

Intermolecular Electron Transfer from Naphthalene Derivatives in the Higher Triplet Excited States

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Abstract: Intermolecular electron transfer (ELT) from a series of naphthalene derivatives (NpD) in the higher triplet excited states (T_n) to carbon tetrachloride (CCl_4) in Ar-saturated acetonitrile was observed using the two-color two-laser flash photolysis method. The ELT efficiency depended on the driving force of ELT. Since the ELT from the T_n state occurred competitively with the internal conversion (IC, $T_n \rightarrow T_1$) and the triplet energy transfer (ENT), the ELT became apparent only when sufficient free energy change of ELT was attained. On the other hand, ELT from the T_1 state was not observed, although ELT from the T_1 state with sufficiently long lifetime has a slightly exothermic driving force. The fast ELT from the T_n state and lack of the reactivity of the T_1 state were explained well by the "sticky" dissociative electron-transfer model based on one-electron reductive attachment to CCl_4 leading to the C–Cl bond cleavage.

Introduction

Photoinduced electron transfer (ELT), one of the fundamental processes in the physical, chemical, and biological aspects, is an attractive subject and has received much attention.¹ Photoinduced ELT converts electronic excitation energy to chemical energy. Usually the lowest excited state participates in photoinduced ELT. Although ELT from the higher excited states is also energetically possible, the studies are limited.² The intermolecular ELT from the higher excited state (S_2) of zinc-tetraphenylporphyrin to dichloromethane was reported by Okada et al.^{2a} LeGourri rec et al. reported the intramolecular ELT from the S_2 state of porphyrin in a covalently linked zinc porphyrin–ruthenium(II) tris-bipyridine dyad.^{2b} The systematic study on the intramolecular ELT from the S_2 state of porphyrins was carried out by Mataga et al.^{2e–g} The dependence of the intramolecular ELT rate from the S_2 state on the free-energy change and solvent was confirmed. The intermolecular ELT quenching of the S_2 states of azulene, benz[*a*]azulene, and xanthione by several electron donors was investigated by Muller

et al.^{2h} Furthermore, the intermolecular ELT from the D_2 state of stilbene radical cation was reported by Majima et al.^{2i,j} These studies clearly demonstrated that the ELT from the higher excited state is possible even when the lifetime of the higher excited state is as short as a few picoseconds. Therefore, intermolecular ELT from the higher triplet excited states (T_n , $n \geq 2$) seems to be also possible. Because large excitation energy of the T_n state affords larger driving force of ELT even when the ELT from the T_1 state is energetically unfavorable, the ELT is expected to occur from the T_n state.

A limited number of studies have been reported on the properties of molecules in the T_n states.^{3–5} Two-color two-laser flash photolysis can be applied to study photoinduced reactions from the T_n states. It has been reported that the main reaction path from the T_n states is the triplet energy transfer (ENT) to the triplet quenchers.⁴ To the best of our knowledge, there has been only one report on ELT from the T_n state. Wang et al. reported ELT from anthracene(T_2) to ethyl bromoacetate.⁵

(1) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001–2002; Vol. 1–5.

(2) (a) Chosrowjan, H.; Taniguchi, S.; Okada, T.; Takagi, S.; Arai, T.; Tokumaru, K. *Chem. Phys. Lett.* **1995**, *242*, 644. (b) LeGourri rec, D.; Andersson, M.; Davidsson, J.; Mukhtar, E.; Sun, L.; Hammarstr m, L. *J. Phys. Chem. A* **1999**, *103*, 557. (c) Andersson, M.; Davidsson, J.; Hammarstr m, L.; Korppi-Tommola, J.; Peltola, T. *J. Phys. Chem. B* **1999**, *103*, 3258. (d) Nakano, A.; Yasuda, Y.; Yamazaki, T.; Akimoto, S.; Yamazaki, I.; Miyasaka, H.; Itaya, A.; Murakami, M.; Osuka, A. *J. Phys. Chem. A* **2001**, *105*, 4822. (e) Mataga, N.; Chosrowjan, H.; Shibata, Y.; Yoshida, N.; Osuka, A.; Kikuzawa, T.; Okada, T. *J. Am. Chem. Soc.* **2001**, *123*, 12422. (f) Mataga, N.; Chosrowjan, H.; Taniguchi, S.; Shibata, Y.; Yoshida, N.; Osuka, A.; Kikuzawa, T.; Okada, T. *J. Phys. Chem. A* **2002**, *106*, 12191. (g) Mataga, N.; Taniguchi, S.; Chosrowjan, H.; Osuka, A.; Yoshida, N. *Chem. Phys.* **2003**, *295*, 215. (h) Muller, P.-A.; Vauthier, E. *J. Phys. Chem. A* **2001**, *105*, 5994. (i) Ishida, A.; Fukui, M.; Ogawa, H.; Tojo, S.; Majima, T.; Takamuku, S. *J. Phys. Chem.* **1995**, *99*, 10808. (j) Majima, T.; Fukui, M.; Ishida, A.; Takamuku, S. *J. Phys. Chem.* **1996**, *100*, 8913.

(3) (a) Kapusta, P.; Machalick y, O.; Hrdina, R.; Nepra s, M.; Zimmt, M. B.; Fidler, V. *J. Phys. Chem. A* **2003**, *107*, 9740. (b) Kamata, Y.; Akiyama, K.; Tero-Kubota, S. *J. Phys. Chem. A* **1999**, *103*, 1714. (c) Redmond, R. W.; Kochevar, I. E.; Krieg, M.; Smith, G.; McGimpsey, W. G. *J. Phys. Chem. A* **1997**, *101*, 2773. (d) Scaiano, J. C.; Arnold, B. R.; McGimpsey, W. G. *J. Phys. Chem.* **1994**, *98*, 5431.

(4) (a) Cai, X.; Hara, M.; Kawai, K.; Tojo, S.; Majima, T. *Chem. Commun.* **2003**, 2, 222. (b) Cai, X.; Hara, M.; Kawai, K.; Tojo, S.; Majima, T. *Chem. Phys. Lett.* **2003**, *368*, 365. (c) Cai, X.; Hara, M.; Kawai, K.; Tojo, S.; Majima, T. *Chem. Phys. Lett.* **2003**, *371*, 68. (d) Cai, X.; Sakamoto, M.; Hara, M.; Sugimoto, A.; Tojo, S.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *Photochem. Photobiol. Sci.* **2003**, *2*, 1209. (e) Bohne, C.; Kennedy, S. R.; Boch, R.; Negri, F.; Orlandi, G.; Siebrand, W.; Scaiano, J. C. *J. Phys. Chem.* **1991**, *95*, 10300. (f) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 335. (g) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2299. (h) Ladwig, C. C.; Liu, R. S. H. *J. Am. Chem. Soc.* **1974**, *96*, 6210. (i) Ladwig, C. C.; Liu, R. S. H. *Chem. Phys. Lett.* **1975**, *35*, 563. (j) Ladwig, C. C.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 8093. (k) McGimpsey, W. G.; Evans, C.; Bohne, C.; Kennedy, S. R.; Scaiano, J. C. *Chem. Phys. Lett.* **1989**, *161*, 342. (5) Wang, Z.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem.* **1993**, *97*, 374.

However, no detailed mechanism of the ELT from the T_n state has been reported. The photoinduced ELT should be regulated by various factors such as free-energy change, electronic coupling between donor and acceptor, and reorganization energy. Therefore, systematic study is required to elucidate ELT from the T_n state.

In this article, we report the intermolecular ELT from a series of naphthalene derivatives in the T_n state ($\text{NpD}(T_n)$) to carbon tetrachloride (CCl_4). It is found that $\text{NpD}(T_n)$ has a sufficiently long lifetime to cause intermolecular reactions. The driving force dependence of the ELT from $\text{NpD}(T_n)$ is examined. This is the first systematic study of the intermolecular ELT from $\text{NpD}(T_n)$ to CCl_4 .

Results

$\text{NpD}(T_1)$ was generated by the triplet-sensitized reaction during the irradiation with the first laser (355 nm, 3 mJ pulse^{-1}) to a mixture of benzophenone (BP) ($7.0 \times 10^{-3} \text{ M}$) and NpD ($7.0 \times 10^{-3} \text{ M}$) in Ar-saturated acetonitrile at room temperature. $\text{NpD}(T_n)$ was generated by the excitation of $\text{NpD}(T_1)$ with the second laser (425 nm, 9 mJ pulse^{-1}) at 100 or 150 ns after the first laser. In the presence of CCl_4 , bleaching of the transient absorption of 1-methoxynaphthalene(T_1) and growth of new transient absorption peaks at 385 and 702 nm were observed immediately after the second laser irradiation as shown in Figure 1A. The new absorption bands were assigned to 1-methoxynaphthalene radical cation (see Supporting Information).⁶ The inset of Figure 1A shows the kinetic traces of $\Delta\text{O.D.}$ at 440 and 702 nm. Line **a** shows the second laser-induced bleaching of the triplet-triplet (T - T) absorption at 440 nm within the second 425-nm laser flash duration of 5 ns. This bleaching indicates that 1-methoxynaphthalene(T_n) generated with the second laser irradiation did not reproduce 1-methoxynaphthalene(T_1). Line **b** shows the growth of the radical cation absorption at 702 nm within the laser pulse duration. Thus, it is clearly indicated that the ELT from 1-methoxynaphthalene(T_n) to CCl_4 occurred to give the 1-methoxynaphthalene radical cation within the laser flash duration. The ELT from the T_n state was also observed for other NpD such as 1-methylnaphthalene and 1-ethylnaphthalene (Figure 1B and C, respectively). It should be noted that a radical cation was not observed without the second laser irradiation even in the presence of CCl_4 , indicating the contribution of the T_n state to the occurrence of the ELT.

In the absence of CCl_4 , no change of the transient absorption of 1-methoxynaphthalene(T_1) with a peak at 440 nm was observed during the irradiation with the second laser. It is suggested that the fast internal conversion (IC) of $T_n \rightarrow T_1$ occurred within the laser flash duration. Furthermore, this finding excludes the photoionization during the two-color two-laser irradiation. Photoionization of NpD can be also ruled out from the energetical consideration. Since the second laser (425 nm) corresponds to 2.9 eV and the T_1 energy of naphthalene is 2.7 eV, the energy level attained by the second 425-nm laser irradiation is 5.6 eV, which is much lower than the photoionization threshold energy of naphthalene in acetonitrile (7.0 eV).⁷

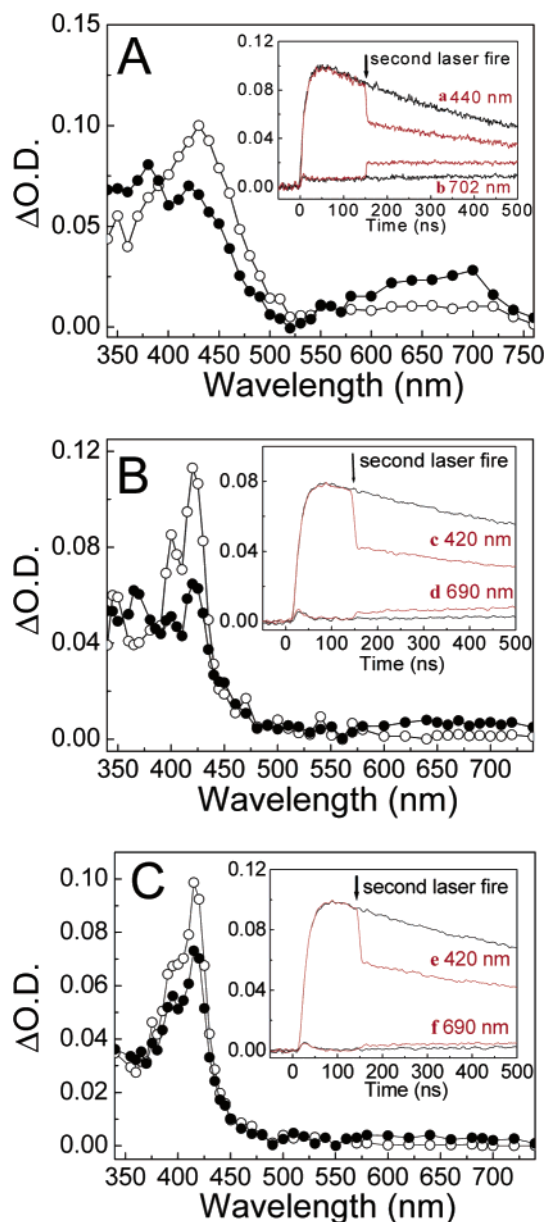


Figure 1. Transient absorption spectra obtained during two-laser (first 355- and second 425-nm) excitation (●) and one-laser (355-nm) excitation (○) of BP ($7.0 \times 10^{-3} \text{ M}$) with 1-methoxynaphthalene (A), 1-ethylnaphthalene (B), or 1-methylnaphthalene (C) ($7.0 \times 10^{-3} \text{ M}$), respectively, in Ar-saturated acetonitrile in the presence of CCl_4 (1.0 M) at room temperature. The second laser was irradiated at 200 ns after the first laser pulse. The insets show the kinetic traces of $\Delta\text{O.D.}$ at 440 (a), 702 (b), 420 (c, e), and 690 (d, f) nm with or without the second 425-nm laser irradiation. The initial growth of $\Delta\text{O.D.}$ in the 50-ns time scale corresponds to the formation of $\text{NpD}(T_1)$ by energy transfer from BP(T_1).

Since no fluorescence from $\text{NpD}(S_1)$ was observed after the second laser irradiation in the absence of CCl_4 , back intersystem crossing ($T_n \rightarrow S_1$) can be neglected. Therefore, $\text{NpD}(S_1)$ is not involved during the second laser irradiation, although ELT from $\text{NpD}(S_1)$ to CCl_4 was reported.⁸ While the T - T absorption of naphthalene is assigned to the $T_1 \rightarrow T_{10}$ transition, fast IC occurs to give the T_2 state.⁹ Contribution of the T_n ($n = 3$ – 10) states seems to be small because of the following reasons. First,

(6) (a) Yamaji, M.; Sekiguchi, T.; Hoshino, M.; Shizuka, H. *J. Phys. Chem.* **1992**, *96*, 9353. (b) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Physical Science Data, 34; Elsevier: Amsterdam, 1988.
(7) Harada, M.; Ohga, Y.; Watanabe, I.; Watarai, H. *Chem. Phys. Lett.* **1999**, *303*, 489.

(8) Bosca, F.; Canudas, N.; Marín, M. L.; Miranda, M. A. *Photochem. Photobiol.* **2000**, *71*, 173.

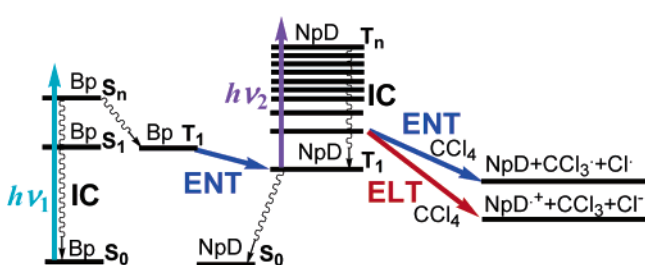
(9) (a) Zgierski, M. Z. *J. Chem. Phys.* **1997**, *107*, 7685. (b) El-Sayed, M. A.; Pavlopoulos, T. *J. Chem. Phys.* **1963**, *39*, 834.

Table 1. Lifetimes of NpD(T₂) (τ(T₂)), Energies of the Lowest and Higher Triplet Excited States (E(T₁) and E(T₂), Respectively), the Driving Force of Electron Transfer (−ΔG_{ELT}), Half-Wave Oxidation Potentials (E_{OX}) in Acetonitrile, Efficiencies of ELT from NpD(T₂) to CCl₄ (f_{ELT}), and Calculated Efficiencies (f_{ELT}(calcd))

NpD	τ(T ₂) (ps)	E(T ₁) (eV)	E(T ₂) ^c (eV)	E _{OX} ^d (V vs SCE)	−ΔG _{ELT} (eV)	f _{ELT} ^e	f _{ELT} (calcd) ^g
naphthalene	9.4 ± 2.0	2.65 ^a	3.8	1.78	1.3	<i>f</i>	0.06
1-methylnaphthalene	9.5 ± 0.8	2.67 ^a	3.9	1.63	1.5	0.11 ± 0.1	0.14
1-ethylnaphthalene	19 ± 4.3	2.59 ^a	4.0	1.63	1.6	0.16 ± 0.1	0.21
1-isopropylnaphthalene	45 ± 1.2	2.58 ^b	4.2	1.63	1.8	0.31 ± 0.1	0.31
1-methoxynaphthalene	61 ± 8.6	2.66 ^a	4.3	1.38	2.2	0.50 ± 0.1	0.34
2-methylnaphthalene	34 ± 6.5	2.62 ^a	4.2	1.65	1.8	0.26 ± 0.1	0.28
2-ethylnaphthalene	36 ± 9.2	2.62 ^a	4.2	1.64	1.8	0.29 ± 0.1	0.29
2-methoxynaphthalene	63 ± 13	2.62 ^a	4.3	1.41	2.2	0.59 ± 0.1	0.34

^a From refs 12 and 17. ^b Calculated from the phosphorescence spectra. ^c Estimated from the equation, E(T₂) = E(T₁) + ΔE. ^d Estimated from cyclic voltammetry measurements. ^e ε_{NpD•+} and ε_T of 1-methylnaphthalene, 1-ethylnaphthalene, 1-isopropylnaphthalene, 1-methoxynaphthalene, 2-methylnaphthalene, 2-ethylnaphthalene, and 2-methoxynaphthalene in acetonitrile are ε₆₉₀ = 3800 and ε₄₂₀ = 20 000, ε₆₉₀ = 4200 and ε₄₂₀ = 21 000, ε₆₉₀ = 2700 and ε₄₂₀ = 19 000, ε₇₀₂ = 3080 and ε₄₄₀ = 9980, ε₆₉₀ = 2500 and ε₄₂₀ = 20 000, ε₆₉₀ = 2800 and ε₄₂₀ = 19 000, and ε₆₃₀ = 4500 and ε₄₄₀ = 18 000 M^{−1} cm^{−1}, respectively.^{6,18,19} ^f No ELT was observed. ^g Error ± 10%

Scheme 1. Energy Level Diagram for NpD and CCl₄ in Their Ground and Excited States^a



^a Winding lines indicate internal conversion and intersystem crossing processes.

in the present experimental condition, there was no CT interaction between NpD and CCl₄ in the ground state since the steady-state absorption of NpD did not change by adding CCl₄. Therefore, static quenching of NpD by CT interaction can be ignored. Second, the T₁₀ → T₂ IC is too fast for the occurrence of bimolecular reactions because of a quite small energy gap between the T_n (n = 2–10) states.⁹ Therefore, ELT is expected to proceed mainly from NpD(T₂) with the longest lifetime among T_n (n = 2–10).⁹

The efficiency of ELT from NpD(T₂) to CCl₄ obviously depends on the properties of NpD(T₂). Both ENT and IC are involved in the NpD(T₂) decay process (Scheme 1).^{4a–d} Therefore, the efficiency of ELT (f_{ELT}) from of NpD(T₂) is represented by eq 1:

$$f_{\text{ELT}} = \frac{\Delta\Delta\text{O.D.}_{702}}{\epsilon_{\text{NpD}\bullet+}[\text{NpD}(\text{T}_2)]_0} \quad (1)$$

where ΔΔO.D.₇₀₂ is the difference of ΔO.D. at 702 nm with and without the second laser irradiation in the presence of CCl₄ (1.0 M), ε_{NpD•+} is the molar absorption coefficient of NpD radical cation, and [NpD(T₂)]₀ is the initial concentration of NpD(T₂). The [NpD(T₂)]₀ value can be estimated from the rate constant of IC and the bleaching of transient absorption of NpD(T₁) in CCl₄ upon the second laser irradiation.¹⁰ The estimated f_{ELT} values for NpD(T₂) are listed in Table 1.

(10) The second laser induced the bleaching of the initial concentration of NpD(T₁) in 56% yield in Ar-saturated neat CCl₄ under the present experimental condition. Since the efficiency of the quenching of NpD(T₂) is expressed as f_q = (k_{ENT}[CCl₄])/(k_{ENT}[CCl₄] + k_{IC}), the initial concentration of NpD(T₂) ([NpD(T₂)]₀) was estimated from [NpD(T₂)]₀ = 0.56[NpD(T₁)]₀/f_q, where [NpD(T₁)]₀ is the concentration of NpD(T₁) before the second laser irradiation. The ratios of [NpD(T₂)]₀ to [naphthalene(T₁)]₀, [1-methylnaphthalene(T₁)]₀, [1-ethylnaphthalene(T₁)]₀, [1-isopropylnaphthalene(T₁)]₀, [1-methoxynaphthalene(T₁)]₀, [2-methylnaphthalene(T₁)]₀, [2-ethylnaphthalene(T₁)]₀, and [2-methoxynaphthalene(T₁)]₀ were estimated to be 90, 89, 78, 68, 66, 71, 70, and 66%, respectively.

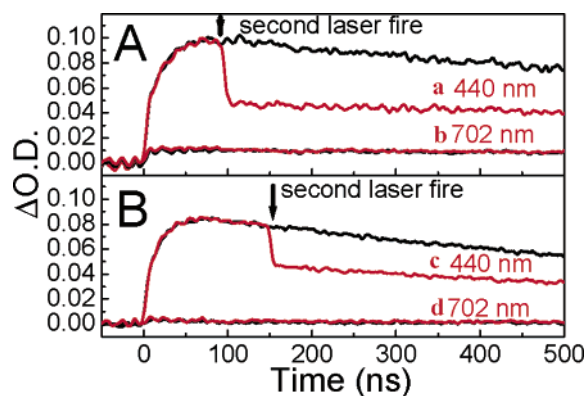


Figure 2. Kinetic traces of ΔO.D. at 440 (a, c) and 702 nm (b, d) during the two-laser (first 355- and second 425-nm, delay time of the second laser after the first laser was 100 or 150 ns) and one-laser (355-nm) excitation of 1-methoxynaphthalene (7.0 × 10^{−3} M) with BP (7.0 × 10^{−3} M) in Ar-saturated neat CCl₄ (A) or cyclohexane in the presence of CCl₄ (1.0 M) (B) at room temperature.

The two-color two-laser photolysis of NpD was carried out in Ar-saturated neat CCl₄ and in the Ar-saturated cyclohexane in the presence of CCl₄ (1.0 M) (Figure 2). In these nonpolar solvents, NpD radical cation was not generated, although bleaching of NpD(T₁) was observed during the irradiation with the second laser. It is reasonably concluded that only ENT from NpD(T₂) to CCl₄ occurred in such nonpolar solvents.⁴ This result indicates that the ELT from the T_n state is favorable in polar solvent, the same as ELT from the lowest excited states.

Discussion

Determination of Lifetime of NpD(T_n). The lifetimes of NpD(T₂) were estimated by the same method as described in previous articles.^{4a–d} In cyclohexane, only ENT occurred from NpD(T₂) to CCl₄. Figure 3 shows the kinetic traces of ΔO.D. at 440 nm for 2-methoxynaphthalene(T₁), in which the second laser irradiation caused bleaching of the T–T absorption in the presence of various concentrations of CCl₄. Since the ENT quenching of NpD(T₂) occurs by the bimolecular process, the ΔΔO.D.₄₄₀ can be represented as a function of the concentration of CCl₄ as shown in eq 2:^{2i,j,4a–d}

$$\frac{1}{\Delta\Delta\text{O.D.}_{440}} = \beta \left(1 + \frac{1}{k_{\text{ENT}}\tau[\text{CCl}_4]} \right) \quad (2)$$

where β is a constant that depends on reaction system,^{2i,j,4a–d} k_{ENT} is the ENT quenching rate constant of NpD(T₂) by CCl₄,

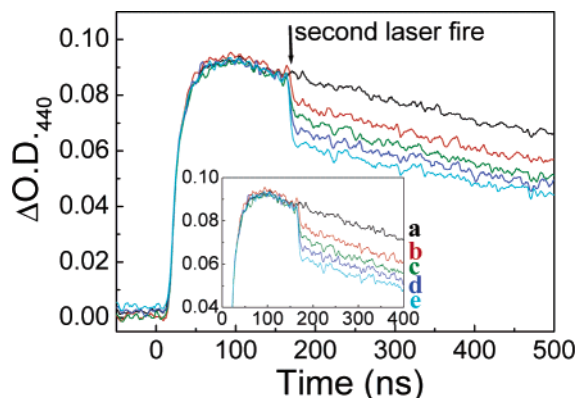


Figure 3. Kinetic traces of $\Delta O.D.$ at 440 nm during the two-color two-laser flash photolysis of 1-methoxynaphthalene (7.0×10^{-3} M) with BP (7.0×10^{-3} M) in Ar-saturated cyclohexane in the absence (a) and presence of CCl_4 (0.05 (b), 0.10 (c), 0.15 (d), and 0.20 (e) M) at room temperature.

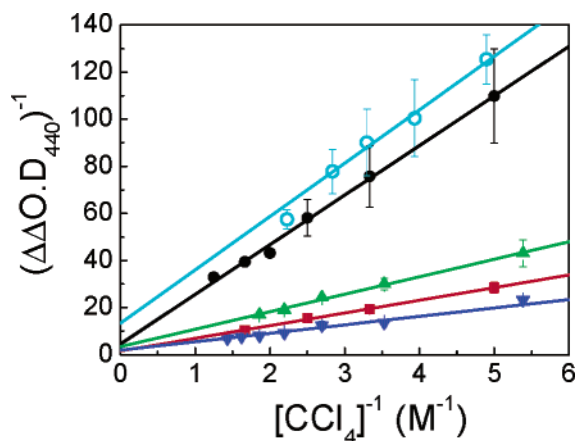


Figure 4. Plots of $(\Delta\Delta O.D._{440})^{-1}$ vs $[CCl_4]^{-1}$ during the two-color two-laser photolysis of naphthalene (\bullet , 7×10^{-3} M), 1-methylnaphthalene (\blacksquare , 7×10^{-3} M), 1-ethylnaphthalene (\blacktriangle , 7×10^{-3} M), 1-isopropylnaphthalene (\circ , 7×10^{-3} M), and 1-methoxynaphthalene (\circ , 7×10^{-3} M) in the presence of various concentrations of CCl_4 .

and τ is the lifetime of $NpD(T_2)$. According to eq 2, the plots of $(\Delta\Delta O.D._{440})^{-1}$ vs $[CCl_4]^{-1}$ gave a linear relation as shown in Figure 4.

The ENT quenching mechanism of $NpD(T_2)$ by CCl_4 cannot be explained by the simple diffusion-controlled process because of the quite short τ of $NpD(T_2)$ and high concentration of CCl_4 . Since the lifetime-dependent quenching should be considered, k_{ENT} is represented as the sum of the lifetime independent and dependent terms (eq 3):^{4a-e,11}

$$k_{ENT} = k_{diff} \left(1 + \frac{\sigma'}{(\pi D \tau)^{0.5}} \right) \quad (3)$$

where σ' is a collisional distance. k_{diff} is a diffusion-controlled rate constant given by eq 4:^{4a-e,12}

$$k_{diff} = 4\pi N \sigma' D \quad (4)$$

where N is the Avogadro number and D is the mutual diffusion coefficient of the excited molecule and quencher in cyclohexane. Here, $\sigma' = 0.6$ nm and $D = 0.8 \times 10^{-5}$ cm² s⁻¹ were

(11) (a) Andre, J. C.; Niclaude, M.; Ware, W. R. *Chem. Phys.* **1978**, *28*, 371. (b) Andre, J. C.; Baros, F.; Reis e Sousa, A. T. *J. Photochem. Photobiol., A* **1988**, *42*, 233.

employed.^{4a-e,11,12} The estimated τ values of $NpD(T_2)$ are summarized in Table 1. The τ value of naphthalene(T_2) is consistent with the value estimated by the theoretical and experimental methods.^{4a,h-j,9a} The $NpD(T_2)$ with the electron-donating substituents showed longer τ . This tendency is similar to that reported for benzophenone derivatives.^{4d}

The energy gap (ΔE) between $NpD(T_2)$ and $NpD(T_1)$ was estimated from eq 5:

$$\tau(T_2)^{-1} = k_{IC} \approx 10^{13} \exp(-\alpha \Delta E) \quad (5)$$

where k_{IC} is the rate constant of IC and given by the reciprocal of the lifetime of $NpD(T_2)$. α is the proportional constant and calculated to be 3.8 from ΔE and estimated τ of naphthalene(T_2).¹³

Dependence of f_{ELT} on $-\Delta G_{ELT}$. The rate of ELT depends on the driving force ($-\Delta G_{ELT}$). It is necessary to estimate ΔG_{ELT} to explain the difference of f_{ELT} . CCl_4 undergoes the C–Cl bond cleavage following the one-electron reduction.^{14,15} According to the ELT mechanism involving the formation of NpD radical cation and the dissociative electron attachment to CCl_4 leading to the C–Cl bond cleavage,^{14,15} ΔG_{ELT} is represented by eq 6:

$$\Delta G_{ELT} = E_{OX} - E_{RCI/R^*+Cl^-} - w_p - E(T_2) \quad (6)$$

where E_{OX} is the oxidation potential of NpD , E_{RCI/R^*+Cl^-} is the reduction potential of the $RCI/R^* + Cl^-$ couple (for CCl_4 , $E_{RCI/R^*+Cl^-} = -0.825$ V vs SCE),^{15c} w_p is the Coulombic energy (0.06 eV), and $E(T_2)$ is the energy level of the T_2 state given by the sum of the energy of the T_1 state ($E(T_1)$) and ΔE . The estimated $-\Delta G_{ELT}$ values are summarized in Table 1. As shown in Figure 5, the f_{ELT} value increases with an increase of the $-\Delta G_{ELT}$ value. From the theoretical calculation (vide infra), the faster ELT is expected for larger $-\Delta G_{ELT}$ in this system. Since ELT from $NpD(T_2)$ occurs competitively with other fast processes such as IC ($T_2 \rightarrow T_1$) and ENT, the large $-\Delta G_{ELT}$ value is necessary for the occurrence of the ELT.

No ELT was observed in the intermolecular quenching of unsubstituted aromatic hydrocarbons(T_n) such as chrysene and dibenz[*a,h*]anthracene by CCl_4 in our previous study,^{4b-d} although they have longer τ than $NpD(T_n)$. This is probably due to insufficient $-\Delta G_{ELT}$ to compete with ENT and IC.

ELT from $NpD(T_n)$ and $NpD(T_1)$. The ELT from $NpD(T_1)$ to CCl_4 was remarkably inefficient despite the long lifetime of

(12) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(13) Hanson, D. M.; Robinson, G. W. *J. Chem. Phys.* **1965**, *43*, 4174.

(14) (a) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. (b) Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595. (c) Andrieux, C. P.; Le Gorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892. (d) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455. (e) Savéant, J.-M. *J. Phys. Chem.* **1994**, *98*, 3716. (f) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864. (g) Andrieux, C. P.; Tallec, A.; Tardivel, R.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 2420. (h) Andrieux, C. P.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1998**, *120*, 4167. (i) Pause, L.; Robert, M.; Savéant, J.-M. *Chem. Phys. Chem.* **2000**, *1*, 199. (j) Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 514. (k) Costentin, C.; Hapiot, P.; Médebielle, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 5623. (l) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4886. (m) Mohanty, J.; Pal, H.; Sapre, A. V. *J. Chem. Phys.* **2002**, *116*, 8006. (n) Mohanty, J.; Pal, H.; Nayak, S. K.; Chattopadhyay, S.; Sapre, A. V. *J. Chem. Phys.* **2002**, *117*, 10744. (o) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 105.

(15) (a) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829. (b) Cardinale, A.; Isse, A. A.; Gennaro, A.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2002**, *125*, 13533. (c) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 10729.

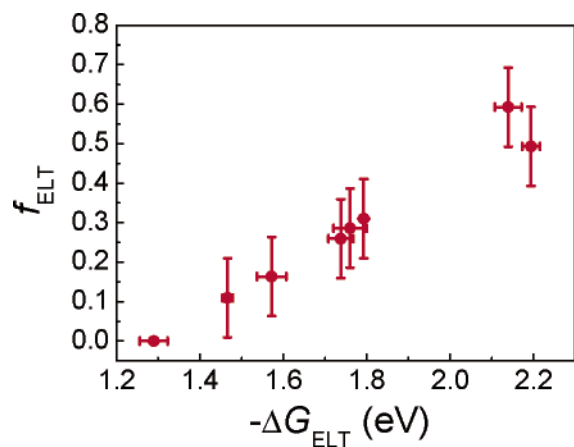


Figure 5. Plots of f_{ELT} vs $-\Delta G_{\text{ELT}}$.

NpD(T_1) and slightly negative ΔG_{ELT} value. For example, ΔG_{ELT} for the ELT from 1-ethylnaphthalene(T_1) to CCl_4 is -0.2 eV.

Since ELT to CCl_4 leads to the concerted C–Cl bond cleavage, contribution of the bond breaking should be considered. The dissociative ELT model, in which the Morse potential curve is employed, has been developed to describe such type of ELT.^{14,15} According to the “sticky” dissociative ELT model, the activation energy (ΔG^*) can be represented by eq 7:¹⁵

$$\Delta G^* = \frac{(\sqrt{D_{\text{R}}} - \sqrt{D_{\text{p}}})^2 + \lambda_0}{4} \left[1 + \frac{\Delta G_{\text{ELT}} - D_{\text{p}}}{(\sqrt{D_{\text{R}}} - \sqrt{D_{\text{p}}})^2 + \lambda_0} \right]^2 \quad (7)$$

where D_{R} is a bond dissociation energy of reactant RX, D_{p} is an interaction energy of radical–ion pair, and λ_0 is the solvent reorganization energy independent of bond breaking. In the present work, the following parameters were employed: $D_{\text{R}} = 2.99$ eV, $D_{\text{p}} = 0.161$ eV,^{15c} and $\lambda_0 = 1.48$ eV.^{16b} In the simplified form, the activation energy-controlled ELT rate constant can be expressed by eq 8:^{14m–n,16}

$$k_{\text{ELT}} = \nu \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (8)$$

where ν is the frequency factor. Here, ν is assumed to be $5.0 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$.^{14m} For the bimolecular reaction, electron-transfer rate constant (k_{ELT}') can be given by eq 9,¹⁶ taking the formation of an encounter complex into account.

$$\frac{1}{k_{\text{ELT}}'} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{ELT}}} \quad (9)$$

Because of the high concentration of CCl_4 and short lifetime of the T_n state, the ELT rate constant (k_{ELT}'') from NpD(T_n) to CCl_4 can be expressed as shown in eq 10:^{4a–e,11}

$$k_{\text{ELT}}'' = k_{\text{ELT}}' \left(1 + \frac{\sigma}{(\pi D' \tau)^{0.5}} \right) \quad (10)$$

where D' is the mutual diffusion coefficient in acetonitrile. According to the literature, $D' = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.^{4a–e,11,12}

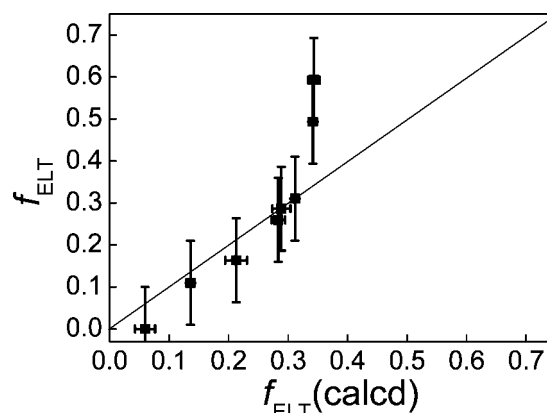


Figure 6. Plots of f_{ELT} vs $f_{\text{ELT}}(\text{calcd})$.

From Scheme 1, the efficiency of ELT from NpD(T_n) ($f_{\text{ELT}}(\text{calcd})$) can be calculated by eq 11:

$$f_{\text{ELT}}(\text{calcd}) = \frac{k_{\text{ELT}}''[\text{CCl}_4]}{(k_{\text{ELT}}'' + k_{\text{ENT}})[\text{CCl}_4] + k_{\text{IC}}} \quad (11)$$

where k_{IC} is the IC rate constant and given by the reciprocal of τ , and $[\text{CCl}_4]$ is a concentration of CCl_4 as a quencher ($[\text{CCl}_4] = 1 \text{ M}$). The estimated $f_{\text{ELT}}(\text{calcd})$ values are summarized in Table 1. As shown in Figure 6, the plots of f_{ELT} vs $f_{\text{ELT}}(\text{calcd})$ showed a good correlation. It is suggested that the efficient ELT from NpD(T_2) to CCl_4 and inefficient ELT from NpD(T_1) to CCl_4 are explained qualitatively by the “sticky” dissociative ELT model.¹⁵ The rate constant of ELT from 1-ethylnaphthalene(T_2) to CCl_4 is calculated to be $k_{\text{ELT}} = 5.9 \times 10^{10} \text{ s}^{-1}$, while the rate constant of ELT from 1-ethylnaphthalene(T_1) to CCl_4 is also calculated to be $k_{\text{ELT}} = 660 \text{ s}^{-1}$. Thus, the dissociative ELT from the triplet excited NpD to CCl_4 occurs only from the T_2 state.

As shown above, no ELT occurred in cyclohexane or CCl_4 as a solvent. The $-\Delta G_{\text{ELT}}$ values of ELT from 1-methoxynaphthalene(T_2) to CCl_4 in cyclohexane and neat CCl_4 were calculated to be 1.2 eV for both cases using Weller’s equation.²⁰ According to the “sticky” dissociative ELT theory, the estimated ΔG_{ELT} value is not enough for ELT to compete with IC and ENT.

It should be noted that the present systematic study on the ELT from NpD(T_2) revealed the following advantageous points. First, since ELT from the T_2 state affords the larger driving force than the ELT from the T_1 state, the ELT, which requires a large driving force such as dissociative ELT, becomes possible to proceed. Larger excitation energy of the T_n states is also beneficial to examine the driving force dependence of ELT in a wide range. Second, under the condition with highly concentrated quencher and short τ , the k_{ELT} value becomes larger than k_{diff} as expected from eq 10, resulting in larger f_{ELT} despite the existence of the fast IC and ENT. Third, larger T_n energy can generate products with higher reactivity, which is favorable to the successive reaction. Consequently, the ELT from the T_n states is expected to show interesting reactivities.

(16) (a) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (b) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (d) Marcus, R. A.; Eyring, H. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(17) Abdel-shafi, A. A.; Wilkinson, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 248. (18) Kelly, J. F. D.; Doyle, M. E.; Guha, M.; Kavanagh, P. V.; Kelly, J. M.; McMurry, T. B. *H. J. Chem. Soc., Perkin Trans. 2* **1998**, 1635. (19) The ϵ_{NpD^+} value was estimated by the same method in ref 16b. (20) Weller, A. Z. *Phys. Chem. Neue Folge* **1982**, *133*, 93.

Conclusions

We have found the intermolecular ELT from a series of $\text{NpD}(T_2)$ to CCl_4 in acetonitrile. The efficient ELT from $\text{NpD}(T_n)$ and inefficient ELT from $\text{NpD}(T_1)$ to CCl_4 were well explained by the “sticky” dissociative ELT model. It is concluded that the ELT from the T_n state can be controlled by $-\Delta G_{\text{ELT}}$ and solvent. In addition, we would like to remark that the present study will bring further work on ELT from various compounds in the higher triplet excited states.

Experimental Section

Materials. 2-Methylnaphthalene, naphthalene, and BP were recrystallized two or three times from ethanol before use. Other compounds were of the highest grade available and used as received. Sample solutions were deoxygenated by bubbling with Ar gas for 30 min before irradiation. All experiments were carried out at room temperature.

Phosphorescence Measurement at 77 K. Phosphorescence spectra were recorded in 1-methylpentane rigid glass at 77 K on a spectrometer (Hitachi 850).

Cyclic Voltammetry Measurements. Cyclic voltammograms were obtained using a conventional three-electrode system (BAS CV-50W) in acetonitrile at 298 K. A platinum electrode was used as the working electrode, and an Ag/AgNO_3 electrode was used as the reference electrode.

Transient Absorption Measurement Using Two-Color Two-Laser Flash Photolysis. Two-color two-laser flash photolysis experiment was carried out using the third harmonic oscillation (355 nm) of a Nd^{3+} :

YAG laser (Quantel, Brilliant; 5-ns fwhm) as the first laser and the 425-nm flash from an OPO laser (Continuum, Surelite OPO) pumped by a Nd^{3+} :YAG laser (Continuum, Surelite II-10; 5-ns fwhm) as the second laser. The delay time of two laser flashes was adjusted to 100 or 150 ns by three four channel digital delay/pulse generators (Stanford Research Systems, model DG 535). Two laser beams were adjusted to overlap at the sample. The monitor light source was a 450 W Xe lamp (Osram, XBO-450) synchronized with the laser flash. The monitor light perpendicular to the laser beams was focused on a monochromator (Nikon, G250). The output of the monochromator was monitored using a photomultiplier tube (PMT) (Hamamatsu Photonics, R928). The signal from the PMT was recorded on a transient digitizer (Tektronix, TDS 580D four channel digital phosphor oscilloscope). To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were employed. The samples were contained in a transparent rectangular quartz cell ($1.0 \times 1.0 \times 4.0 \text{ cm}^3$) at room temperature.

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Supporting Information Available: The absorption spectra of 1-methylnaphthalene, 1-ethylnaphthalene, and 1-methoxynaphthalene radical cation (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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