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Study of the photophysics and energy transfer of 9,10-diphenylanthracene in solution

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Abstract

Photophysics of 9,10-diphenylanthracene (DPA) in benzene solution was studied with time-resolved thermal lensing (TRTL) technique. The TRTL signal was composed of the fast and slow-rising components. The heat conversion efficiency, which is defined as the ratio of energy released as heat against energy absorbed, was determined to be 0.31±0.01, revealing that the fluorescence quantum yield is fairly large (0.88±0.03), while the quantum yield for triplet formation is quite small (0.04±0.02) by analyzing the slow component of the TRTL signal. The triplet–triplet (T–T) absorption of DPA in benzene appeared for the wavelength region of 420–470 nm, obtained by energy transfer with triplet benzophenone used as a photosensitizer. The quenching rate constant of DPA by triplet benzophenone was determined to be $(3.6\pm0.3)\times10^{9}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ with Stern–Volmer plots. The intrinsic energy transfer rate was also estimated by analyzing the time profile of the TRTL signal. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Time-resolved thermal lensing; 9,10-Diphenylanthracene; Energy transfer

1. Introduction

It has been extensively discussed about the precise fluorescence quantum yield of 9,10-diphenylanthracene (DPA), which is used as a fluorescent standard, since its fluorescence quantum yield was reported to be unity [1]. Later, many researchers reported the fluorescence quantum yield (0.80–0.96) in the several solvents [2–13]. Medinger and Wilkinson [5,6] also estimated the quantum yield of the triplet formation to be 0.12 in liquid paraffin at 20°C. Chattopadhyay et al. [14] reported data concerning triplet absorption and triplet yields for DPA, based on the study of reversible triplet energy transfer between anthracene and DPA in toluene. The yield of intersystem crossing was surprisingly low compared with other aromatic compounds such as naphthalene and anthracene derivatives [2,15]. Although some parts of the photophysical parameters are rather ambiguous, characteristic behavior (quite high fluorescence quantum yield and low triplet formation yield) presumably results from the rotational motion of two phenyl groups about the inter-ring bonds [4,11]. It may not be so surprising because the internal rotational motion of the methyl group on the toluene derivatives should play an important role for the nonradiative processes, even in the spectral region around the S_1 origin studied by laser-induced fluorescence measurement in a supersonic jet expansion [16,17]. Therefore, accurate photophysical parameters should be required as a fluorescence standard as same as a photodynamical information with respect to the phenyl internal rotational motion.

Photothermal methods including time-resolved thermal lensing (TRTL) and photoacoustic spectroscopy (PAS) are a powerful technique for the studies on nonradiative and radiative processes [18–26]. It can provide not only kinetic information (lifetime of the triplet state etc.) but also thermodynamical information (heat of reaction, triplet energy etc.). When one will obtain the absolute fluorescence quantum yield, photothermal techniques can eliminate some of the experimental errors, which come out with the conventional optical methods. The techniques are also applicable to intermolecular processes. Kaya et al. reported the application of PAS to the study on energy transfer from benzene to biacetyl in the gas phase [25]. Terazima and Azumi studied energy transfer between the upper triplet states of 2-acetylphenanthrene and biphenyl using the TRTL [26]. In this article, the TRTL technique combined with the nanosecond laser flash photolysis is applied for the first time to the study on photophysical and energy transfer processes of DPA. Quantum yields of fluorescence and triplet formation, intrinsic energy transfer efficiency, and the extinction coefficient of triplet–triplet (T–T) absorption can be obtained.

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2. Experimental

An experimental setup for the TRTL method was described elsewhere [19–23]. A XeCl excimer laser (Lumonics TE-860-4; 110 mJ/pulse, 10 ns pulse duration), used as an excitation light source, was focused into the sample with a 150 mm focal length lens. The laser power was monitored with a silicon photodiode (Hamamatsu S1336-5BQ) calibrated with a pyroelectric detector (Gentec ED100). A He–Ne laser (Uniphase 1103P; 2 mW) equipped with a stabilized power supply (Takasago; ARH500) was used as a probe light for a thermal lens. The sample solution flowed into a cuvette (NSG T-59FL-10; 10 mm optical path length). The probe light sampled through a pinhole (Corion 2401; 300 μm diameter) and a monochromator (Nikon P-250) was detected by a photomultiplier tube (Hamamatsu R928). The output signals were measured by a digital oscilloscope (Sony Tektronix TDS380P; 2 GS/s), and transferred to a personal computer. The TRTL signals were averaged over 50 shots. The error bar shows the accuracy of 1σ for the obtained data.

Transient absorption spectra were measured with the conventional laser flash photolysis system, consisting of the excimer laser and a steady-state Xe lamp (Ushio UXL-300DO; 300 W) for a monitoring light source. The sample solution flowed in a cuvette (40 mm optical path length). Absorption spectra were measured with a double beam spectrometer (Jasco Ubest V-550).

Benzophenone and 2-hydroxybenzophenone (Tokyo Kasei, GR grade) were purified by recrystalization twice with methanol and hexane. DPA (Tokyo Kasei, GR grade) was recrystallized with benzene. Benzene (Kanto Chemical, GR grade) was used from a freshly opened bottle. All samples were deaerated by bubbling Ar gas (purity 99.95%) purged by benzene vapor for 0.5 h before use. All measurements were carried out at room temperature.

3. Results and discussion

3.1. TRTL measurements on DPA in benzene

Fig. 1a shows the TRTL signal of DPA in benzene solution with the 308 nm laser excitation under quite low excitation power (1 μJ). After the laser excitation, the signal rose steeply, grew up slowly, and became plateau in this time window. The fast (U_F) component corresponds to the heat released through the relaxation processes from the first excited singlet state (vibrational relaxation, internal conversion to the S_0 state, and intersystem crossing to the T_1 state) and the slow rising component (U_S) to the heat resulting from intersystem crossing from the T_1 to S_0 states. The TRTL signal for 2-hydroxybenzophenone (HBP) is also presented in Fig. 1b. HBP is a well-known calorimetric standard, which emits the absorbed energy as heat into the solvent within a single laser pulse [18].

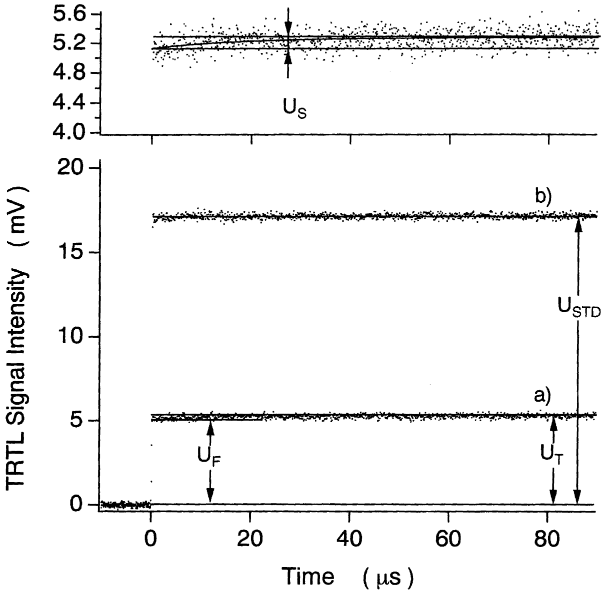

Fig. 1. Time profiles of the TRTL signal of (a) DPA and (b) 2-hydroxybenzophenone in benzene. The expanded view for the TRTL signal of DPA are also presented.

To obtain the quantum yields of fluorescence and triplet formation, we quantitatively analyzed the TRTL signal intensity. The total heat, U_T (=U_F+U_S), is described as

$$U_T = K\alpha I_L(1 - 10^{-OD}) \quad (1)$$

where K is the instrumental factor including thermal properties of the solvent, I_L the laser energy, OD the absorbance at 308 nm, and α denotes the heat conversion efficiency, namely, the fraction of energy released as heat against energy absorbed [19]. The laser power dependence of the TRTL signal intensity at 400 μs when all photophysical processes were completed, was measured at various concentrations of DPA, shown in Fig. 2a. The signal intensity increased more rapidly against the laser power under the higher laser power region, revealing that multi-photon absorption should occur. The solid line shows the best fitting curve obtained with the least squares' fitting method using the following relation:

$$U_T = a_1 I_L + a_2 I_L^2 \quad (2)$$

where a_1 and a_2 denote the coefficients of linear and quadratic terms, respectively. Alternative analysis was carried out with the equation.

$$\frac{U_T}{I_L} = a_1 + a_2 I_L \quad (3)$$

The results are shown in Fig. 2b. The plots of U_T/I_L against I_L show good linear relation. These results indicate that there should be two different heat sources released through single- and two-photon absorption processes even under relatively low laser power region of *ca.* 3 μJ.

There are two candidates responsible for the quadratic power dependence term; $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ absorption.

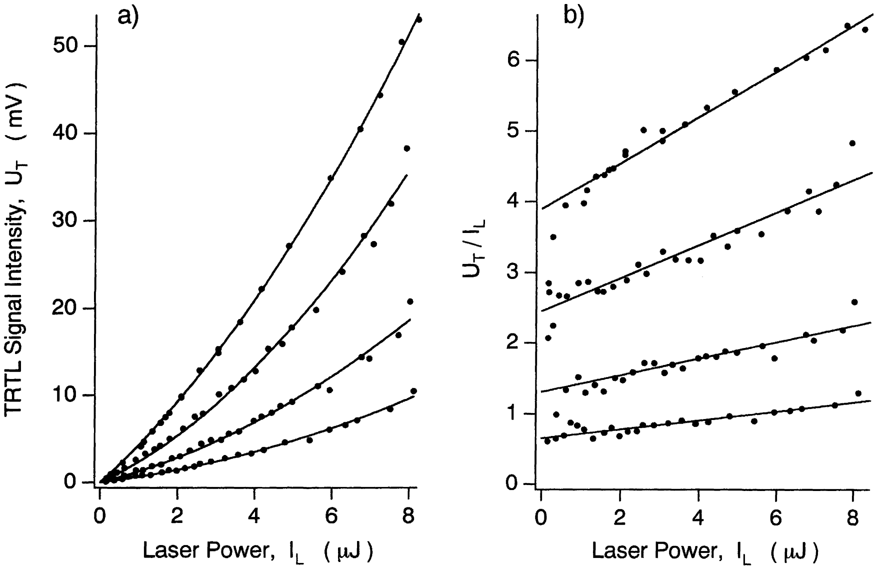

Fig. 2. (a) Plots of the total heat U_T of DPA in benzene vs. excitation laser power I_L. The signal intensity slightly curved, revealing multi-photon absorption should occur. The solid lines show the best fitting curve obtained with the least squares' fitting of $U_T = a_1 I_L + a_2 I_L^2$. (b) Plots of U_T/I_L vs. I_L. The solid lines shows the best fitting curves obtained with the least square fitting of $U_T/I_L = a_1 + a_2 I_L$.

Benzophenone has been reported to show also two-photon absorption phenomena [20,21]. The two-photon absorption process at 308 nm excitation was elucidated to be the first $S_1 \leftarrow S_0$ absorption followed by a rapid intersystem crossing to the T_1 state and the second $T_n \leftarrow T_1$ absorption to dissociate into two phenyl radicals and a carbon monoxide molecule. In the case of naphthalene, the two-photon process at 308 nm was realized as $S_n \leftarrow S_1$ absorption followed by accelerated internal conversion into the S_0 state with quantum yield of *ca.* 0.2 due to quite large excess energy [19]. In these cases, the laser power dependence of the TRTL signal (U_T) showed a large quadratic term ($a_2 > 0$) and the a_2 coefficient for U_S was negative. However, the linearity of the plots of U_S versus I_L for DPA was maintained even in the range where the two-photon event occurred remarkably. It suggests that two-photon phenomena do not affect the photophysical processes caused by single photon absorption. In other words, even when excited into higher excited states (S_n and/or T_n) with two-photon absorption, the excited molecules should be relaxed to the corresponding first excited states (S_1 and/or T_1) through rapid internal conversion, and their excess energies were emitted into the solvent as heat.

Plots of slope a_1 in Fig. 2 against absorptivity, $1–10^{-OD}$, are shown as blank squares in Fig. 3. Good linear relation was observed. The solid line denotes the best fitting curve. The plots for the calorimetric standard of HBP are also presented as solid circles. The signals were carefully measured under the exactly same conditions as the DPA system. Therefore, the instrumental factor *K* in Eq. (1) is same in both the cases. The ratio of two slopes in Fig. 3 gave the α value to be 0.31±0.01 because the α value for the standard is known to be unity [18]. The α value is written as

$$\alpha = \frac{E_{ex} - \phi_f E_S}{E_{ex}} \tag{4}$$

where ϕ_f and E_S are the fluorescence quantum yield and the S_1 energy, respectively, and E_{ex} is the energy of the excitation light. With the values of E_S=304 kJ/mol [15] and E_{ex}=388 kJ/mol (308 nm), the fluorescence quantum yield was successfully obtained to be 0.88±0.03, which agrees to the reported ones [8,11,12]. Next, the triplet formation quantum yield is related to the ratio of the slow and total heats,

$$\frac{U_S}{U_T} = \frac{\phi_{ISC} E_T}{E_{ex} - \phi_f E_S} = \frac{\phi_{ISC} E_T}{\alpha E_{ex}} \tag{5}$$

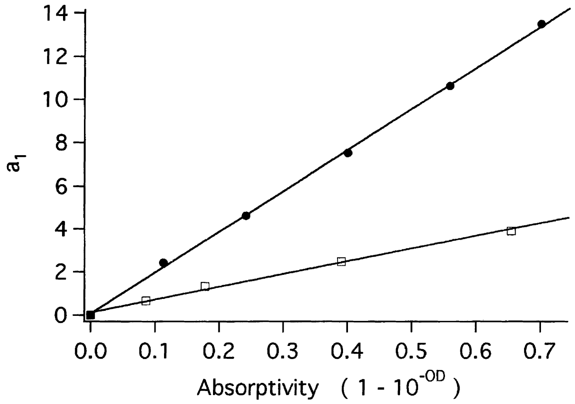

Fig. 3. Plots of slope a_1 in Fig. 2 (□) versus absorptivity, $1–10^{-OD}$. Good linear relation was observed. The plots for the calorimetric standard of HBP are also presented (●). The solid lines show the best fitting curves. The ratio of two slopes gave the heat conversion efficiency to be 0.31.

where ϕ_{ISC} and E_{T} are quantum yield of triplet formation and triplet energy, respectively. The $U_{\mathrm{S}}/U_{\mathrm{T}}$ value was obtained to be 6.2×10^{-2} from the result in Fig. 1 and the reported E_{T} value is 171 kJ/mol [14,15]. Thus, ϕ_{ISC} was determined to be 0.04±0.02. Medinger and Wilkinson reported the triplet formation quantum yield to be 0.12 in liquid paraffin [5,6]. Our result suggests that the ϕ_{ISC} value is found to be extremely small, however, it agrees within an experimental error to the one reported by Chattopadhyay et al. (0.01–0.03) [14]. The large difference on the quantum yield may result from the property of the solvent.

On radiationless deactivation processes of anthracene derivatives in the S_1 state, intersystem crossing was reported to be important processes [12,13,27,28]. The higher excited triplet state(s) was expected to lie near or very slightly below the S_1 state. Therefore, indirect intersystem crossing $S_1\rightarrow T_n\rightarrow T_1$ would be the most important process to populate the T_1 state. In comparison with anthracene and other aromatics, the photophysical properties characteristic to DPA, namely, quite large fluorescence quantum yield (0.88), extremely low triplet formation yield (0.04) and internal conversion (0.08), may be attributed to the conformational change in between the excited and ground states. Two phenyl rings were reported to be twisted by about 66° with respect to the anthracene framework in the ground state, and the angle decreased about 6° for the excited state [4]. Darmanyan [11] carried out the quenching experiment of DPA in the excited states by oxygen, and pointed out the importance of the phenyl ring conformation on both the ground and excited states. Phillips and co-workers measured the fluorescence lifetime and its quantum yield of DPA in the solution and the vapor phase [12,13]. The quantum yield dropped off and the fluorescence decay changed from single-to dual-exponential decay with temperature. They speculated the T_2 state lying near the S_1 state. However, the intersystem crossing from the S_1 to the T_2 states is unlikely without any perturbations because the S_1 state has $^1\mathrm{B}^+_{1g}$ symmetry and the T_2 state has $^3\mathrm{B}^+_{1g}$, according to the D_{2h} point group to which DPA belongs. We reported that large amplitude vibration of the methyl group on the benzene ring for toluene derivatives such as chlorotoluenes and methylanisoles, should play an important role for the nonradiative processes even in the spectral range around the S_1 origin with laser-induced fluorescence and photosensitized phosphorescence excitation techniques in a supersonic jet expansion [16,17]. The vibration presumably induces the intersystem crossing process. Therefore, the dynamical motion of the phenyl groups with respect to the anthracene frame presumably affect the photophysical processes for DPA. In order to further obtain information on influence of the phenyl internal rotation in the deactivation processes, we are doing laser-induced fluorescence and photosensitized phosphorescence measurements in a supersonic jet expansion with phenyl substituted aromatic molecules [29].

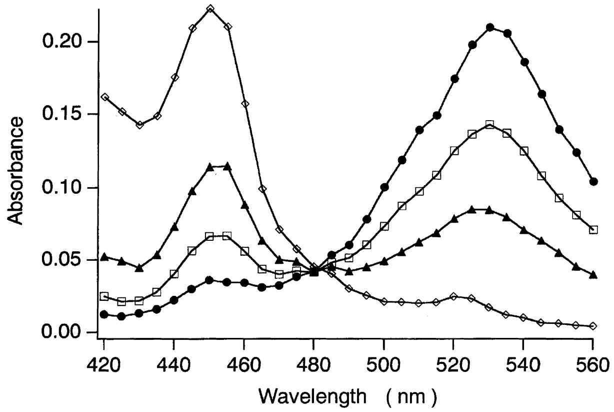

Fig. 4. Transient absorption spectra of benzophenone and DPA (151 μM) in benzene excited at 308 nm: 0 (●), 0.3 (□), 0.7 (▲), and 3.5 (◇) μs after the laser. New absorption band appeared around 420–470 nm while absorption at 530 nm decreased. An isosbestic point was clearly observed at 480 nm.

3.2. Transient absorption measurements on benzophenone-DPA system

Fig. 4 shows transient absorption spectra of benzophenone and DPA (150 μM) in benzene. The absorption band around 530 nm due to the triplet benzophenone decayed while new absorption band around 420–470 nm appeared. An isosbestic point was clearly observed at 480 nm. It should be noted here that no transient signal was observed for an excitation of sole DPA. The new band observed in Fig. 4, well agreed with T–T absorption spectrum of DPA reported previously [14]. Fig. 5a shows the time profiles of the transient absorption monitored at 450 and 530 nm. The risetime at 450 nm corresponded to the decay time at 530 nm. Therefore, it reveals that T–T energy transfer between benzophenone and DPA should occur. The decay rate of triplet benzophenone (530 nm) became larger with DPA concentration as shown in Fig. 5b. The solid lines denote the best fitting curves. Fig. 6 shows Stern–Volmer plots of the deactivation rate of triplet benzophenone against DPA concentration. The solid line indicates the best fitting curve. The quenching rate constant, k_{q}, was determined to be $(3.6\pm0.3)\times10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The obtained value of k_{q} is regarded as the summation of the energy transfer rate (k_{et}) between benzophenone and DPA and the collisional quenching rate (k_{d}). The substantial energy transfer efficiency was successfully obtained with the TRTL technique, as described below.

3.3. TRTL measurements on benzophenone-DPA energy transfer

Fig. 7 shows the time profile of the TRTL signal for the benzophenone-DPA (0.3 mM) system excited at 308 nm. The measurements were carried out under the low photon density region because of being avoided multi-photon absorption described above. The signal is composed of three rising

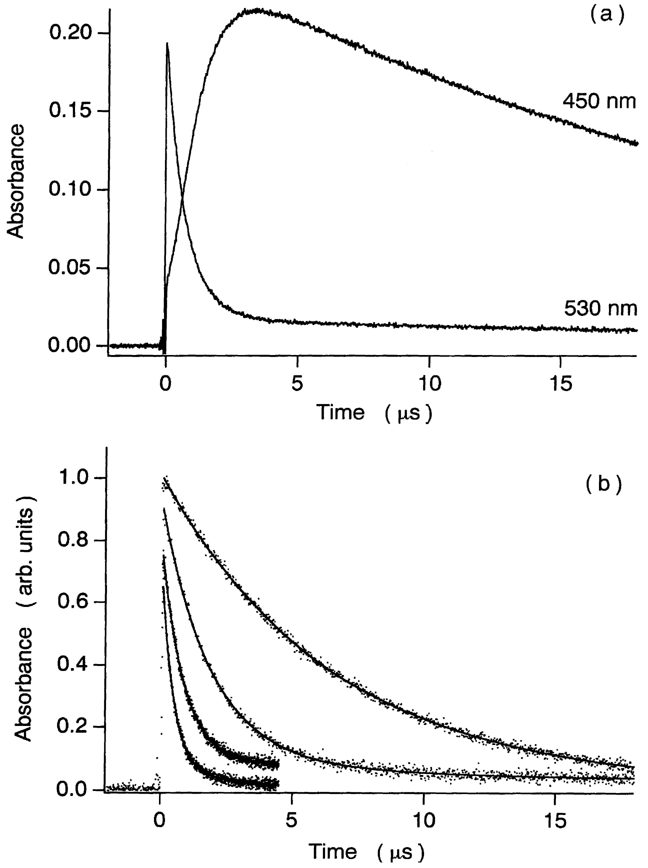

Fig. 5. (a) Time profiles of transient absorption monitored at 450 and 530 nm. The absorption at 450 nm rose with the absorption at 530 nm decayed. (b) Time profiles of the transient absorption monitored at 530 nm with several DPA concentrations; 0, 50, 151, and 201 μM.

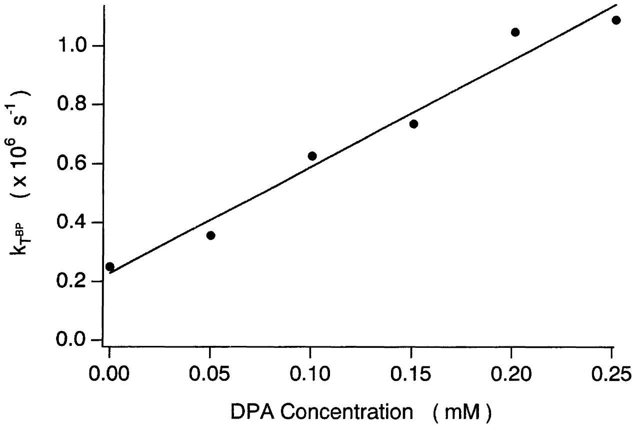

Fig. 6. Stern–Volmer plots of deactivation rate for triplet benzophenone, k_T^{BP}, against DPA concentration. Good linear relation was observed. The solid line was obtained with the least squares' fitting method. The slope gave a quenching rate constant to be k_q=(3.6±0.3)×10^9 M^{-1} s^{-1}.

components, one fast and two slow ones (medium slow and slow). The medium slow component corresponds to the lifetime of triplet benzophenone also shown in Fig. 7, while the slow component to the lifetime of triplet DPA produced by the energy transfer (38 μs) described in the previous section. Therefore, analyzing the time profile of the TRTL signal will give us the information on intrinsic energy transfer rate, k_{et}. The heat conversion efficiency of the total heat for energy transfer was unity, determined at 500 μs after the laser irradiation with the same procedure described above on the assumption that only benzophenone absorbs the laser light. The assumption seems to be valid because of the quite low absorbance for DPA in addition to the small α value (0.31).

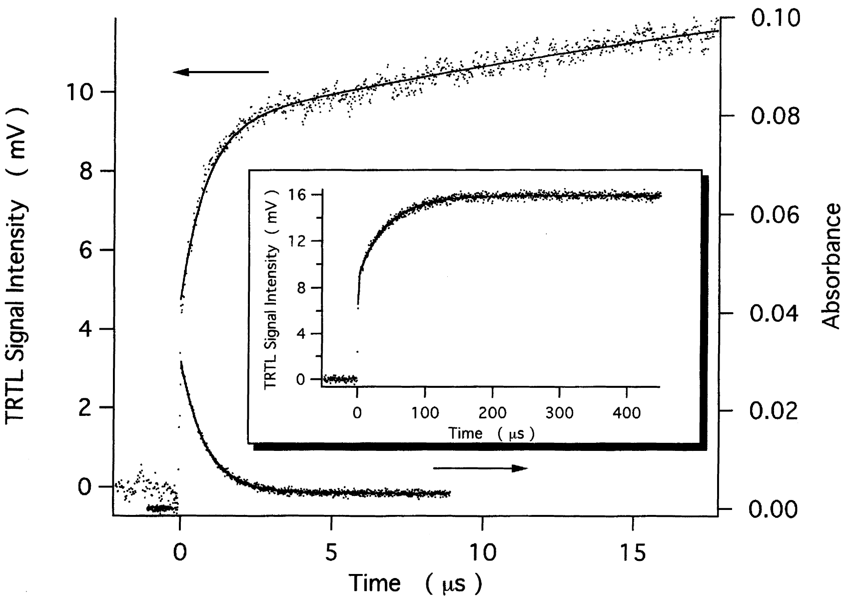

Fig. 7. Time profile of the TRTL signal for the benzophenone-DPA (0.3 mM) system excited at 308 nm. The time profile showed one fast and two slow components: medium slow and slow ones. The medium slow component corresponded to the decay of triplet benzophenone, which is also indicated in the fig. The solid line was obtained with the least squares' fitting method of Eq. (6). See text in detail.

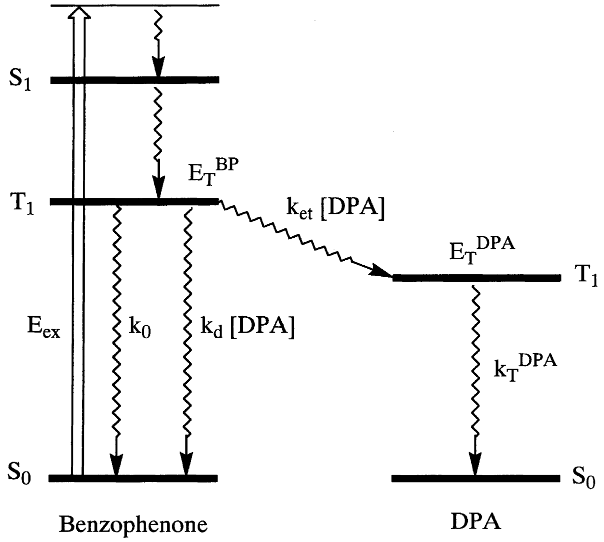

Fig. 8. Schematic energy diagram for benzophenone and DPA. E_{ex}, $E_{\mathrm{T}}^{\mathrm{BP}}$, and $E_{\mathrm{T}}^{\mathrm{DPA}}$ denote energies of the excitation laser, triplet energies for benzophenone and DPA, respectively. $k_{\mathrm{T}}^{\mathrm{BP}}$ and $k_{\mathrm{T}}^{\mathrm{DPA}}$ are the deactivation rate constants for triplet benzophenone and DPA, respectively. k_0 is the unimolecular decay rate constant for triplet benzophenone, and k_{et} and k_{d} are the rate constants for collisional quenching by DPA with and without energy transfer, respectively. $k_{\mathrm{T}}^{\mathrm{BP}}=k_0+k_{\mathrm{q}}[\mathrm{DPA}]$ and $k_{\mathrm{q}}=k_{\mathrm{d}}+k_{\mathrm{et}}$.

Schematic energy diagram for the benzophenone-DPA system is described in Fig. 8. The released heat is related to the concentrations and energies of excited states. The concentrations of triplet benzophenone and DPA are expressed as follows:

$$[^3\mathrm{BP}^*] = C_0 \exp(-k_{\mathrm{T}}^{\mathrm{BP}} t),$$

$$[^3\mathrm{DPA}^*] = \left\{ \frac{k_{\mathrm{et}}[^1\mathrm{DPA}]C_0}{(k_{\mathrm{T}}^{\mathrm{BP}} - k_{\mathrm{T}}^{\mathrm{DPA}})} \right\} \{\exp(-k_{\mathrm{T}}^{\mathrm{DPA}} t) - \exp(-k_{\mathrm{T}}^{\mathrm{BP}} t)\}$$

where C_0 and $[^1\mathrm{DPA}]$ are concentrations of initially excited benzophenone, and DPA in the ground state, $k_{\mathrm{T}}^{\mathrm{BP}}$ and $k_{\mathrm{T}}^{\mathrm{DPA}}$ are deactivation rate constants for triplet benzophenone and triplet DPA, and k_{et} is the T–T energy transfer rate constant. Therefore, with the triplet energies of $E_{\mathrm{T}}^{\mathrm{BP}}$ (benzophenone) and $E_{\mathrm{T}}^{\mathrm{DPA}}$ (DPA), the time-dependent heat is described as

$$\frac{U(t)}{K} = p - q \exp(-k_{\mathrm{T}}^{\mathrm{DPA}} t) - r \exp(-k_{\mathrm{T}}^{\mathrm{BP}} t) \tag{6}$$

where

$$p = C_0 E_{\mathrm{ex}}, \qquad q = p - r, \qquad r = \frac{C_0 E_{\mathrm{T}}^{\mathrm{DPA}} k_{\mathrm{et}}[^1\mathrm{DPA}]}{(k_{\mathrm{T}}^{\mathrm{BP}} - k_{\mathrm{T}}^{\mathrm{DPA}})}.$$

The time profile of the TRTL signal in Fig. 7 was analyzed with the least squares' fitting method of the bi-exponential equation (Eq. (6)). The best fitting curve is shown as a solid line in Fig. 7. The k_{et} value was successfully obtained to be $3.6\times10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ by using the ratio of pre-exponential factors, r/p=0.40, the $E_{\mathrm{T}}^{\mathrm{DPA}}$ value (171 kJ/mol [14,15]), and the values of $k_{\mathrm{T}}^{\mathrm{BP}}$ and $k_{\mathrm{T}}^{\mathrm{DPA}}$, which have been already obtained with the transient absorption. Hence, it concluded that the energy transfer efficiency ($k_{\mathrm{et}}/k_{\mathrm{q}}$) becomes almost unity, since k_{q} obtained with the quenching experiment for triplet benzophenone is exactly equal to k_{et}. When triplet benzophenone was deactivated into the S_0 state by collision with DPA in the ground state, energy transfer to produce triplet DPA does occur effectively.

The photosensitization is a powerful technique to obtain the extinction coefficient of the target triplet molecule. However, it stands on the notable assumption that the efficiency would be unity. With the efficiency determined above, we estimated the absorption coefficient of DPA triplet as follows,

$$\frac{\mathrm{OD}_{4.5\,\mu s}^{450}}{\mathrm{OD}_0^{530}} = \left(\frac{\varepsilon_{\mathrm{DPA}}^{450}}{\varepsilon_{\mathrm{BP}}^{530}}\right)\left(\frac{k_{\mathrm{et}}[\mathrm{DPA}]}{k_{\mathrm{T}}^{\mathrm{BP}}}\right) \tag{7}$$

where OD_t^{λ} is absorbance monitored at λ nm at time t, $\varepsilon_{\mathrm{BP}}^{\lambda}$and $\varepsilon_{\mathrm{DPA}}^{\lambda}$ are extinction coefficients at λ nm for benzophenone and DPA, respectively. The ratio of $\varepsilon_{\mathrm{DPA}}^{450}/\varepsilon_{\mathrm{BP}}^{530}$ was obtained to be 1.77 because $\mathrm{OD}_{4.5\,\mu s}^{450}/\mathrm{OD}_0^{530} = 1.06$ when [DPA]=0.3 mM. Hence, the $\varepsilon_{\mathrm{DPA}}^{450}$ value was successfully determined to be $1.28\times10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ with the reported $\varepsilon_{\mathrm{BP}}^{530}$ value ($7220\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ [30]). It well agrees with the averaged extinction coefficient for DPA, reported to be $15600\pm5240\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ [31].

The energy transfer technique method is one of the most widespread methods of measuring the T–T absorption coefficient. However, there still remains an uncertainty even after some kinetic corrections are made (e.g. unimolecular disappearance of the excited donor and acceptor). It has become apparently not to need this type of correction in the system of benzophenone-DPA dilute solution because of the efficiency of unity. If the acceptor deactivates the excited donor without the acceptor itself being excited (k_{d}), a correction has to be required. The TRTL technique is applicable to obtain the substantial energy transfer efficiency.

4. Conclusion

Photophysical character of DPA in benzene was studied with the TRTL technique with the XeCl excimer laser excitation. The time profile of the TRTL signal was composed of the fast part and the slow one. The total heat was quantitatively analyzed with the calorimetric standard of HBP, and the heat conversion efficiency was determined to be 0.31, revealing that the fluorescence quantum yield was 0.88. The quantum yield of triplet formation was also obtained to be quite low (0.04). The photophysical character, quite high fluorescence quantum yield and low triplet formation yield, will be explained with the internal rotation of two phenyl at the inter-ring single bonds. The T–T absorption spectrum for DPA was obtained with benzophenone photosensitization technique. The new absorption band was observed in the spectral range of 420–470 nm, which well agrees with the reported one. The TRTL signal was also measured in the benzophenone-DPA system. It was found to be three rising components: one fast and two slow ones (medium slow and slow). The slow one results from the triplet DPA relaxation produced by energy transfer from triplet benzophenone. The slow component was quantitatively analyzed, and the intrinsic energy transfer rate constant, k_{et}, was successfully determined to be the same rate constant as the k_{q} value. It reveals that the energy transfer efficiency is almost unity. We estimated the extinction coefficient of DPA's T–T absorption.

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