ~4 cm and the travelling rate was 3.1 and 7.1 mm per day and the ingot was about 30 cm long.

‡ The details will be described in Appendix.

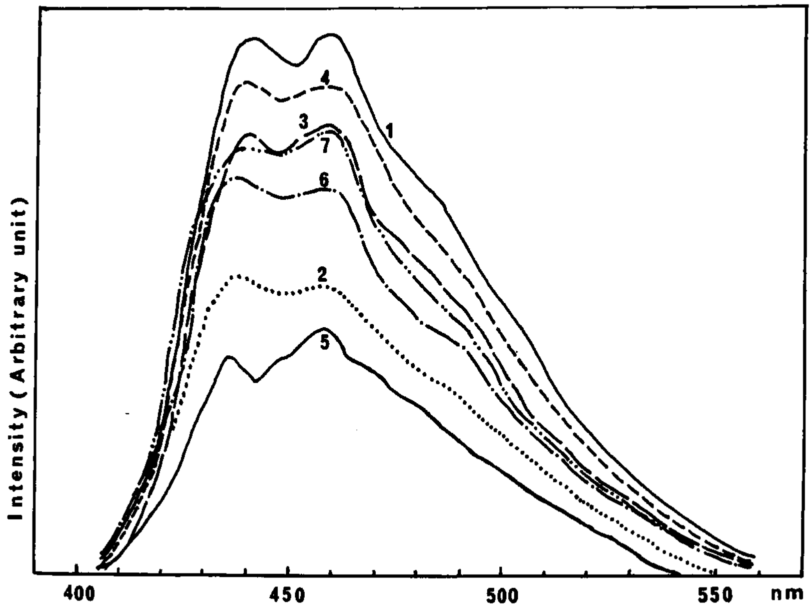

Figure 1. Fluorescence spectra of fluoranthene in microcrystalline state at a room temperature (296 °K). Curves 1, 2, 3, 4, 5, 6, and 7 are for *U*, *S*, *Z* (7.1 mm/day, 450 passes, 2 cm), *Z* (3.1 mm/day, 100 passes, 2 cm), *Z* (3.1 mm/day, 100 passes, 25 cm), *M*, and *MZ* (7.1 mm/day, 450 passes, 2 cm), respectively.

impurities concentrated at the bottom part (20–30 cm from the top of the tube) of the refining tube.

The patterns of fluorescence spectra at 77 °K are similar to each other for all the samples except for *U*, although the effect of reabsorption on the spectra is strongly dependent on the samples.

From the above description, it can be concluded that the spectral shape of the fluorescence of the fluoranthene crystal is not the relevant criterion of its purity. The fluorescence spectra of fluoranthene in cyclohexane solution are also useless as criterions for purity because their patterns are also found to be very similar to each other.

Since we could not estimate the purity of fluoranthene with the aid of the spectral shape, we undertook to measure fluorescence lifetimes at various wavelengths. Figures 3 and 4 show the results of the solid fluoranthene samples at 296 °K and at 77 °K, respectively.

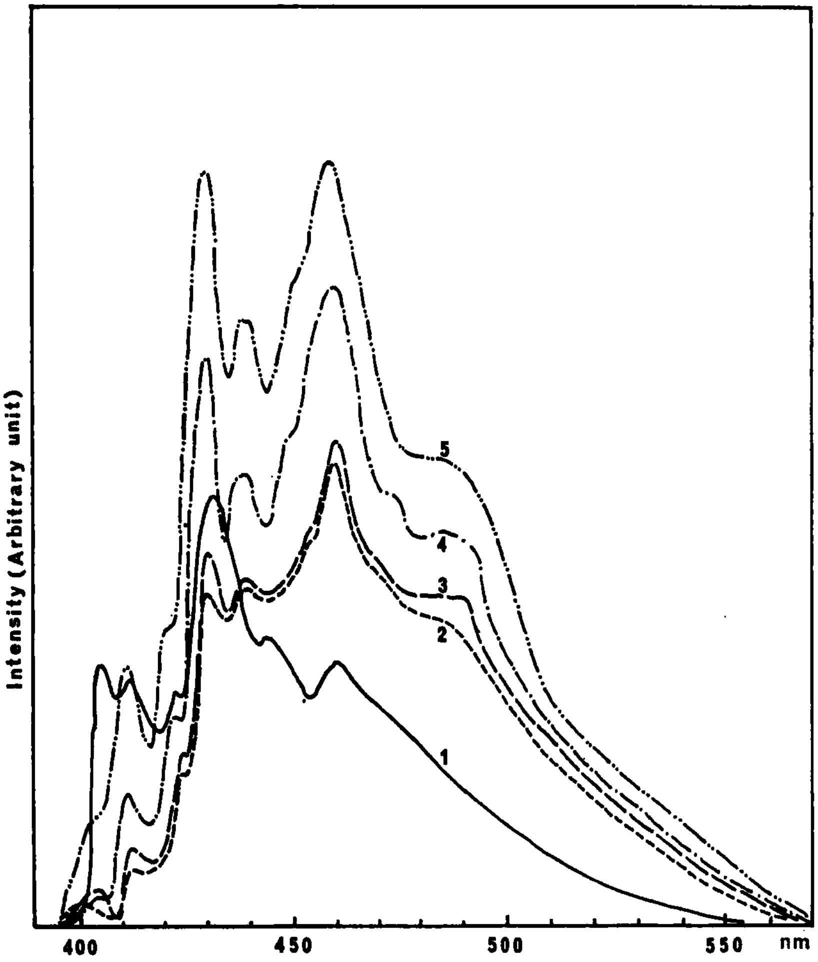

Figure 2. Fluorescence spectra of fluoranthene in microcrystalline state at 77°K. Curves 1, 2, 3, 4, and 5 are for *U*, *S*, *Z* (7.1 mm/day, 450 passes, 2 cm), *M*, and *MZ* (7.1 mm/day, 20 passes, 2 cm), respectively.

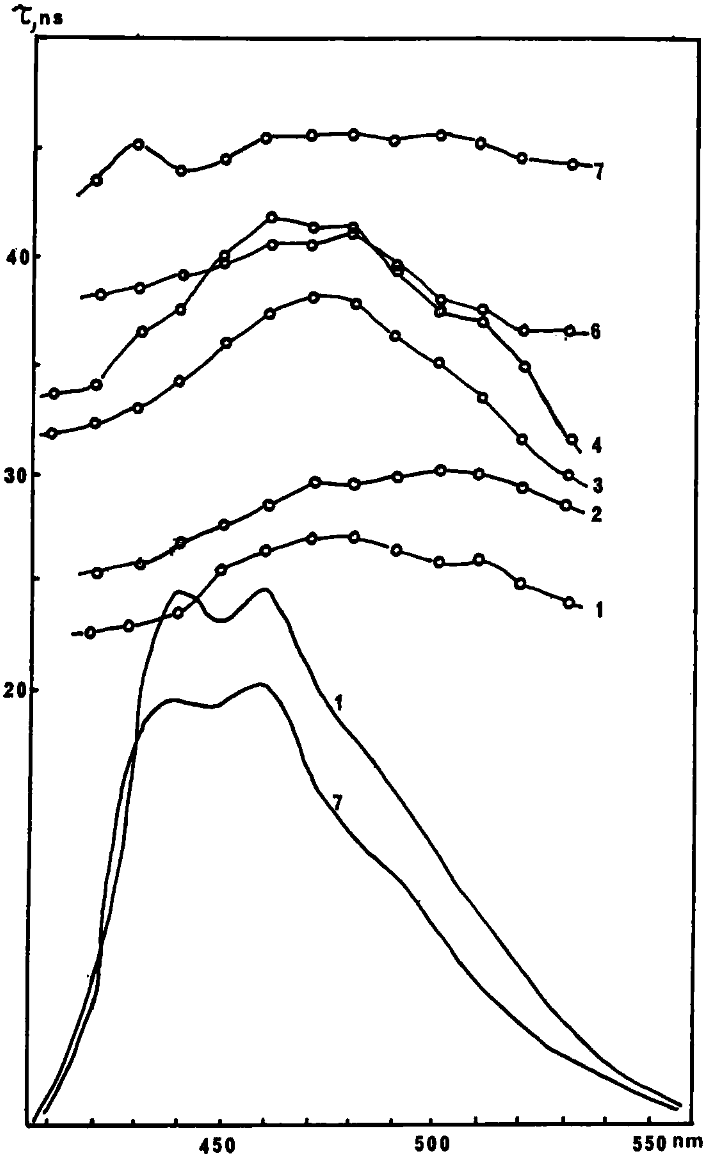

Figure 3. Spectral dependence of fluorescence lifetime for fluoranthene in microcrystalline state at room temperature. The numbering of curves is the same as Fig. 1.

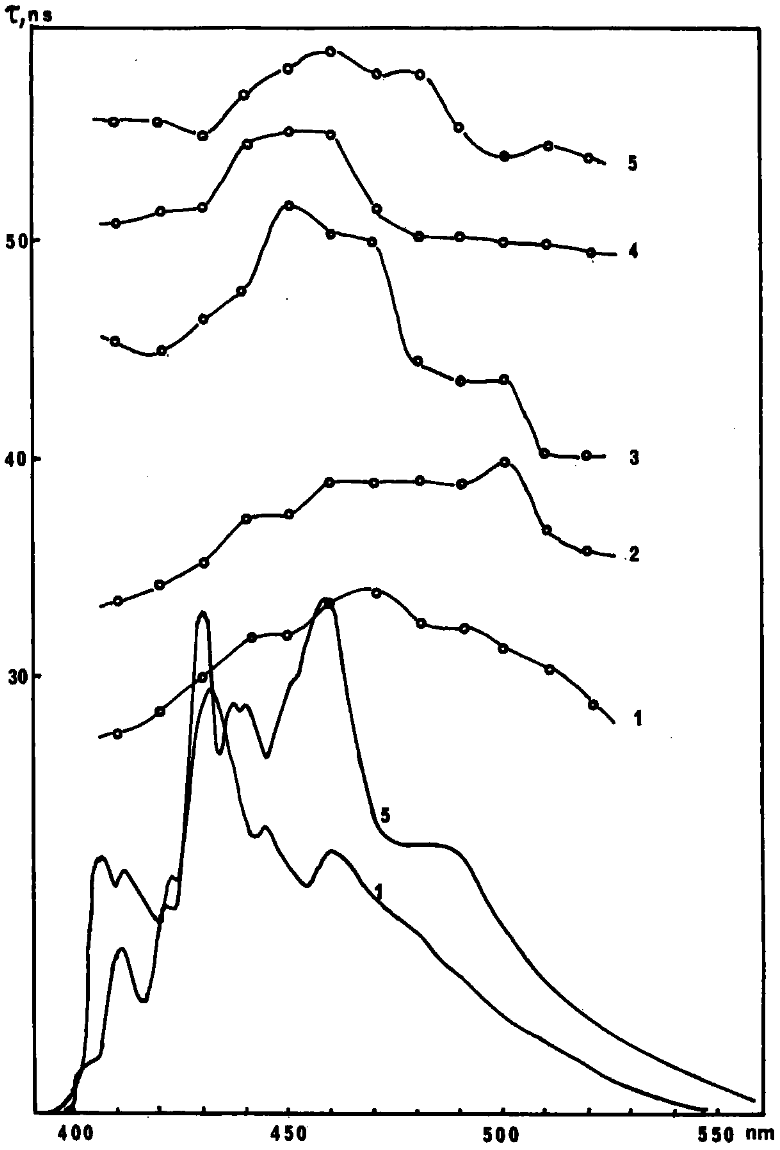

Figure 4. Spectral dependence of fluorescence lifetime for fluoranthene in microcrystalline state at 77 °K. The numbering for curves is the same as Fig. 2.

The weight-average fluorescence lifetime, $\tau_{av}$,† the longest lifetime, $\tau_m$, and the difference between longest and shortest lifetimes, $\Delta\tau$, at various wavelengths from 410 to 530 nm are listed in Table 1.

TABLE 1 Fluorescence Lifetimes (ns) of Fluoranthene Crystals at Room Temperature (296 °K)

| | Temp. | Sample | | | | | |
|---|---|---|---|---|---|---|---|
| | | *MZ* | *M* | $Z_1^a$ | $Z_2^a$ | *S* | *U* |
| $\tau_{av}$ | 296 °K | 45.1 | 40.2 | 34.8 | 39.4 | 28.1 | 25.2 |
| $\tau_m$ | 296 °K | 45.6 | 40.9 | 41.7 | 38.1 | 31.0 | 27.0 |
| $\Delta\tau$ | 296 °K | 2.1 | 4.4 | 10.1 | 8.1 | 5.6 | 4.5 |
| $\tau_{av}$ | 77 °K | 57.4 | 53.9 | | 47.6 | 38.7 | 32.2 |
| $\tau_m$ | 77 °K | 58.9 | 55.2 | | 50.5 | 40.0 | 34.0 |
| $\Delta\tau$ | 77 °K | 4.8 | 5.4 | | 10.1 | 4.0 | 5.0 |

[a] $Z_1$ and $Z_2$ are *Z* (3.1 mm/day, 100 passes, 2 cm) and *Z* (7.1 mm/day, 450 passes, 2 cm), respectively.

From Figs. 3 and 4 the following four general tendencies can be derived:

(1) The fluorescence lifetimes increase in the following order in the wavelength region of 410–530 nm, with only a small number of exceptions.

$U < S < Z$ (7.1 mm/day, 450 passes, 2 cm) $< Z$ (3.1 mm/day, 100 passes, 2 cm) $< M < MZ$ (7.1 mm/day, 20 passes, 2 cm).

(2) The lifetimes of *MZ* measured at room temperature are about 45 ns and are almost constant through the observed wavelength region of 410–530 nm. This constancy is also held for the observed values at 77 °K. $\Delta\tau$ is only 2.1 ns at room temperature and is 4.8 ns at 77 °K.

(3) The lifetime of *Z* (7.1 mm/day, 450 passes, 2 cm) is shorter than that of *Z* (3.1 mm/day, 100 passes, 2 cm) through the observed wavelength region.

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† $\tau_{av}$ is obtained by the following equation:

$$\tau_{av} = \frac{\sum_i \tau_i I_i}{\sum_i I_i}$$

where $\tau_i$ and $I_i$ are lifetime and intensity of the fluorescence at the wavelengths between 410 nm and 530 nm.

(4) The lifetimes of *Z* (7.1 mm/day, 450 passes, 2 cm) are shorter than those of *M*, and the difference between these two samples are larger in 410–440 nm or 480–530 nm region than that in 450–470 nm region.

The fluorescence lifetime should be constant through the measured wavelength region when the emission is due to only one origin. Hence, the observed spectral dependence of fluorescence lifetime may be regarded as due to the overlapping of emissions from impurities with different lifetimes. Therefore, from the above results (1)–(3), the following conclusions are derived:

(1) The purity of the sample increases in the following order: $U < S < Z < M < MZ$.
(2) Among the samples studied, *MZ* is the purest one, but the fluorescence spectra is still contaminated to a very small extent by emissions from impurities. These findings show that the newly developed purification method combining the chemical process with zone refining is excellent but is not perfect.
(3) The travelling rate of the zone refining strongly affects the efficiency of purification. Zone refining with travelling rate of 3.1 mm/day can give a purer sample than that with 7.1 mm/day rate in a shorter period.

Experimental result (4) can be explained as follows: commercially available fluoranthene is extracted from coal tar pitch and contains small amounts of several aromatics, anthracene, fluorene, naphthacene, phenanthrene, carbazole, naphthalene, and chrysene, and so on. Naphthalene, fluorene, chrysene, anthracene, carbazole, phenanthrene, and naphthacene exhibit fluorescences in the wavelength regions of 335–350 nm, 380–430 nm, 370–400 nm, 390–430 nm, 390–440 nm, 390–470 nm, and 490–565 nm, respectively.(3) Hence, the fluorescence of fluoranthene is found to be unaffected by those of naphthalene and chrysene. The emissions from fluorene, anthracene, and carbazole, from phenanthrene, and from naphthacene overlap the fluorescence of fluoranthene in the shorter and in the shorter and intermediate, and in the longer wavelength regions, respectively. The spectral dependence of the fluorescence lifetime measured for

*Z* (3.1 mm/day, 100 passes, 2 cm) and *M* at room temperature shows that zone refining is better for eliminating phenanthrene than the chemical process with maleic anhydride and chloranil, while, anthracene, carbazole, and naphthacene can be eliminated by the chemical process much better than by zone refining. This fact may be expected because anthracene and carbazole react easily with maleic anhydride.

In order to clarify the effect of the several kinds of impurities on the fluorescence lifetime, we undertook to measure the lifetimes of the crystals of the purest fluoranthene, *MZ* (7.1 mm/day, 20 passes, 2 cm), with anthracene ($10^{-5}$, $10^{-3}$, $10^{-2}$ and $10^{-1}$ mole/mole), fluorene ($10^{-1}$ mole/mole), carbazole ($10^{-1}$ mole/mole), and naphthacene ($10^{-1}$ mole/mole), at room temperature. Tables 2 and 3 show the impurity effect on the fluorescence lifetime.

TABLE 2 Fluorescence Lifetimes (ns) of Fluoranthene–Anthracene Mixed Crystals at Room Temperature (23 °C)

| | Concentration of anthracene (mole/mole) | | | | |
|---|---|---|---|---|---|
| Wavelength (nm) | 0 | $10^{-5}$ | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ |
| 420 | 43.5 | 40.0 | 38.0 | 37.5 | 36.0 |
| 460 | 45.5 | 42.5 | 42.0 | 42.0 | 41.5 |
| 500 | 45.5 | 43.5 | 42.5 | 42.5 | 41.0 |
| $\tau_{av}$ | 45.1 | 42.2 | 41.7 | 41.1 | 40.6 |
| $\tau_m$ | 45.6 | 43.5 | 42.5 | 42.0 | 41.7 |
| $\Delta\tau$ | 2.1 | 3.5 | 4.5 | 4.5 | 5.7 |

As shown in Table 2, the fluorescence lifetime of fluoranthene contaminated by $10^{-5}$ mole/mole anthracene is found to be shorter than that of *MZ* by about 3 ns in the wavelength region of 420–500 nm. The lifetime of fluoranthene decreases drastically by adding a small amount of anthracene; even at concentration as low as $10^{-5}$ mole/mole. Therefore, the measurement of lifetime is useful to detect qualitatively anthracene in fluoranthene.

Table 3 shows that the lifetime decreases in the order of *MZ*, *MZ* + anthracene, *MZ* + carbazole, *MZ* + fluorene and *MZ* + naphthacene. In particular, it is much shorter for *MZ* + naphthacene

TABLE 3 Fluorescence Lifetimes (ns) of Fluoranthene Crystals Containing $10^{-1}$ mole/mole of Anthracene, Carbazole, Fluorene, or Naphthacene

| | Sample | | | | |
|---|---|---|---|---|---|
| Wavelength (nm) | Pure crystal | Anthracene | Carbazole | Fluorene | Naphthacene |
| 420 | 43.5 | 36.0 | 32.7 | 27.5 | 14.2 |
| 460 | 45.5 | 41.5 | 33.6 | 28.3 | 13.0 |
| 500 | 45.5 | 41.0 | 34.3 | 30.0 | 15.0 |
| $\tau_{av}$ | 45.1 | 40.6 | 33.6 | 28.7 | 13.7 |
| $\tau_m$ | 45.6 | 41.7 | 34.3 | 31.0 | 15.0 |
| $\Delta\tau$ | 2.1 | 5.7 | 1.6 | 4.0 | 2.0 |

system than for the others. This is because the energy transfer from fluoranthene to an impurity is more effective for this system than for the others. The lowest excited singlet state of naphthacene is lower than that of fluoranthene while the reverse is the case for the other impurities.

As concluding remarks, we list the merits of the application of the spectral response of fluorescence lifetime as a monitor of the purity of organic molecular crystals.

(1) The contribution of the short-lived component to the observed emissions is predominant at the first stage after flash, and the logarithmic plot reveals its presence even if it is only a few percent of the total emission. Therefore, the emissions from impurities with short lifetimes may be detected, even if unobserved by steady excitation.

(2) The purity of the organic compounds can be estimated without destroying the sample.

(3) The purity of samples can be checked by the principles: (a) The decay curve should be exponential throughout the whole wavelength region of fluorescence spectra. (b) When the purity is sufficiently high, the lifetime should be constant over the whole spectral region. (c) Generally, the longer the lifetime the higher the purity of the samples.

## Appendix

### PURIFICATION BY CHEMICAL REACTION

The crude fluoranthene (10 g) was treated for about 2 hours with 150 g boiling maleic anhydride containing 8 g of chloranil as an oxidizing agent. The solution was once cooled down to 50 °C, and thereafter was added to hot toluene. The toluene solution was boiled further for 2 hours. After hot filtration, the filtrate was cooled down to room temperature. The precipitates containing the reaction products and the unreacted maleic anhydride and chloranil were removed from the parent solution by filtration. The solvent, toluene, was distilled under reduced pressure to isolate fluoranthene crystals, which were further purified by repeated recrystallizations from benzene.

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