

Excited State Structural Changes of 10-Cyano-9-tert-butyl-anthracene (CTBA) in Polymer Matrices

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Abstract Two main deactivation processes are suggested to be present in the electronic excited state of 10-cyano-9-tert-butyl-anthracene (CTBA): one leading to the Dewar structure resulted from photochemical effect, similar to the case of 9-tert-butyl-anthracene (TBA), which is enhanced in solution, and another leads to a more planar structure leading to a Charge Transfer (CT) state and is enhanced in polymers. The presence of donor (tert-butyl group) and an acceptor (cyano group) along the line of 9,10 positions in CTBA confirm our hypothesis of CT state. Our suggestions were supported by steady state and time resolved fluorescence spectra results.

Keywords Fluorescence · Polymers · Lifetime · Aromatics · Charge transfer · Dewar anthracene · Tert-butylanthracene · Photoreaction

Introduction

In 1978, Schoof and coworkers [1] showed that 9-tert-butyl-anthracene (TBA) in solution has a very low fluorescence quantum yield (~ 0.011) which was found to increase significantly as the viscosity of the medium is increased. They attributed their results [2] to the photochemical valence isomerization of TBA to 9,10-Dewar anthracene in solution. This process was found to be quenched as the medium becomes more rigid.

Jahn and Dreeskamp suggested a model [3] to explain the photochemical behavior of 9-tert-pentyl-anthracene which was found to be prefolded by an angle of $\sim 13^\circ$ in its ground

state, and prefolded by $\sim 60^\circ$ in a higher energy state with a Dewar isomer structure.

The competition between different routes (fluorescence, radiationless transitions, and isomerization to a Dewar structure) from the ($S_1 \rightarrow S_0$) state of TBA was the core of a study by Hirayama and Shimono [4]. They measured the fluorescence excited state lifetime for TBA in a set of non-viscous solvents and found its decay to be single exponential and to increase from 0.2 ns at room temperature to 15.9 ns at 123 K. Moreover they studied the fluorescence lifetimes of TBA in the high viscous media of poly(methylmethacrylate) (PMMA) polymer matrix and found its spectra not to be appreciably different from those in solution. However the quantum yield was enhanced and the decays were not monoexponential. They suggested two different frequency factors, associated with temperature dependent radiationless processes, to explain differences between the non-viscous solvents and PMMA polymer matrix, which implies the existence of two different temperature dependent radiationless processes from (S_1). Their hypothesis assumed very fast ($S_1 \rightarrow S_0$) internal conversion to be dominant in non-viscous solvents. In PMMA polymer matrix however, they suggested that this internal conversion is totally suppressed and the decay occurs via an intermediate X, which may finally take place. They suggested that the photochemical pathway to compete with the fluorescence of the parent compound, and thus a double exponential decay was observed.

Hirayama and coworkers [5] extended their work and showed the effect of temperature on the fluorescence band of 10-cyano-9-tert-butyl-anthracene (CTBA) in PMMA polymer matrix. An obvious increase of the fluorescence band quantum yield as the temperature decreased was observed. Careful inspection of Fig. 1 of their paper in reference [5] shows a red shift of the fluorescence as the temperature is lowered but unfortunately was not explained.

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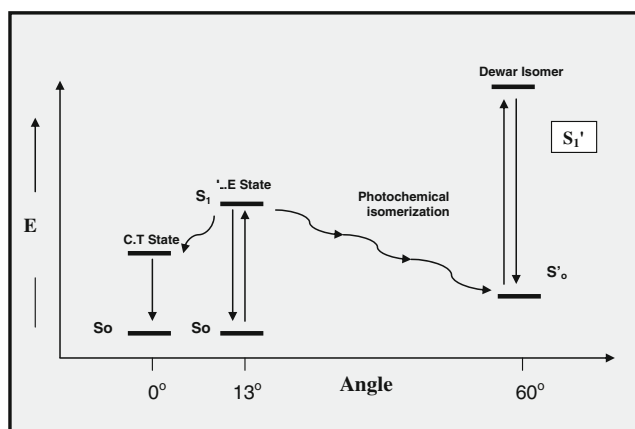


Fig. 1 Suggested scheme for the photochemical behavior and deactivation processes of CTBA during excited state lifetime

A similar study was carried out by Fritz et al. [6] who used CTBA molecule as a probe to check the role of poly(butylmethacrylate) (PBMA) polymer free volume on its emission. They suggested that the multiexponential fluorescence decay of CTBA in polymer matrices implies the presence of several conformers of CTBA molecules in the excited state ranging from slightly prefolded CTBA (as that in the ground state) to the higher folded Dewar isomer, which simply makes what they called “butterfly” motion.

These observations motivated us to use the red edge effect (REE) phenomena [7–12] as a probe to study such butterfly motions of CTBA and related compounds in various polymers. Instead, we observed a blue shift and more structured fluorescence, for the case of CTBA, as the polymer becomes softer, and found to be consistent with Hirayama and coworkers results. These observations lead us to add one more state, namely a Charge Transfer (CT) state, to the scheme suggested by Jahn and Dreeskamp [3].

The scheme, Fig. 1, built according to our hypothesis suggests two main deactivation processes to compete in the electronic excited state of CTBA; one leading to the Dewar isomer and is dominant as the medium becomes soft and nonpolar, and another leading to the charge transfer state, and is enhanced as the medium becomes more rigid and more polar. Therefore, we believe, the fluorescence can be observed from three different states: namely from; the locally excited state, the CT state and the Dewar isomer state depending on the conditions of the experiment. This most probably explains the multiexponential decay of this molecule in various polymers.

Experimental

10-cyano-9-tert-butyl-anthracene (CTBA) was a gift from Prof. W. Rettig (Technical University of Berlin)

and was used as received. The procedure of PMMA and PBMA polymer matrices sample preparation from monomer solutions, were the same as in our previous works [13].

Fluorescence spectra (corrected) were measured using FS900 CDT steady-state L-geometry Spectrofluorometer from Edinburgh Analytical instruments (EAI). Fluorescence decay lifetime measurements were obtained by time-correlated single photon counting technique (TCSPC) using an Edinburgh Instruments unit Model 199. The details of the instrument and the method of measurements were described earlier [14].

Results & Discussion

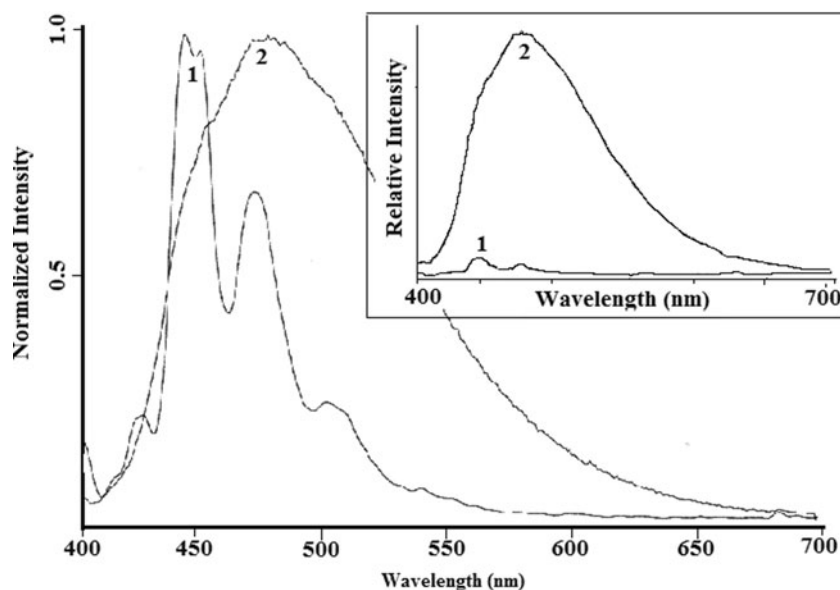
All our results [15] show that the main fluorescence band of CTBA undergoes a red shift as the medium becomes more rigid. This is unusual in the fluorescence spectroscopic studies [7, 11], where the fluorescence emission usually occurs from the unrelaxed Franck-Condon excited states, that are of higher energy as compared to the equilibrium position of the relaxed excited state, as the medium becomes more rigid. Therefore a blue shift (and not a red shift) is expected.

The fluorescence spectrum of CTBA in the viscous PMMA polymer matrix is broad, undergoes a red shift of $\sim 1,400\text{ cm}^{-1}$, and has a higher quantum yield as compared to fluid methylmethacrylate (MMA) monomer. Actually, the fluorescence spectrum of CTBA in the monomer is structured as compared to its fluorescence in PMMA polymer matrix as shown in Fig. 2.

This observation lead us to suggest that the fluorescence spectrum of CTBA in PMMA polymer matrix to be composed of two fluorescence bands: namely, the locally excited (LE) band located $\sim 450\text{ nm}$, and an intramolecular charge transfer (CT) band located $\sim 480\text{ nm}$. The presence of tert-butyl-group (as a donor), and cyano-group (as an acceptor) along the line of 9,10 positions in anthracene support our hypothesis of the presence of CT state.

Excitation of CTBA will put the molecule in the Franck-Condon state of the (LE) state. Beside the normal non-radiative processes taking the molecule to the equilibrium position of the locally excited (LE) state which leads to a fluorescence around 450 nm , we suggest the presence of two main non-radiative processes competing during the excited state lifetime. One nonradiative process takes the excited molecule to state “X” as proposed previously [3] (that finally leads to the Dewar isomer, (due to photochemical reaction [2])) and found to be enhanced in fluid and non-polar media. This isomer has fluorescence maximum $\sim 350\text{ nm}$. The other non-radiative process takes the excited molecule to

Fig. 2 Normalized fluorescence spectra of CTBA: (1) in methylmethacrylate monomer, and (2) in PMMA polymer matrix at room temperature. *Inset:* unnormalized fluorescence spectra of CTBA



a charge transfer (CT) state which is more planar than the (LE) state, and is enhanced in viscous and polar media. The presence of *t*-butyl group (as a donor), and cyano group (as an acceptor) at the opposite sides (9, 10 positions) of anthracene is required for the presence of such (CT) state. This state leads to fluorescence around 480 nm. The excited state lifetimes and the quantum yields of the fluorescence of CTBA in polymer is thus determined by the competition of the above processes beside medium relaxations around the excited conformers trapped in the sites of the polymer. A better conceptualization of our suggestions can be traced using the potential energy diagram shown in Fig. 1. This most probably explains the higher quantum yield of emission of CTBA in PMMA polymer matrix as compared to its fluorescence in MMA fluid monomer, and are shown in Fig. 2, and inset. The fluorescence quantum yield quenching observed in solution for the (LE) band, ~450 nm, due to a photochemical isomerization to Dewar structure, is largely converted, in rigid and slightly polar polymer, to a relatively high quantum yield (CT) emission ~480 nm, since PMMA has an appreciable free volume and polarity for CTBA to accommodate sufficient planarity needed for a charge transfer emission domination. The fluorescence of CTBA during polymerization of MMA monomer towards PMMA polymer matrix was traced, a red shift and an increase in quantum yield as the polymerization process proceed was observed [15]. One of the major basis in the judgment that the fluorescence of CTBA, observed in Fig. 2 is a red shift and not redistribution of intensities of the LE vibronic bands as the medium become rigid. This can be seen in comparing the emission spectra of TBA, where a CT band is not expected

to be observed, with that of CTBA, where a CT band is clearly observed, in the same PMMA polymer matrix. For the case of TBA, only enhancement of the structured fluorescence and sharpening of the vibronic bands was observed without changes in the position of peak fluorescence band ~430 nm or its half-width, $\Delta\bar{\nu}_{1/2} \sim 3000 \text{ cm}^{-1}$, in going from solution to rigid glass and /or to PMMA polymer matrix [3, 4]. Therefore emission is simply attributed to occur mainly from the LE state. On the other hand, the fluorescence of CTBA undergoes enhancement and red shift ($\lambda_{\text{max}} \sim 480 \text{ nm}$) and band broadening ($\Delta\bar{\nu}_{1/2} \sim 4400 \text{ cm}^{-1}$) in PMMA polymer matrix as compared to its fluorescence in MMA monomer ($\lambda_{\text{max}} \sim 450 \text{ nm}$ and $\Delta\bar{\nu}_{1/2} \sim 2100 \text{ cm}^{-1}$) as shown in Fig. 2. It seems that the presence of CN, as an electron withdrawing group, at the opposite side of the *tert*-butyl group in CTBA is the driving force for relaxation of the prefolded anthracene moiety in the ground state to a planer configuration, during the excited state lifetime, leading to emission from the CT state besides the LE state. Thus enhancement, red shifted and broadening in the fluorescence band of CTBA as compared to that of TBA in the same polymer matrix is expected and being observed. In solution, the relaxation of CTBA or TBA to this CT state is overwhelmed by the photoreaction, during the excited state lifetime, leading to the Dewar form. Therefore emission occurs mainly from the LE excited state with low quantum yield, structured for both, and blue shifted for the case of TBA as compared to CTBA. It must be mentioned that Hirayama and co-workers [5] observed broadening, red shift and enhancement of the fluorescence of CTBA in PMMA polymer matrix and didn't exclude the presence of another state beside the LE state to be responsible for the multiexponential decay in the excited state. Actually they later [16] reported that, "The total absence of fluorescence from the electronic origin suggests the

involvement of an intermediate electronic state other than triplet state. This could be a charge-transfer state, they say, considering the strong electron-withdrawing and electron-donating nature of cyano and tert-butyl groups respectively”, in interpreting the absence of fluorescence of CTBA in the supersonic free jet experiment, from room temperature to 77 K. These are in line of our results and suggestions.

It is therefore obvious that the existence of both a donor (tert-butyl group) and an acceptor (cyano group) are responsible for inducing the CT state leading to the red shift and enhancement of fluorescence observed for CTBA as compared to that observed for TBA in polymer matrices. These observations and suggestions are confirmed below by comparing the fluorescence and decay lifetimes of CTBA in PBMA to that in PMMA polymer matrix.

Figure 3 shows a blue shift (however with lower quantum yield) of the fluorescence of CTBA in PBMA (softer and less polar) as compared to the rigid and more polar PMMA polymer matrix. Actually the softer PBMA polymer matrix enhances the Dewar structure formation over the CT resulted from photochemical deactivation of the LE excited state [15] indicating that the CT band is enhanced for the case of CTBA in more rigid and more polar media. Moreover, and similar to the previous investigators [4–6], we have found the decay of fluorescence of CTBA in PBMA and PMMA polymer matrices is not monoexponential. Figure 4 shows one of the decays and Table 1 shows the lifetimes of CTBA in PMMA and PBMA polymer matrices at different emission wavelengths. CTBA in PMMA polymer matrix shows a double exponential decay with

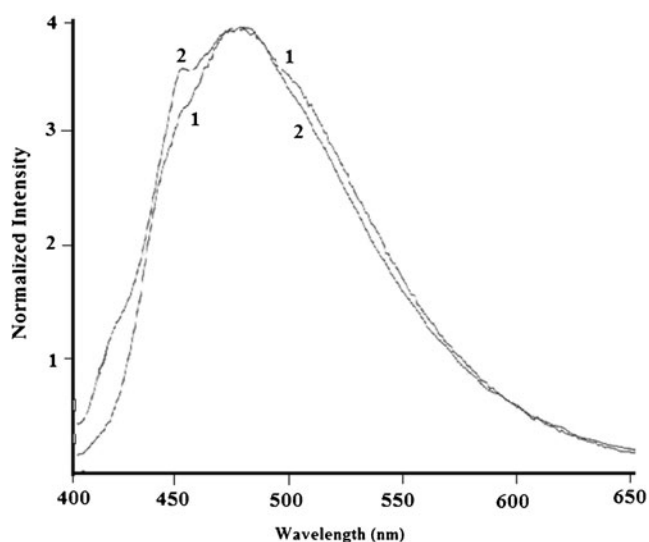


Fig. 3 Normalized fluorescence spectra of CTBA: (1) in PMMA polymer matrix, and (2) in PBMA polymer matrix at room temperature

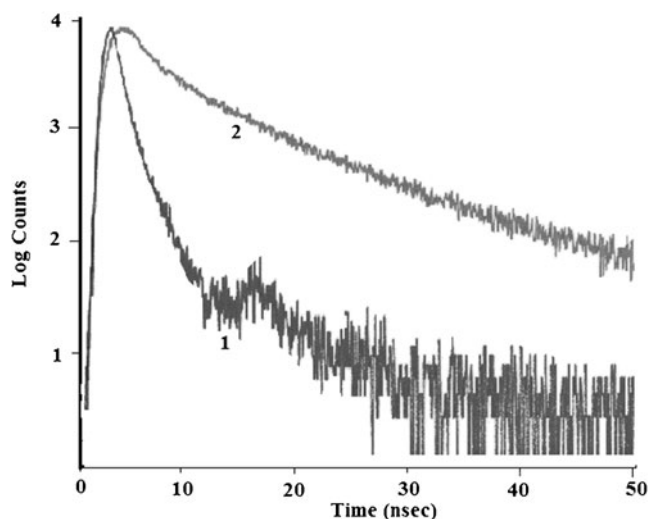


Fig. 4 Fluorescence decay curve of CTBA in PMMA polymer matrix: (2) as compared to lamp decay (1) at room temperature, monitored at 480 nm

a mean lifetime of 5.32 ns, when the decay was monitored at 480 nm. The presence of two components in the decay pattern shown in (Fig. 4 and Table 1) is an evidence and most probably confirms our hypothesis concerning the composite nature of the long fluorescence band observed for CTBA in rigid media, namely the LE state band and the CT band. We assign the long excited state lifetime (7.2 ns) to the CT fluorescence while the shorter lifetime (0.94 ns) to the LE fluorescence. In contrast, the mean lifetime for CTBA in PBMA polymer matrix was found to be 1.44 ns, is lower than that in PMMA polymer matrix at the same emission reading wavelength, as its demonstrated in Table 1. However, the relative abundance (Q) for the CT lifetime in PBMA is significantly lower than that for CTBA in PMMA. This is an expected result because charge transfer emission of CTBA is favored in the more rigid and relatively polar PMMA polymer matrix.

The role of molecular weights and types of polymer matrices, like: polyalkyl methacrylates, polyvinylchlorides, polyvinylalcohols, ...etc., on the competition of these two

Table 1 Fluorescence excited state lifetimes of CTBA in PMMA and PBMA polymer matrices at different emission wavelengths

Polymer	λ_{exc} (nm)	$\lambda_{em.}$ (nm)	$\tau_{1/ns}$	Q_1	$\tau_{2/ns}$	Q_2	$\langle\tau\rangle/ns$
PMMA	337	480	0.94	0.30	7.2	0.70	5.32
PMMA	337	400	0.77	0.41	5.2	0.59	3.39
PBMA	337	480	0.42	0.79	5.3	0.21	1.44
PBMA	316	360	0.02	0.69	2.2	0.31	0.69

fluorescence bands in CTBA, are under our attention for further investigation.

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