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Naphthalene in the higher triplet excited state†

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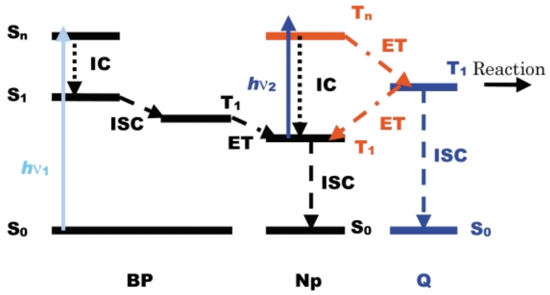
Naphthalene in the higher triplet excited state Np(T_n) was generated from the two-step excitation method using two-colour two-laser flash photolysis technique and the lifetime of Np(T_n) was estimated to be 4.5 ps from the triplet energy quenching by quenchers such as *p*-dichlorobenzene, *o*-dicyanobenzene and carbon tetrachloride.

Naphthalene (Np) is one of the most important aromatic compounds and has been extensively studied in photochemistry and photophysics. Since Np exhibits rich vibronic structure in its electronic transition compared with benzene, Np has been extensively studied by theoretical chemists.[1–6] The vibronic structures of fluorescence and phosphorescence spectra of Np calculated from quantum chemistry methods agree with the experimental results. The triplet–triplet absorption spectrum with a peak at 415 nm is identified as the $T_{10} \leftarrow T_1$ transition in polar solvents such as acetonitrile.[1–3,6,7] Although Np in the higher triplet excited state Np(T_n) is a very interesting research subject,[8,9] no experiment has been reported on Np(T_n). In the present paper, we report on Np(T_n) based on the triplet energy transfer quenching by triplet quenchers (Q) such as *p*-dichlorobenzene (DCB), *o*-dicyanobenzene (DCNB) and carbon tetrachloride (CCl_4) using the two-colour two-laser flash photolysis technique.

Since the quantum yield of fluorescence of Np ($\phi_f = 0.19$) is high,[7] the best way to get Np in the lowest triplet excited state Np(T_1) is the triplet energy transfer method.[10,11] Np(T_n) is obtained by excitation of Np(T_1) with irradiation of laser light at 425 nm tuned to the absorption of Np(T_1). Scheme 1 shows the energy diagram involving Np(S_0), Np(T_1), Np(T_n), Q(S_0), and Q(T_1).

When benzophenone (BP) (6.0×10^{-3} M) was selected as a triplet sensitizer of Np (6.0×10^{-3} M) in Ar-saturated acetonitrile solution at room temperature, Np(T_1) with an absorption peak at 415 nm was obtained during irradiation with a Nd:YAG laser (355 nm, 6 mJ pulse^{-1}). Excitation of Np(T_1) with an OPO laser (425 nm, 9 mJ pulse^{-1}) pumped by another Nd:YAG laser (355 nm, 150 mJ pulse^{-1}) with a delay time of 100 ns after the first Nd:YAG laser gave Np(T_n). No change of the transient absorption of Np(T_1) was observed during irradiation with two lasers. It is suggested that the fast internal conversion of $T_n \rightarrow T_1$ occurs within the laser flash duration (~5 ns). However, entirely different consequences were observed in the presence of CCl_4. The bleaching of the transient absorption of Np(T_1) was observed and increased with increasing concentration of CCl_4. No change of transient absorption of Np(T_1) was observed under irradiation by one laser at 355 or 425 nm in the presence of CCl_4. The bleaching was observed only in the presence of CCl_4 and with irradiation of two lasers as shown in Fig. 1.

Similar experimental results were observed in the presence of CH_2Cl_2. The decomposition of CCl_4 or CH_2Cl_2 sensitized by Np(T_n) occurred to give CCl_3 + Cl or CH_2Cl + Cl, respectively. Formation of the Cl–benzene complex was observed by detection of the transient absorption with a peak at 490 nm in the presence of benzene in CCl_4 solution, confirming Np(T_n)-sensitized cleavage of the C–Cl bond in CCl_4.‡ It is well known that Cl reacts with various arenes to give Cl–arene complexes with an absorption peak around 500 nm.[9,12,13] Therefore, triplet energy transfer from Np(T_n) to CCl_4 or CH_2Cl_2 occurs to cause the C–Cl bond cleavage. In order to elucidate the mechanism involving these phenomena, several Qs such as DCB and DCNB were used. These Qs are transparent at 355 and 425 nm and their triplet energies (E_T) are higher than those of BP and Np. The bleaching and recovery of the transient absorption of Np(T_1) were observed. The bleaching increased with increasing concentration of Q ($0.3 < [Q] < 1.0$ M) as shown in Fig. 2. The recovery was accomplished in 100% yield without formation of a new peak and the recovery time range was almost constant. If DCNB could act as an electron acceptor for the quenching of Np(T_n), Np radical cation and DCNB radical anion would be observed. In the separate experiment with 308 nm excimer laser irradiation of Np and DCNB mixture in acetonitrile, we observed Np radical cation and Np dimer radical cation with absorption peaks at 625 and 685 nm and 570 nm, respectively.[14] The yield of Np(T_n) from Np(T_1) was calculated from the



Scheme 1 Energy level diagram and reaction mechanism involving Np(T_n), BP: benzophenone, Q: triplet energy quenchers of Np(T_n), $h\nu_1$: 355 nm laser, $h\nu_2$: 425 nm laser, solid and dotted lines indicate radiation and radiationless processes.

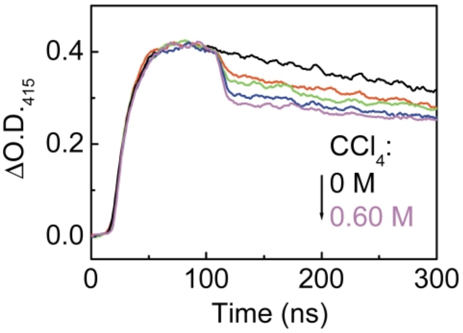


Fig. 1 Kinetic traces illustrating the time profiles of ΔO.D.$_{415}$ in the two-colour two-laser flash photolysis of Np in the absence and presence of CCl_4: 0.25, 0.35, 0.50, 0.60 M, in Ar-saturated acetonitrile solution at room temperature.

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† Electronic supplementary information (ESI) available: yield of Np(T_n), evidence for the formation of a Cl–benzene complex induced by Np(T_n), evidence for no electron transfer from NP(T_n) to Q. See http://www.rsc.org/suppdata/cc/b2/b210118a/

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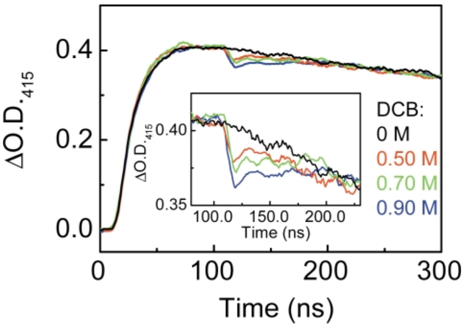

Fig. 2 Kinetic traces illustrating the time profiles of ΔO.D.$_{415}$ in the two-colour two-laser flash photolysis of Np in the absence and presence of DCB: 0.50, 0.70, 0.90 M, in Ar-saturated acetonitrile at room temperature.

bleaching of transient absorption of Np(T_1) to be 65% after the 425 nm laser irradiation in CCl_4. Therefore, Np radical cation must be detected if it is produced from Np(T_n). No change of the transient absorption of Np(T_1) was observed during two-colour two-laser photolysis of Np in 1,2-dichloroethane as a good electron acceptor in place of CCl_4. Therefore, no electron transfer quenching occurred, but energy transfer quenching did.

It is well established that the T–T energy transfer occurs at the diffusion-controlled rate (k_{diff}) when E_T of the triplet excited molecule is 13 kJ mol^{-1} higher than that of the triplet energy acceptor.[11,15] Since, the E_T values of DCB and DCNB in the T_1 state (335 and 305 kJ mol^{-1}, respectively) are much higher than E_T of BP(T_1) and Np(T_1) (289 and 253 kJ mol^{-1}, respectively),[7] and the recovery time range of transient absorption of Np(T_1) is almost constant when CCl_4 was replaced by various concentration of DCB or DCNB as Q. Therefore, the triplet energy transfer from Q(T_1) to Np occurred at k_{diff} to give Np(T_1) and Q(S_0). The triplet energy transfer processes of Q(T_1) $\rightarrow$ BP(S_0) $\rightarrow$ Np(S_0) and Q(T_1) $\rightarrow$ Np(S_0) are involved because of the 1 : 1 ratio of [BP] : [Np]. Since formation of BP(T_1) from the triplet energy transfer of Q(T_1) $\rightarrow$ BP(S_0) and quenching of BP(T_1) by Np(S_0) occur at the same rate, no transient absorption of BP(T_1) at 525 nm was observed.

Since, the formation and decay of Np(T_n) occur within the duration of the 425 nm laser flash, the transient phenomena of Np(T_n) cannot be monitored directly. The bleaching of ΔO.D.$_{415}$ with laser irradiation (ΔΔO.D.$_{415}$ = ΔO.D.$_{before}$ − ΔO.D.$_{after}$) in the presence of CCl_4 results from the energy transfer from Np(T_n) to CCl_4 and increases with increase in the concentration of CCl_4. The inverse of ΔΔO.D.$_{415}$ is represented by the concentration of CCl_4 as in the following equation,[16,17]

$$(\Delta\Delta \mathrm{O.D.}_{415})^{-1} = \alpha + \alpha(k_{ET}\tau[\mathrm{CCl_4}])^{-1}, \qquad (1)$$

where α is a constant depending on the experimental conditions, k_{ET} is the rate constant of the triplet energy transfer from Np(T_n) to CCl_4, and τ is the lifetime of Np(T_n). According to eqn. 1, the Stern–Volmer plots of (ΔΔO.D.$_{415}$)$^{-1}$ *vs.* [CCl_4]$^{-1}$ gave a linear line with an intercept of α and slope of α($k_{ET}\tau$)$^{-1}$ as shown in Fig. 3. From E_T of Np(T_1), 253 kJ mol^{-1},[7] E_T of Np(T_n) is estimated to be 534 kJ mol^{-1} under 425 nm laser excitation in our experiments. E_T of Np(T_n) is much higher than those of Qs(T_1). Therefore, it is reasonably suggested that the energy transfer from Np(T_n) to Qs(S_0) occurs at k_{diff}. However, the energy transfer kinetics from Np(T_n) to Q(S_0) is different from that from Q(T_1) to Np(S_0). The concentration of Q (0.3 < [Q] < 1.0 M) is high and τ is short, while concentration of Np (6 mM) is low and lifetime of Q(T_1) is long (several 100 μs).[7] Therefore, the lifetime dependent quenching should be considered in the case of quenching of short-lived species such as Np(T_n).[18,19] In such cases k_{ET} is indicated from the lifetime independent and dependent terms (eqn. 2),

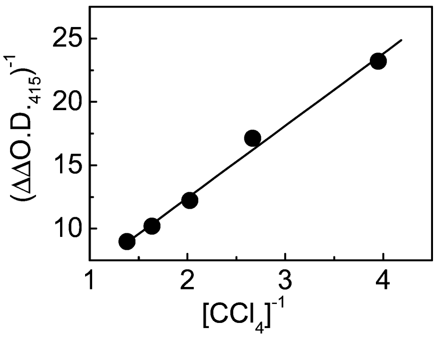

Fig. 3 Plots of (ΔΔO.D.$_{415}$)$^{-1}$ *vs.* [CCl_4]$^{-1}$ in the two-colour two-laser photolysis of Np in the presence of CCl_4.

$$k_{ET} = k_{diff} + k_{diff}\sigma'/(\pi D\tau)^{0.5}, \qquad (2)$$

where $k_{diff} = 4\pi N\sigma' D$, N is the Avogadro number, σ' is the reaction distance, D is the sum of the diffusion coefficients for the excited molecule and quencher molecule. Therefore, τ of Np(T_n) was found to be 4.5 ps at $\sigma' = 0.6$ nm and $D = 2.0 \times 10^{-7}$ dm^2 s^{-1}.[19] Similar results were obtained when CCl_4 was replaced by DCB or DCNB. This is the first report on τ ~ 4.5 ps of Np(T_n).

Np(T_{10}) has a larger transition dipole moment than those of Np($T_{m,\,10 > m > 2}$) according to theoretical calculations using the QCFF/PI + CISD method.[6] All $T_1 \rightarrow T_m$ transitions are forbidden or have very small oscillator strengths. Therefore, the triplet state in the triplet–triplet absorption spectrum was assigned to the $T_1 \rightarrow T_{10}$ transition.[3,6] In other words, the T_{10} state is generated from the 425 nm laser irradiation in the acetonitrile.

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Notes and references

‡ Two-colour two-laser excitation experiments were performed in the presence of various concentrations of benzene (0 ~ 2.0 M) in Ar-saturated CCl_4 solution at room temperature. In the absence of benzene, the bleaching at 490 nm was observed and found to be similar to that at 415 nm. No change of transient absorption of Np(T_1) at 415 nm was observed at various concentrations of benzene in the solutions. However, the bleaching at 490 nm decreased with increasing concentration of benzene. These results show that a Cl–benzene complex with absorption at 490 nm,[9,12,13] is generated from the reaction of benzene and Cl formed by dissociation of CCl_4(T_1) during 425 nm laser radiation.

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