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(Tn) by CCl4.
Fig. 1 Time profiles of the transient absorption of DBA(T₁) at 570 nm during two-color two-laser flash photolysis of DBA (3.6 × 10⁻⁴ M) in the absence and presence of CCl₄ (0.01, 0.08, and 0.15 M), in Ar-saturated acetonitrile solution. The growth of the transient absorption of DBA(T₁) in the time scale of few tens ns was due to the formation of DBA(T₁) through intersystem crossing from DBA(S₁).

(2) The quenching of CHR(Tₙ) 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(T₁) at 415 nm (d) and the bleaching and recovery of CHR(T₁) 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 CHR(T₁) at 580 nm in the time scale of few tens ns corresponds to the intersystem crossing from CHR(S₁) to CHR(T₁). The large minus signal of ΔO.D. at 415 nm in the range of 100 ns is due to the fluorescence of CHR(S₁) 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.

DBA** and CHR** 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 DBA** and CHR**, respectively. The transient absorption spectra assigned to DBA** and CHR** were observed and similar to the reported results¹ (Figs. 3 and 4).

![Transient absorption spectra](image)

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.
When 1,2-dichloroethane or CH$_2$Cl$_2$ was used as Q and solvent in place of CCl$_4$, ELT was supposed to occur from AH(T$_n$) to Q. However, no change of transient absorptions of DBA(T$_1$) or CHR(T$_1$) was observed during the two-color two-laser flash photolysis (Figs. 5 and 6).
Consequently, it is clearly evidenced that no ELT occurred from NAP(Tₙ), DBA(Tₙ), or CHR(Tₙ) to Q.

(4) The evidence for AH(Tₙ)-sensitized cleavage of C-Cl bond of CCl₄ through TENT and the formation of benzene/Cl complex.

When CCl₄ was used as a Q of NAP(Tₙ), DBA(Tₙ), and CHR(Tₙ), the bleaching and no recovery of the transient absorptions of AH(T₁) were observed. Since neither AH⁺⁺ nor AH⁺ was observed during the two-color two-laser flash photolysis of AH in the presence of CCl₄, the decomposition of C-Cl bond of CCl₄(T₁) occurred to give *CCl₃ and *Cl radicals.⁴ 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 CCl₄. 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 ∆O.D.₄₉₀
decreased with an increase of [benzene] (Fig. 7). No change of \( \Delta O.D._{415} \) of NAP(T₁) was observed at various [benzene] in the solutions.

Fig. 7 Time profiles of \( \Delta O.D._{490} \) 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 CCl₄ 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 NAP(Tₙ)-sensitized cleavage of the C-Cl bond in CCl₄(T₁). Generation of \( \cdot \text{Cl} \) can be attributed to the TENT quenching not to the ELT quenching, because no change of \( \Delta O.D._{415} \) of NAP(T₁) was observed during the two-color two-laser photolysis of NAP in 1,2-dichloroethane as a good electron acceptor in place of CCl₄. Similar AH(Tₙ)-sensitized scission of the C-Cl in CCl₄(T₁) was found to occur during the quenching of DBA(Tₙ) and CHR(Tₙ) by CCl₄.⁴,⁵

References