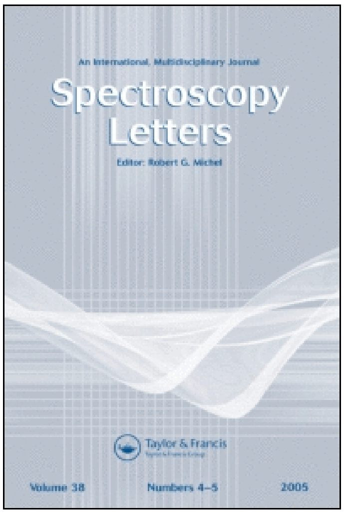

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High Resolution B-Type Delayed Fluorescence of Dibenzanthracene in PMMA

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High Resolution B-Type Delayed Fluorescence of Dibenzanthracene in PMMA

Key words: B-type of delayed fluorescence, Delayed fluorescence, Fluorescence, Dibenzanthracene, *T-T* absorption

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B-Type delayed fluorescence of 1,2,3,4-dibenzanthracene in PMMA was experimentally observed for the first time. Dibenzanthracene molecules were excited in a two-step process. In the first step, an excited singlet S_1 is created, which undergoes intersystem crossing to T_1 then *T-T* absorption creates an excited triplet dibenzanthracene molecule, which returns to the first excited singlet level by intersystem crossing. The recreated first excited singlet of dibenzanthracene decays back to the ground state by emitting this new type of delayed fluorescence.

INTRODUCTION

Polymer matrices are convenient for the study of singlet and triplet related phenomena over a wide temperature range. Such amorphous solids, as polymethylmethacrylate (PMMA), remain rigid up to 100°C, Schafer et al,[1]. The temperature dependence, of triplet processes, has been reported in several polymer matrices. Invariably, the phosphorescence lifetime of aromatic solutes, (larger than benzene) in plastics, shortens when the temperature is raised. Above 30°C the triplet lifetime drops precipitously, since the molecular environment is not well defined in polymer matrices, the temperature depended mechanism remains largely obscure above room temperature. High pressures eliminate diffusional quenching by oxygen molecules in polymer matrix, Rodriquez and Offen,[2]. Therefore a large pressure dependence of the thermally activated processes is predicted, if the bimolecular quenching is responsible for the diminished phosphorescence at high temperatures. The visible and near ultraviolet absorption spectrum of a centrosymmetric molecule is shifted to longer wavelengths in the presence of an electric field because the polarizabilities of the ground and excited states are different, Barnet et al,[3]. Excitation spectra of 1,2,3,4-dibenzanthracene at very high concentrations are characterized by the appearance of broad bands, decreased lifetimes, and a marked decrease in the quantum yield of the triplet state, Slifkin and Chalabi,[4]. The magnetic circular dichroism (MCD) of 1,2,3,4-dibenzanthracene has been measured in the alpha absorption region. The sign and magnitude of the MCD observed were in good agreement with those calculated using CNDO wavefunctions, Larkindale and Simkin,[5]. Due to the low vapor pressure of dibenzanthracenes, their vapor spectra could not be recorded, Morales and Traverso,[6]. B-type delayed fluorescence was observed experimentally for the first time for rubrene in solution by one and two photon excitations, Bayrakçeken,[7].

EXPERIMENTAL

The solutes of 1,2,3,4-dibenzanthracene (Eastman Kodak), and other chemicals (Aldrich) were chosen for this study at a concentration of 2.5×10^{-4}M. The PMMA samples were prepared by thermal polymerization. The singlet and triplet transient phenomena were excited with a flash photolysis set-up consisted of two-parallel photo-tubes arranged in series, contained in a reflector which was flushed with nitrogen. The Photoflash energies used were 780-1125 J, and the flash duration time was five nanoseconds. All quartz components were spectrosilica grade. Spectra were recorded on a Hilger medium quartz spectrograph, slit-width 0.025 mm Ilford XK fast blue sensitive plates sensitized with sodium salicylate, and were developed in Ilford PQ universal developer. The spectra were photometered on a Joyce-Loebel double beam recording microdensitometer, Model-MKIIB. Calibrated optical densities on the photographic plate were obtained with a seven-step filter, Hilger F-1273. All kinetic spectroscopy was carried out for single flashes.

RESULTS AND DISCUSSION

Absorption of light raises the molecule from the ground state to one of the upper electronically excited singlet states. At room temperature most molecules are in the lowest vibrational level of the ground state and it is from here that transitions upward by absorption of light take place. For many organic compounds the pattern of vibrational levels is complex and all the transitions to the various levels of the first excited state appear as one broad absorption band. From the first excited singlet energy level, the molecule can return to any one of the vibrational levels of the ground state with the emission of fluorescence. The shape of fluorescence emission spectrum is independent of the wavelengths used to excite the molecule, because the emission always takes place from the level S_1. The rate of emission of fluorescence is by definition equal to the rate of light absorption measured in quanta, multiplied by the quantum efficiency of fluorescence. All types of delayed fluorescence involve a metastable state which is first converted to an excited singlet state before emitting. For this study the molecule 1,2,3,4-dibenzanthracene was especially selected, because this molecule (a) belongs to a C_{2v} symmetry, which allows to a clear-cut polarization assignment, (b) has a singlet lifetime of the order of 100 nanoseconds and, (c) has a reasonable absorption coefficient at the flash and the laser flash excitations wavelengths in the ultraviolet - visible region, Lavalette et al,[8]. The triplet states have lower energies than their corresponding singlet states. However, cases are claimed in which S_1 lies below T_1, because of strong coupling between excited states. The solvent or polymer matrix may cause a breakdown of the spin conservation rule for molecules facilitate a charge in multiplicity, and permit weak $S_0 \rightarrow T_1$ absorption to be observed, as it is seen at 480-640 nm band in Figure 1. However, this is not a necessary criterion concerning singlet-triplet mixing. Under favorable conditions, (rigid medium, absence of quenchers), emission of phosphorescence often can compete favorably with delayed fluorescence and intersystem crossing. Although the natural radiative lifetime of phosphorescence is independent of temperature, the actual observed rate of decay of the triplet state is the sum of all competing processes, phosphorescence, intersystem crossing back to the excited state S_1, intersystem crossing to the ground state S_0, and bimolecular reactions with other substances.

Dibenzanthracene molecules was excited in a two-step process involving the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ transitions. Dibenzanthracene molecules in the T_2 state returned to the first excited singlet state S_1 by intersystem crossing from the excited triplet T_2. The recreated electronically excited S_1 state decayed back to the ground state S_0 by emitting B-type delayed fluorescence. The lifetime of B-type delayed fluorescence will be the lifetime to T_2 state, instead of T_1, because the T_2 state is responsible for repopulating the S_1 state of the molecule.

The mechanism of "B-type = Bayrakçeken type" of delayed fluorescence is the following, Bayrakçeken,(7,9).

1) $^1DBA + h\nu$(200 - 700 nm band, photolysis flash)$\rightarrow$ $^1DBA^\bullet$

(one photon absorption, $S_0 \rightarrow S_n$, rate $= I_a$)

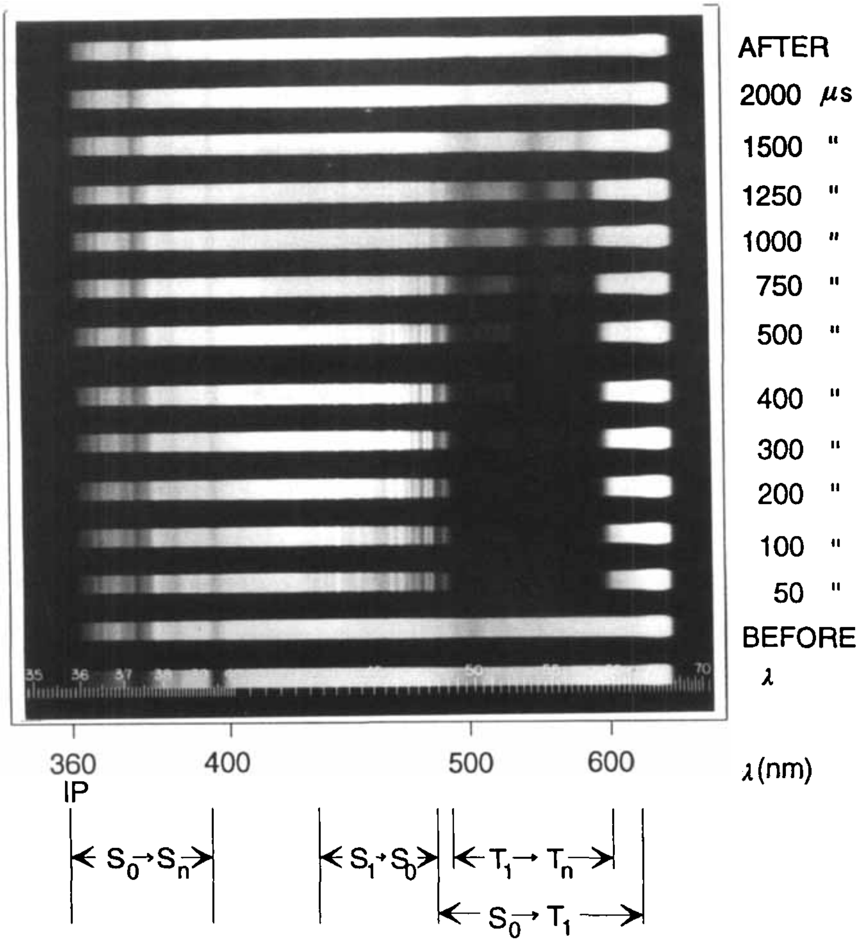

Figure 1. Singlet-singlet and triplet-triplet absorption spectra and B-type of delayed fluorescence spectrum of DBA in PMMA and their decay at room temperature.

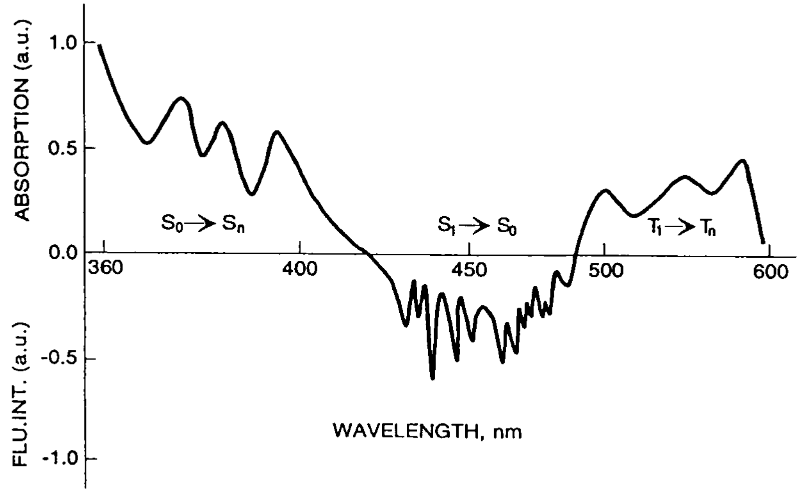

Figure 2. $S_0 \rightarrow S_n, T_1 \rightarrow T_n$ absorption spectra and B-type of delayed fluorescence spectrum of DBA in PMMA at room temperature.

2) $^1DBA^* \rightarrow {}^3DBA^\bullet$(intersystem crossing, $S_1 \rightarrow T_1$)

3) $^3DBA^\bullet + h\nu$ (480 - 640 nm band, spectral flash) $\rightarrow {}^3DBA^{**}$
($T_1 \rightarrow T_2$, one photon absorption, creation of T_2, rate $= I_a$)

4) $^3DBA^{**} \rightarrow {}^1DBA^\bullet$(intersystem crossing from T_2 to S_1)

5) $^1DBA^\bullet \rightarrow {}^1DBA + h\nu'$ (425-490 nm, B-type delayed fluorescence,
rate $= k_f = [T_2]$)

Figure 1 shows $S_0 \rightarrow S_n, T_1 \rightarrow T_n$ allowed transitions and, spin and parity forbidden $S_0 \rightarrow T_1$ absorption spectra of 2.5 x 10^{-4}M, 1,2,3,4-dibenzanthracene in PMMA at room temperature, recorded by flash photolysis technique. Values of the rate of triplet decay, as determined by the decrease in $T_1 \rightarrow T_n$ absorption, where in substantial agreement with those made by determining the rate of decay of phosphorescence. Figure 2 shows the singlet and triplet related spectra of DBA in PMMA. Continuous absorption started at 360 nm, therefore the first ionization potential of DBA via singlets was calculated from this edge and found to

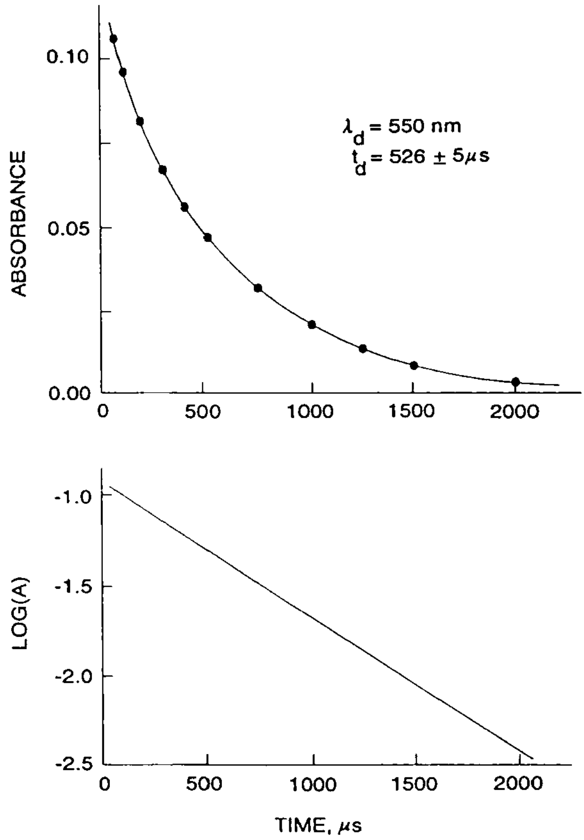

Figure 3. Triplet decay (disappearance of T_1 state) of DBA in PMMA at room temperature.

be 3.44 eV. The longest wavelength member of the $S_0 \rightarrow S_n$ absorption observed at 395 nm, therefore if the autoionization discreate energy states were formed during the flash photolysis, we should observe them at 197.5 nm and below. Due to the very strong continuous absorption below 360 nm, no autoionization discreate energy levels were observed.

The triplet state of DBA in PMMA was stable at room temperature, the absorption spectrum was structured, and the peaks of triplet state were easily identified in the range 490-600 nm. This conclusion is reinforced by the appearance of delayed fluorescence. The wide singlet-triplet energy gap, (395-425 nm band), would appear to preclude an E-type mechanism as well as P and

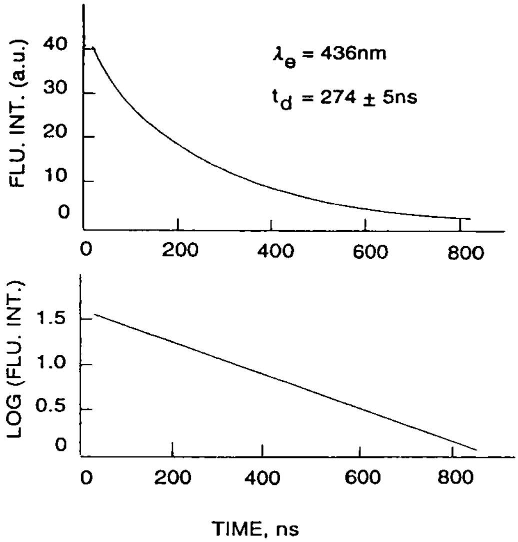

Figure 4. B-type of delayed fluorescence decay, (decay of T_2 state via S_1 state), of DBA in PMMA at room temperature.

B-type mechanisms. The identity of the delayed fluorescence and prompt fluorescence spectra excludes the possibility of the triplet state spectra observed being due to an impurity with a low-lying triplet state. Decay curves for the DBA triplet were found to follow an exponential decay law.

$$\left|{}^3DBA\right|_t = \left|{}^3DBA\right|_0 e^{-kt}$$

where k is a constant. In order to get best triplet-triplet absorption spectrum and B-type delayed fluorescence, the concentrations of DBA in PMMA were tested and 2.5×10^{-4}M concentrations was selected for all the experiments. Figure 3 shows the exponential decay of DBA - triplet, (T_1 state), in PMMA at room temperature, measured at 550 nm, and decay time of T_1 (disappearance of T_1) was found to be 526±5 microseconds. The decay time of B-type delayed fluorescence is much shorter than P-type delayed fluorescence, because T_2 state is responsible to repopulate the S_1 state. As it is seen in Figure 1, due to the multiple emissions coming from S_1 state, (i.e. normal fluorescence, recombination delayed fluorescence, E, P, and B-type delayed fluorescences), the lifetime of B-type delayed fluorescence could not be measured from the emission spectrum of Figure 1. In order to measure the decay time of B-type delayed fluorescence, a combination of glass filters were used between the sample, photolysis flash and spectral flash lamps to eliminate the recombination delayed fluorescence by cutting the emissions below 365 nm which was coming from the photolysis flash lamp. During the optical pumping to create S_1, T_1, and T_2 states, oxygen-free nitrogen was flushed through the optical cavity to keep the temperature constant for the sample. Therefore the possibility of E-type delayed fluorescence was also eliminated. The delay time, between the photolysis and the spectral flash lamps, was selected as 100 nanoseconds to eliminate prompt (normal) fluorescence. Spectral flash emits 480-640 nm band, therefore DBA is transparent at this band, this means, no normal fluorescence emissions are possible from DBA by optical pumping of spectral flash. B-type delayed fluorescence decay was measured at different emission lines and found to be the same within the experimental error. The best signal was obtained at 436 nm emission line, by using a Tektronix oscilloscope, and the decay time of T_2 state via S_1 state was found to be 274±5 nanoseconds at room temperature in PMMA. Figure 4 shows the decay curve for B-type delayed fluorescence of DBA in PMMA at room temperature. The observed long triplet lifetimes are made feasible merely by inaccessibility from the rigidity of the local microenvironment.

Abbreviations:

PMMA = Polymethylmethacrylate

DBA = Dibenzanthracene

CNDO = Complete Neglect of Differential Overlap

MCD = Magnetic Circular Dichroism

$^1M = S_0$ = Ground State
$^1M^* = S_1$ = First Excited Singlet State
$^3M^* = T_1$ = Lowest Excited Triplet State
$^3M^{**} = T_2$ = Upper Excited Triplet State
I_a = Photon Intensity
k_f = Rate of Fluorescence

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