

Supporting information for:

Quenching Processes of Aromatic Hydrocarbons in the Higher Triplet Excited States – Energy Transfer vs Electron Transfer

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(1) The quenching of DBA(T_n) by CCl_4 .

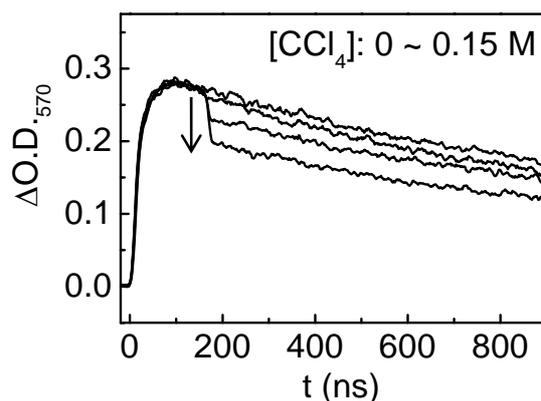


Fig. 1 Time profiles of the transient absorption of DBA(T_1) at 570 nm during two-color two-laser flash photolysis of DBA (3.6×10^{-4} M) in the absence and presence of CCl_4 (0.01, 0.08, and 0.15 M), in Ar-saturated acetonitrile solution. The growth of the transient absorption of DBA(T_1) in the time scale of few tens ns was due to the formation of DBA(T_1) through intersystem crossing from DBA(S_1).

(2) The quenching of CHR(T_n) by NAP

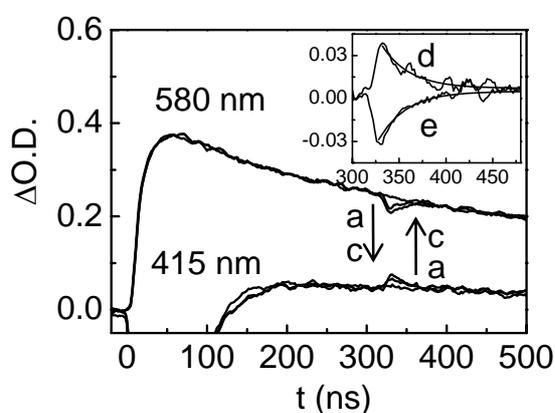


Fig. 2 Time profiles of the transient absorption at 580 and 415 nm during the two-color two-laser flash photolysis of CHR (3.0×10^{-3} M) in the absence (a) and presence of NAP at 0.3 (b) and 0.7 (c) M in Ar-saturated acetonitrile solution. Inset shows the amplification of the growth and decay of NAP(T_1) at 415 nm (d) and the bleaching and recovery of CHR(T_1) at 580 nm (e) which were obtained by

subtraction of (a) from (c). The trace lines were obtained from fits to the pseudo-first-order reactions. The initial growth of the transient absorption of $\text{CHR}(T_1)$ at 580 nm in the time scale of few tens ns corresponds to the intersystem crossing from $\text{CHR}(S_1)$ to $\text{CHR}(T_1)$. The large minus signal of $\Delta\text{O.D.}$ at 415 nm in the range of 100 ns is due to the fluorescence of $\text{CHR}(S_1)$ with the lifetime of 40 ns.

(3) The evidences for no formation of DBA and CHR radical cations produced during two-color two-laser flash photolysis.

$\text{DBA}^{\bullet+}$ and $\text{CHR}^{\bullet+}$ can be observed from the two-photon ionization of DBA and CHR in the polar solvents. With the 355-nm laser irradiation of DBA and CHR in Ar-saturated acetonitrile solution at 50 mJ pulse^{-1} , the two-photon ionization of DBA and CHR occurred to give $\text{DBA}^{\bullet+}$ and $\text{CHR}^{\bullet+}$, respectively. The transient absorption spectra assigned to $\text{DBA}^{\bullet+}$ and $\text{CHR}^{\bullet+}$ were observed and similar to the reported results¹ (Figs. 3 and 4).

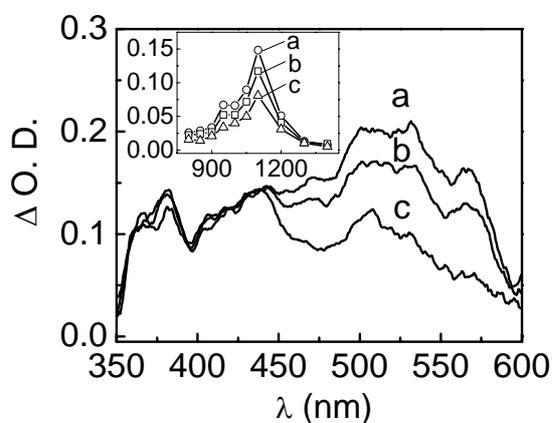


Fig. 3 Transient absorption spectra observed at (a) 0.5, (b) 1.0, and (c) 2.0 μs after the 355-nm laser irradiation of DBA at 50 mJ pulse^{-1} in Ar saturated acetonitrile solution. Inset shows the transient absorption spectra in the region of 800 – 1400 nm.

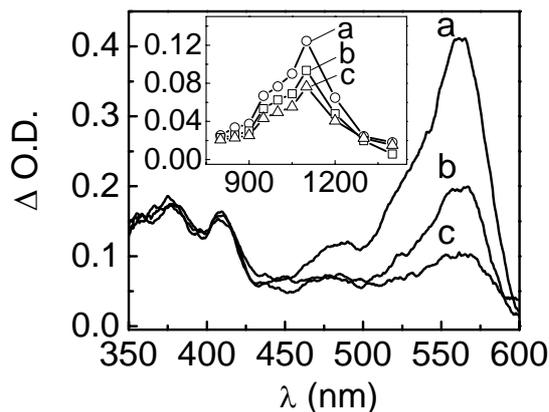


Fig. 4 Transient absorption spectra observed at (a) 0.5, (b) 1.0, and (c) 2.0 μs after the 355-nm laser irradiation of CHR (3.0×10^{-3} M) at 50 mJ pulse^{-1} in Ar-saturated acetonitrile solution. Inset shows the transient absorption spectra in the region of 800 – 1400 nm.

When 1,2-dichloroethane or CH_2Cl_2 was used as Q and solvent in place of CCl_4 , ELT was supposed to occur from $\text{AH}(\text{T}_n)$ to Q. However, no change of transient absorptions of $\text{DBA}(\text{T}_1)$ or $\text{CHR}(\text{T}_1)$ was observed during the two-color two-laser flash photolysis (Figs. 5 and 6).

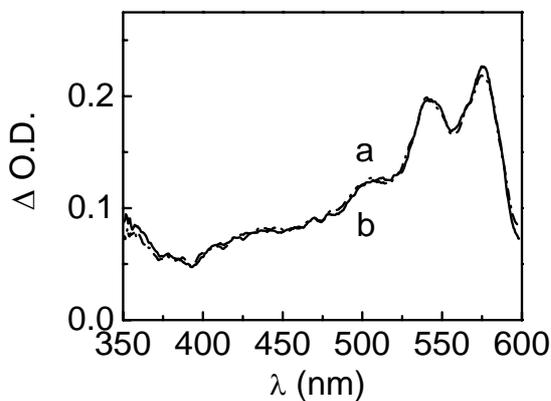


Fig. 5 Transient absorption spectra observed at 260 ns after the first 355-nm laser irradiation (a) (broken line), and at 100 ns after the second 532-nm laser irradiation during the two-color two-laser flash photolysis of DBA (b) (solid line) in Ar-saturated 1,2-dichloroethane solution.

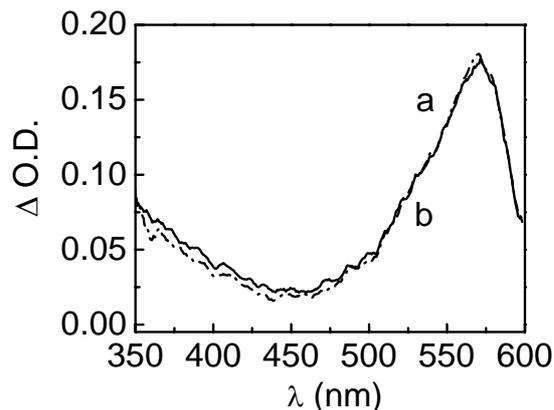


Fig. 6 Transient absorption spectra observed at 260 ns after the first 355-nm laser irradiation (a) (broken line), and at 100 ns after the second 532-nm laser irradiation during the two-color two-laser flash photolysis of CHR (b) (solid line) in Ar-saturated CH_2Cl_2 solution.

Consequently, it is clearly evidenced that no ELT occurred from $\text{NAP}(\text{T}_n)$, $\text{DBA}(\text{T}_n)$, or $\text{CHR}(\text{T}_n)$ to Q.

(4) The evidence for $\text{AH}(\text{T}_n)$ -sensitized cleavage of C-Cl bond of CCl_4 through TENT and the formation of benzene/Cl complex.

When CCl_4 was used as a Q of $\text{NAP}(\text{T}_n)$, $\text{DBA}(\text{T}_n)$, and $\text{CHR}(\text{T}_n)$, the bleaching and no recovery of the transient absorptions of $\text{AH}(\text{T}_1)$ were observed. Since neither AH^+ nor AH^- was observed during the two-color two-laser flash photolysis of AH in the presence of CCl_4 , the decomposition of C-Cl bond of $\text{CCl}_4(\text{T}_1)$ occurred to give $\cdot\text{CCl}_3$ and $\cdot\text{Cl}$ radicals.² To confirm this decomposition mechanism, the two-color two-laser excitation experiment of NAP was performed in the presence of benzene with various [benzene] (0 - 2.0 M) in Ar-saturated CCl_4 . In the absence of benzene, bleaching of the transient absorption at 490 nm was observed similarly to that at 415 nm. However, the bleaching of $\Delta\text{O.D.}_{490}$

decreased with an increase of [benzene] (Fig. 7). No change of $\Delta\text{O.D.}_{415}$ of $\text{NAP}(\text{T}_1)$ was observed at various [benzene] in the solutions.

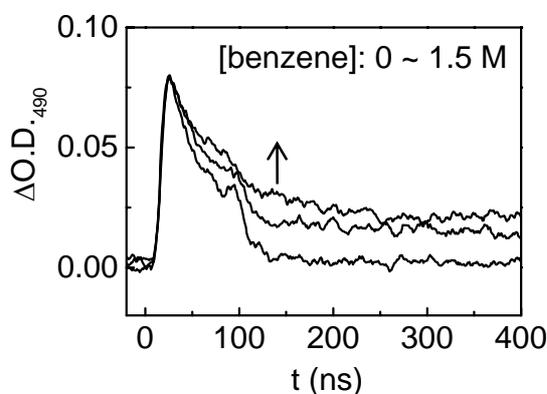


Fig. 7 Time profiles of $\Delta\text{O.D.}_{490}$ during the two-color two-laser flash photolysis of a mixture of NAP and benzophenone as the triplet sensitizer in the absence and presence of benzene (1.0 and 1.5 M) in Ar-saturated CCl_4 solution.

A benzene/Cl complex has been reported to have a peak around 500 nm.^{2,3} Therefore, the results shown in Fig. 8 are interpreted by the formation of the benzene/Cl complex, indicating the $\text{NAP}(\text{T}_n)$ -sensitized cleavage of the C-Cl bond in $\text{CCl}_4(\text{T}_1)$. Generation of $\cdot\text{Cl}$ can be attributed to the TENT quenching not to the ELT quenching, because no change of $\Delta\text{O.D.}_{415}$ of $\text{NAP}(\text{T}_1)$ was observed during the two-color two-laser photolysis of NAP in 1,2-dichloroethane as a good electron acceptor in place of CCl_4 . Similar $\text{AH}(\text{T}_n)$ -sensitized scission of the C-Cl in $\text{CCl}_4(\text{T}_1)$ was found to occur during the quenching of $\text{DBA}(\text{T}_n)$ and $\text{CHR}(\text{T}_n)$ by CCl_4 .^{4,5}

References

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