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Zone Refining and the Triplet Lifetime of Naphthalene, Phenanthrene and *p*-Terphenyl

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The triplet lifetime has been used as a monitor to follow the zone refining process. The triplet lifetime at room temperature has been found to be a sensitive parameter for the purity of naphthalene, phenanthrene and *p*-terphenyl crystals, the impurity concentration of which is below the limit of the detectability by ordinary analytical methods. The purity dependence of the singlet lifetime has also been compared with that of triplet one.

The triplet lifetime of anthracene and naphthalene crystals is known to be reduced by small concentration of impurities and imperfections which quench triplet excitons.[1,2] Port *et al.*[1] have shown that the triplet lifetime of the naphthalene crystal is reduced from 20 to 0.6 msec with an increase of the concentration of anthracene from 10^{-8} to 10^{-5} mol/mol. The triplet lifetime of anthracene crystals has also been studied in relation to the purity.[2] The maximum triplet lifetime of anthracene crystals reached 25 msec after the extensive zone purification process. In this paper, the author attempts to correlate the triplet lifetime to the crystal purity which cannot be determined by ordinary analytical methods, for example, gas chromatography, liquid chromatography, UV absorption etc. The limit of detectability by ordinary analytical methods is about 10^{-6} mol/mol in molecular crystals. The triplet lifetime has been used as a monitor to follow the progress of purification during the zone refining of naphthalene, phenanthrene and *p*-terphenyl in the present work. The singlet lifetime has also been measured to compare its purity dependence with that of the triplet. The technique is not useful for non-interacting impurities, but for impurities which can trap triplets or singlets.

NAPHTHALENE

Naphthalene (Merck 6200, scintillation grade) was purified by the automatic zone refining apparatus for organic compounds, which was fabricated in our laboratory.[3] The zone travel rate was 5 cm per hour. The rotation of the zone tube (44 rpm) prevents the effective distribution coefficients from approaching one. This often occurs in zone refining at such a high speed. The length of the zone ingot was about 85 cm, and its diameter was 0.8 cm. After a vacuum of 10^{-5} mm Hg pressure was reached, the pyrex zone refining tube was filled with 0.5 atmosphere of helium gas. The triplet lifetime was measured from the decay time of the delayed fluorescence, and monitored along the zone ingot following a specific number of zone passes. Triplet excitons were directly excited by the light through Hoya glass filters L39, 40, 41 and LB145 from a 1000 W xenon lamp (Ushio Co. Ltd. UXL1000D). The delayed fluorescence from the zone ingot was separated from the prompt fluorescence with a Becquerel-type phosphoroscope, detected with a photomultiplier (Hamamatsu TV R376) through an interference filter (Oriel 340 nm) and three glass filters UVD25 (Toshiba). The photomultiplier output was fed to a multi-channel analyzer (Tracor Northern TN-1505), and integrated to raise the S/N ratio. A $\frac{1}{4}$ spectrometer (Nikon G250) was used for spectral measurement. The singlet exciton lifetime was measured by a single photon counting method (Ortec Co. Ltd.).

Delayed fluorescence spectra were measured at 77 K and room temperature, and were the same as the prompt one in the purified ingot. No emission due to impurities was observed in the delayed fluorescence spectra. The intensity of the delayed fluorescence proved to be linear with the square of that of the excitation light. The triplet lifetime at room temperature was monitored after a specific number of zone passes. The results are shown in Figure 1 for 132, 206, 292 and 386 zone passes. Delayed fluorescence intensity and the maximum triplet lifetime increase as the zone purification process increases. The change of the triplet lifetime after 132 zone passes is small. After 206 zone passes, there is a large decrease at the top and bottom of the zone ingot. The maximum triplet lifetime which is observed around $1/L = 0.2$ has reached 380 msec. It is obvious that most impurities have moved to the bottom part of the zone ingot, and a few to the top. After 292 zone passes, the maximum value has reached 500 msec, which is as long as the longest value in the literature.[4] After 386 zone passes, the maximum value is 540 msec, and a third of the zone ingot shows the

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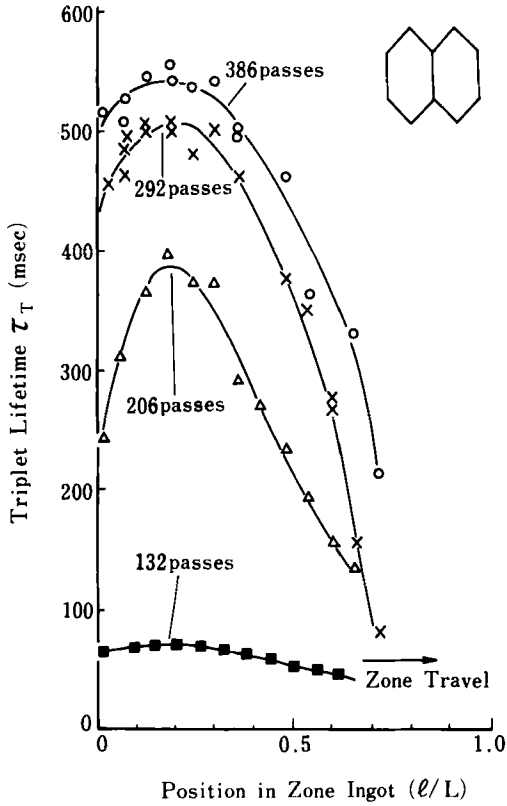

FIGURE 1 Variation of the triplet lifetime of naphthalene with position in the zone ingot following 132, 206, 292 and 386 passes at room temperature.

triplet lifetime over 500 msec. The experimental results show that the triplet lifetime is a sensitive parameter for the purity, and that extensive zone refining affords ultrapure naphthalene crystals efficiently.

The plateau of the triplet lifetime at 77 K after 386 zone passes indicates that the triplet lifetime at 77 K is less sensitive to the chemical impurities than that at room temperature (Figure 2). This suggests that the shallow traps originating from the structural defects quench the triplet exciton effectively at 77 K. The similar quenching is also observed at 77 K in phenanthrene crystals. The singlet lifetime at room temperature is also illustrated in Figure 2. The singlet lifetime is constant in most of the zone ingot, and is shortened only at the colored bottom part. This shows that the singlet lifetime is less sensitive to the chemical impurities than the triplet one in the very pure crystals. Sin-

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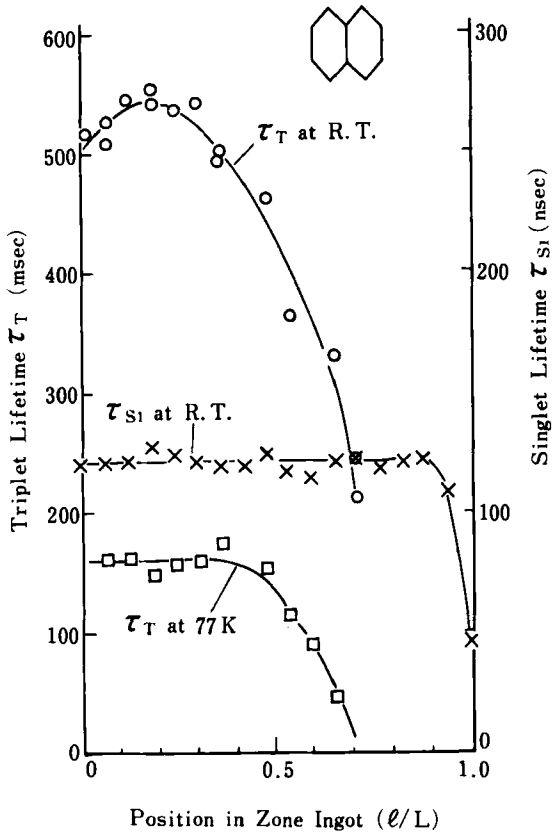

FIGURE 2 Variation of the triplet and singlet lifetimes of naphthalene with position in the zone ingot after 386 zone passes.

glet lifetime has been reported to be affected by the impurity concentrations above 10^{-6} mol/mol.[5] Hence, 90 percent of the zone ingot is considered to contain impurities, the concentration of which is below 10^{-6} mol/mol.

PHENANTHRENE

Phenanthrene (Eastman Kodak X599, fluorescent grade) was zone refined without any previous purification. The initial concentration of anthracene impurity in the sample was determined to be below 10^{-6}

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mol/mol by the UV absorption spectrum of a benzene solution. Glass filters UV39, VY42 and VY43 (Toshiba) were used for excitation, the interference filter (Oriel 365 nm) and three glass filters UVD25 for emission.

Anthracene impurity has moved to the top portion after 160 zone passes. The concentration of anthracene at the top was determined to be 5×10^{-6} mol/mol by the UV absorption spectrum of a benzene solution. The delayed fluorescence spectrum of the purified ingot at room temperature consists of the anthracene and phenanthrene components, while the prompt fluorescence shows only the phenanthrene emission. The delayed and prompt fluorescence spectra of the purified ingot at 77 K show only the phenanthrene emission. This suggests that the quenching of triplet excitons by shallow traps also occurs in phenanthrene crystals at 77 K, as observed in naphthalene crystals. The intensity of the delayed fluorescence I_{DF} at room temperature is related to that of the excitation light $I_{ex.}$ by the formula $I_{DF} \propto I_{ex.}^{k}$ (k varies from 1.9 to 1.7). This suggests that the lifetime of the phenanthrene triplet excitons rules the decay of the delayed fluorescence. The decay time of the delayed fluorescence after 160 zone passes is shown in Figure 3. The maximum value 242 msec is observed around $1/L = 0.2$. As the square law exists approximately ($k = 1.9$), the maximum triplet lifetime is calculated to be about 480 msec, which is about as long as the longest value 410 msec in the literature.[6] The singlet lifetime along the zone ingot is also shown in Figure 3. The decrease of the singlet lifetime is observed at the top and bottom parts. The plateau of the singlet lifetime and the variation of the triplet lifetime indicate that the singlet lifetime is less sensitive to the chemical impurities than the triplet one, as observed in naphthalene crystals.

p-TERPHENYL

p-Terphenyl (Eastman 13057, scintillation grade) was zone refined without any previous procedure. No impurity above 10^{-3} mol/mol was detected by liquid chromatography. No impurity emission was detected in the fluorescence spectrum. The zone tube was filled with 1 atmosphere of helium gas to prevent the movement of the sample by sublimation. Three glass filters L39 and LB165 (Hoya) were used for excitation. The emission at 3720 Å was observed through a spectrometer the slit width of which was 2 mm.

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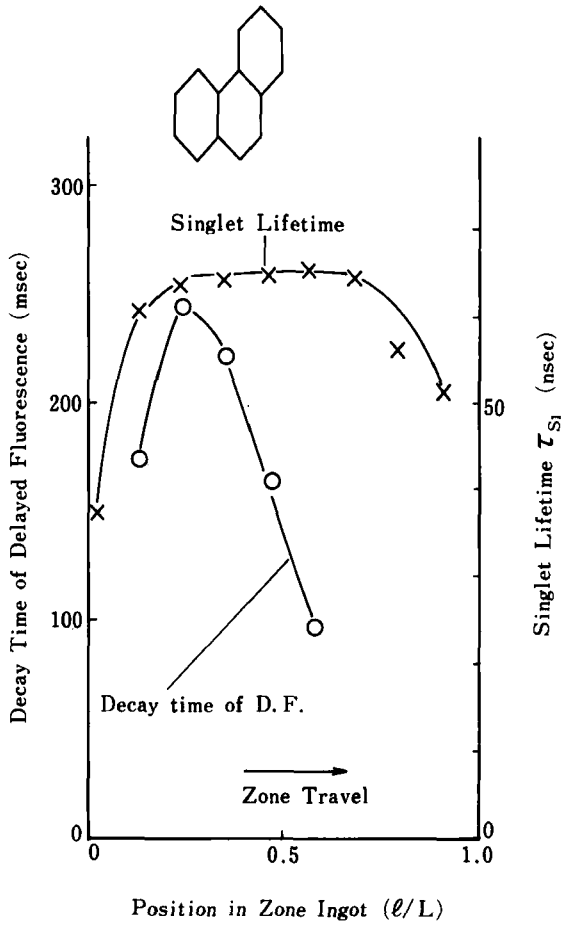

FIGURE 3 The variation of the triplet and singlet lifetimes of phenanthrene with position in the zone ingot after 160 zone passes.

Figure 4 illustrates the triplet lifetime along the zone ingot. As the zone purification process advances, the maximum triplet lifetime increases and the lifetime at the top and bottom parts decreases. The maximum triplet lifetime 28 msec is observed around the middle of the zone ingot after 400 passes. It is longer than the value 20 msec in the literature.[7] The plateau of the triplet lifetime suggests the saturation of the zone purification effect after 400 passes. The delayed fluorescence spectrum shows only the emission from *p*-terphenyl and is similar to the prompt one.

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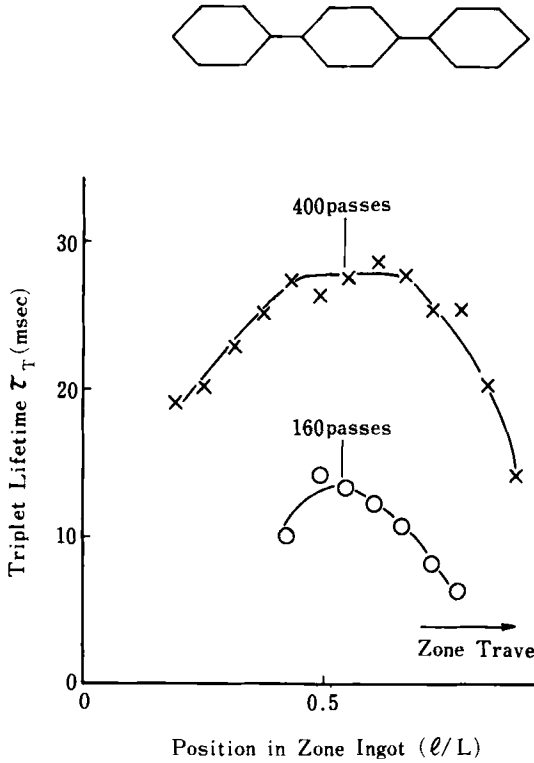

FIGURE 4 Variation of the triplet lifetime of *p*-terphenyl with position in the zone ingot following 160 and 400 zone passes.

CONCLUSION

Long triplet lifetime shows a high degree of purity with respect to compounds which quench triplet excitons. The triplet lifetime is expected as a parameter for purity, particularly in the ultrapure range where the purity cannot be determined by ordinary analytical methods. The use of the triplet lifetime as a purity parameter has the possibility of application to other molecular crystals. It affords a simple non-destructive measurement to follow the zone refining process.

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