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Some triplet energy-transfer reactions initiated by photoexcitation of triplet excited state of dibenz[*a*,*h*]anthracene to the higher triplet excited states

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Abstract—Some triplet energy-transfer reactions initiated by photoexcitation of the triplet excited state of dibenz[*a*,*h*]anthracene to higher triplet excited states (DBA(T_n)) were observed in the presence of the triplet energy quenchers (Q) such as naphthalene, biphenyl, *p*-dichlorobenzene, and *o*-dicyanobenzene. In the case of carbon tetrachloride (CCl_4) as Q, DBA(T_n)-sensitized decomposition of CCl_4 occurred.

Polycyclic aromatic hydrocarbons (PAH) such as naphthalene (Np), anthracene, dibenz[*a*,*h*]anthracene (DBA), and chrysene have attracted much attention from the chemical and biological aspects.[1] Reactions of PAH in the singlet (S_1) and lowest triplet (T_1) excited states have been extensively studied.[2,3] Similarly, reactions involving PAH in the higher excited states such as anthracene and its substituted compounds in the T_2 state have been investigated.[4–7] However, work on the reactions involving PAH in the higher triplet excited states (T_n, $n \geq 2$) is still limited.[8–10] Recently, we found that the triplet energy transfer occurs from chrysene(T_n) and Np(T_n) to quenchers (Q) such as biphenyl (Bp), *p*-dichlorobenzene (DCB), and *o*-dicyanobenzene (DCNB), and that the decomposition of carbon tetrachloride (CCl_4) is sensitized by chrysene(T_n) and Np(T_n).[11,12] According to the electron transfer theories, the electron transfer quenching of chrysene(T_n) or Np(T_n) by Q should occur competitively with the triplet energy transfer quenching. However, the electron transfer did not occur between them. It is necessary to study the properties of PAH(T_n) for a variety of PAH.

PAH, having absorption at around 355 nm, high yield of intersystem crossing to give PAH(T_1), and PAH(T_1) with a long lifetime, and intense absorption at 532 nm, can be a candidate for study under our experimental conditions using the 355 nm first laser and 532 nm second laser.[11] DBA was used as a PAH in this study because of its properties (S_0 state absorption peak, 395 nm; ISC yield, 0.9; T_1 state absorption peak, 580 nm).[3] We found the triplet energy transfer quenching of DBA(T_n) by Q such as Np, Bp, DCB, DCNB, and CCl_4, and DBA(T_n)-sensitized decomposition of CCl_4.

DBA(T_1), generated from irradiation of DBA (3.6×10^{-4} M) with the first 355 nm Nd:YAG laser (5 mJ pulse^{-1}) in Ar-saturated acetonitrile solution, showed absorption peaks in the range of 400–600 nm (Fig. 1(a)), similarly to those reported.[2,3] The second 532 nm Nd:YAG laser (50 mJ pulse^{-1}) was irradiated to the sample at the delay time of 160 ns after the first 355 nm laser excitation, giving DBA(T_n). However, no change in the transient absorption of DBA(T_1) was observed. It is suggested that the internal conversion $T_n \rightarrow T_1$ was fast and accomplished within the laser flash duration of 5 ns. It is also found that no photoionization occurred during the 355 and 532 nm two-laser irradiation of DBA.

On the other hand, bleaching ($\Delta\Delta O.D._{570}$) and recovery of the transient absorption of DBA(T_1) at 570 nm and formation of a new absorption peak at 415 nm were

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Keywords: dibenz[*a*,*h*]anthracene (DBA); higher triplet excited states; triplet energy transfer; sensitized reactions; decomposition of carbon tetrachloride.

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observed in the presence of Np, which increased with increasing the concentration of Np ($0.3<[Np]<1.0$ M). The spectral changes and time profiles of the transient absorption of $Np(T_1)$ at 415 nm[2,3] and $DBA(T_1)$ at 570 nm are shown in Figures 1 and 2.

The experimental results show that a reaction of $DBA(T_n)$ and Np occurred. Neither a radical cation nor a radical anion of Np and DBA was observed, suggesting no occurrence of the electron transfer. The transient absorptions of $Np^{\bullet+}$, $Np^{\bullet-}$, $DBA^{\bullet+}$, and $DBA^{\bullet-}$ are well known to have the corresponding peaks at 690, 755, 753, and 790 nm, respectively,[13] and are easily detected. When Np (E_{T1}: 253 kJ mol^{-1}) was replaced by Bp (E_{T1}: 274 kJ mol^{-1}), DCB (E_{T1}: 335 kJ mol^{-1}), or DCNB (E_{T1}: ~295kJ mol^{-1}) with the T_1 state energy (E_{T1}) higher than that of $DBA(T_1)$ (E_{T1}: 218 kJ mol^{-1})[3] but lower than that of $DBA(T_n)$ (E_{T_n} of $DBA(T_n)$ was estimated to be 443 kJ mol^{-1} from E_{T1} of $DBA(T_1)$ and 532 nm photon energy), $\Delta\Delta O.D._{570}$ and the recovery of the transient absorption of $DBA(T_1)$ was observed similarly to the case of Np.

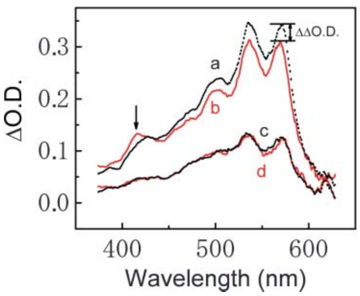


Figure 1. Transient absorption spectra observed at 30 ns after the second 532 nm laser irradiation during two-laser two-step flash photolysis of DBA in the absence (a) and presence of Np (0.9 M) (b) in Ar-saturated acetonitrile solution. (c) and (d) were observed at 2.5 μs after the 532 nm laser irradiation of (a) and (b), respectively.

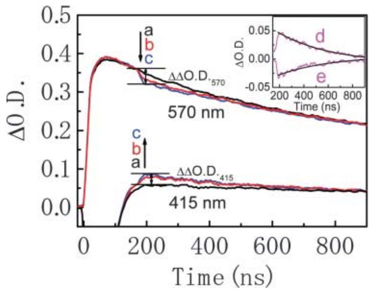


Figure 2. Time profiles of the transient absorption at 570 and 415 nm assigned to $DBA(T_1)$ and $Np(T_1)$, respectively, during two-laser two-step flash photolysis of DBA in the absence (a) and presence of Np at 0.7 (b) and 0.9 (c) M in Ar-saturated acetonitrile solution. Inset shows the amplification of the growth and decay of $Np(T_1)$ at 415 nm (d) together with the bleaching and recovery of $DBA(T_1)$ at 570 nm (e) which were obtained by subtraction of (a) from (c). The trace lines were obtained from calculation according to the first-order rate equation. The initial growth of the transient absorption of $DBA(T_1)$ at 570 nm in the time scale of few tens ns corresponds to the intersystem crossing from $DBA(S_1)$ to $DBA(T_1)$. The large minus signal of ΔO.D. at 415 nm in the range of 100 ns is due to fluorescence of $DBA(S_1)$ with 30 ns lifetime.

The free energy change in the energy transfer between $DBA(T_n)$ and DCNB, $\Delta G_{en}=-E_{Tn}(DBA)+E_{T1}(DCNB)$, was calculated to be −138 kJ mol^{-1}. For the electron transfer between $DBA(T_n)$ and DCNB, $\Delta G_{el}=96.488\times[E^{ox}_{1/2}(DBA)-E^{red}_{1/2}(DCNB)]-E_{T_n}(DBA)$ was calculated to be −124 kJ mol^{-1}, where $E^{ox}_{1/2}(DBA)$ is the oxidation potential (+1.19 V) in acetonitrile versus standard calomel electrodes (SCE), and $E^{red}_{1/2}(DCNB)$ is the reduction potential (−2.12 V) in *N*,*N*-dimethylformamide (DMF) versus $Ag/AgClO_4$, the difference in the potentials between versus $Ag/AgClO_4$ and versus SCE is ±0.3 V.[3] According to the electron transfer theories,[3,14,15] the energy and electron transfer rate constants (k_{en} and k_{el}) were calculated from ΔG_{en} and ΔG_{el}, to be $k_{en}=k_{el}=6.6\times10^{10}$ M^{-1} s^{-1}.[16] Therefore, it is suggested that the energy and electron transfer reactions from $DBA(T_n)$ to DCNB should occur competitively. However, the experimental results show that only triplet energy transfer occurred from $DBA(T_n)$ to DCNB and other Qs (Eq. (1)).

$$DBA(T_n)+Q(S_0)\rightarrow DBA(T_1)+Q(T_1) \qquad (1)$$

It is suggested that ΔG_{el} are too negative to cause the electron transfer in the inverted region.[14,15] It is also suggested that, because of the different properties of $DBA(T_n)$ from those of $DBA(T_1)$, the reactions of $DBA(T_n)$ with Q can not be explained using the electron transfer theories for molecules in the S_1 or T_1 states.[14,15]

Since E_{T1} of Q is higher than that of $DBA(T_1)$, the second triplet energy transfer occurred from $Q(T_1)$ to $DBA(S_0)$ (Eq. (2)).

$$Q(T_1)+DBA(S_0)\rightarrow DBA(T_1)+Q(S_0) \qquad (2)$$

The decay of $Np(T_1)$ and growth of $DBA(T_1)$ after the 532 nm second laser excitation occurred in the same time scale as shown in Figure 2 inset. Since $[Np(T_1)]=1.0\times10^{-6}$ M estimated from $\Delta\Delta O.D._{570}$ and $\Delta\Delta O.D._{415}$ was much lower than [DBA], both of the decay and growth were fitted to the first-order rate equation. The rate constants of both the growth (k_g) and the decay (k_d) were calculated to be 2.0×10^{10} M^{-1} s^{-1}, which is equivalent to the diffusion-controlled rate constant ($k_{diff}=1.9\times10^{10}$ M^{-1} s^{-1}).[3]

However, when Np was replaced with CCl_4 ($0.01<[CCl_4]<0.2$ M), entirely different experimental results were observed. $\Delta\Delta O.D._{570}$ was similarly observed and increased with increasing $[CCl_4]$, while no recovery of the transient absorption of $DBA(T_1)$ at 570 nm was observed (Fig. 3).

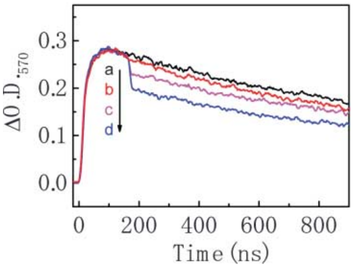


Figure 3. Time profiles of the transient absorption of DBA(T_1) at 570 nm during two-laser two-step flash photolysis of DBA in the absence (a) and presence of CCl_4 with 0.01 (b), 0.08 (c), and 0.15 (d) M, in Ar-saturated acetonitrile solution. The growth of the transient absorption of DBA(T_1) in the time scale of few tens ns was due to the formation of DBA(T_1) through intersystem crossing from DBA(S_1).

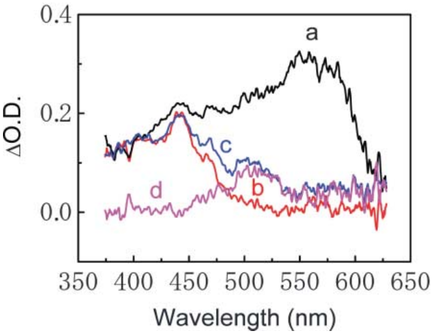


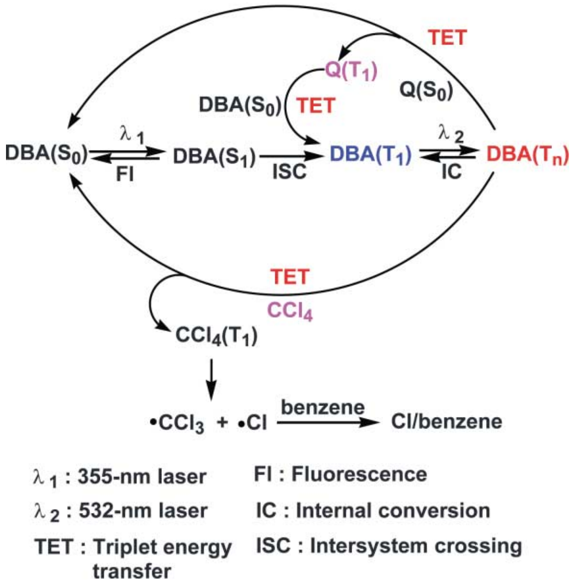
Figure 4. Transient absorption spectra observed at 360 ns after 355-nm laser without 532-nm laser irradiation (a) and with 532-nm laser irradiation during two-laser two-step flash photolysis of DBA (3.6×10^{-4} M) in the absence (b) and presence (c) of benzene 0.85 M, in Ar-saturated CCl_4 solution at room temperature. The delay time of the second 532-nm laser was 160 ns after the first 355-nm laser. The broad absorption with a peak at 510 nm obtained by subtraction of spectra (b) from (c) is assigned to Cl/benzene complex (d).

When CCl_4 was replaced by CH_2Cl_2 or 1,2-dichloroethane, no ΔΔO.D.$_{570}$ was observed. If electron transfer would occur from DBA(T_n) to CH_2Cl_2 or 1,2-dichloroethane as a good electron acceptor,[17,18] ΔΔO.D.$_{570}$ could be observed similarly to the case of CCl_4. The experimental results suggest the occurrence of the triplet energy transfer from DBA(T_n) to CCl_4 and DBA(T_n)-sensitized decomposition of CCl_4 giving a trichloromethyl radical ($^{\bullet}CCl_3$) and a chlorine atom ($^{\bullet}Cl$) (Eq. (3)).[19]

$$\mathrm{DBA}(T_n)+CCl_4\rightarrow \mathrm{DBA}(S_0)+{}^{\bullet}Cl+{}^{\bullet}CCl_3 \qquad (3)$$

The formation of $^{\bullet}Cl$ was confirmed by observation of the Cl/benzene complex with a broad absorption around 510 nm during two-laser, two-step flash photolysis of DBA in CCl_4 in the presence of benzene (Fig. 4).[20,21]

Consequently, the reaction mechanism involving DBA(T_n) and Q was shown in Scheme 1.



Scheme 1. Reaction mechanism involving DBA(T_1), DBA(T_n), and Q.

Other PAH(T_n) such as benz[*a*]anthracene(T_n) and benzo[*e*]pyrene(T_n) also sensitized the decomposition of CCl_4 to give $^{\bullet}CCl_3$ and $^{\bullet}Cl$. It is considered that the triplet energy transfer from PAH(T_n) to Q and PAH(T_n)-sensitized decomposition of CCl_4 are common properties of PAH(T_n) such as DBA(T_n), Np(T_n), chrysene(T_n), benz[*a*]anthracene(T_n), and benzo[*e*]pyrene(T_n) with various structures.

In summary, some triplet energy-transfer reactions initiated by photoexcitation of DBA(T_1) to DBA(T_n) were observed in the presence of Q such as Np, Bp, DCB, and DCNB to give Q(T_1). No electron transfer occurred between DBA(T_n) and Q, which suggested that the properties of DBA(T_n) are different from those of DBA(S_1) and DBA(T_1). In the case of CCl_4 as Q, DBA(T_n)-sensitized decomposition of CCl_4 occurred to give $^{\bullet}CCl_3$ and $^{\bullet}Cl$ radicals with high reactivity. These reactions can not be initiated by DBA(S_1) or DBA(T_1) states. In other words, they can be initiated only by the two-laser excitation method. The T_n-state chemistry will become clear with further theoretical and experimental investigation.

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