Competitive Marcus-Type Electron Transfer and Energy Transfer from the Higher Triplet Excited State

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Electron transfer (ELT) and energy transfer (ENT) from the higher excited triplet state (T_n) ($n > 1$) of various naphthalene derivatives (NpDs) to some polychlorobenzenes (CBs) such as chlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene were examined. It is confirmed that the ELT process from the NpDs (T_n) to CBs obeys Marcus's theory from the driving force dependence of the ELT yield. This is the first example of the Marcus-type ELT from the T_n state. As a competitive process of the ELT, the ENT from NpDs (T_n) to CBs giving the higher excited state of CBs (T_n) (NpD (T_n) + CB (S_0) → NpD (S_0) + CB (T_n)) was observed although a part of CBs (T_n) decomposed by the C−Cl bond dissociation giving chlorocyclohexadienyl radical and chloride radical. This is also the first example of intermolecular ENT from molecules in the T_n state to quenchers giving the quenchers in the T_n state.

Introduction

When a molecule absorbs photon with sufficiently large energy, the higher excited states are generated and quickly deactivate to the lowest excited state via internal conversion (IC) followed by intersystem crossing (ISC). Usually, photochemical reactions proceed from the lowest excited state because of the longest lifetime among the excited states. It is known as Kasha's rule.[1] Reports on reactions from the higher excited states are rather limited compared to those from the lowest excited states.[2−6] It is noteworthy that the triplet energy transfer (ENT) occurs from the higher excited triplet state (T_n) even when the ENT from the lowest excited triplet state is energetically impossible, indicating a different reactivity of T_n from T_1 due to the large excitation energy.[4]

Similar to ENT from the higher excited state, electron transfer (ELT) is also energetically possible, although limited numbers of ELTs from the higher excited singlet state have been reported.[5] The intermolecular ELT from the higher excited state (S_2) of zinc tetraphenylporphyrin to dichloromethane was reported by Okada et al.[5a] LeGourriérec et al. reported the intramolecular ELT from the S_2 state of porphyrin in a covalently linked zinc porphyrin−ruthenium(II) tris-bipyridine dyad.[5b] A systematic study on the intramolecular ELT from the S_2 state of porphyrins has been carried out by Mataga et al.[5e−g] The ELT from the S_2 state of azulene was discussed by Muller et al.[5h] Furthermore, the ELT from the D_2 state of a stilbene radical cation was reported by Majima et al.[5i,j] To the best of our knowledge, there had been only one report on ELT from the T_n state. Wang et al. reported ELT from anthracene (T_2) to ethyl bromoacetate.[6a] In a previous paper, we reported photoinduced dissociative ELT from some naphthalene derivatives (NpDs) in the second excited triplet state (T_2) to carbon tetrachloride (CCl_4) leading to the concerted C−Cl bond cleavage.[6b] The driving force dependence and solvent effect on the ELT from NpD (T_2) to CCl_4 were confirmed. Because ELT from the T_2 state affords the larger driving force than that from the T_1 state, the ELT, which requires a large driving force such as the dissociative ELT, becomes possible to proceed.

In this paper, we examined the ELT and ENT from the higher excited triplet state of various NpDs to some polychlorobenzenes (CBs) such as chlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene. The ELT from NpDs to CBs is energetically impossible from the T_1 state but expected to proceed from the T_n state. We found ELT from NpDs (T_n) to CBs for the first time, in which the dissociative ELT is not operative. Thus, a different ELT mechanism should be included in the present ELT. From the driving force dependence, we confirmed the ELT from NpDs (T_n) to CBs obeys Marcus's theory. This is the first example of the Marcus-type ELT from the higher excited triplet state. As a competition process of the ELT, the two-step ENT from NpD (T_n) (NpD (T_n) + CB (S_0) → NpD (S_0) + CB (T_n) → NpD (S_0) + CB (T_1) → NpD (T_1) + CB (S_0)) was observed although a part of the CB (T_n) decomposed through the bond dissociation generating the corresponding chlorocyclohexadienyl radical (Cl−CHD$^•$). This is also the first example of intermolecular ENT from molecules in the higher excited triplet state to quenchers giving higher triplet excited states of the quenchers.

Results

NpD (T_1) was generated by the triplet sensitized reaction during the irradiation with the first laser (355 nm) to a mixture of benzophenone (BP) and NpD in Ar-saturated acetonitrile. NpD (T_n) was generated by the excitation of NpD (T_1) with the second laser (425 nm) at 250 ns after the first laser. In the presence of the CBs, bleaching of the transient absorption of 2-methoxynaphthalene (T_1) and growth of new transient absorption peaks around 380 and 600 nm were observed immediately after the second laser irradiation as shown in Figure 1. The new absorption bands were assigned to the 2-methoxynaphthalene radical cation (Supporting Information).[7]

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TABLE 1: Lifetimes of NpD (T_2) (τ), Energies of the Lowest and the Second Triplet Excited States (E (T_1) and E (T_2)), Energy Gap between the Lowest and Higher Triplet Excited States (ΔE) and Oxidation Potentials (E_{OX}) of NpD

NpD	τ^a (ps)	E (T_1)^b (eV)	E (T_2) (eV)	ΔE (eV)	E_{OX} (V vs SCE)
naphthalene	9.4 ± 2.0	2.64	3.8	1.2	1.78
1-methylnaphthalene	9.5 ± 0.77	2.63	3.9	1.2	1.63
1-ethylnaphthalene	18 ± 4.3	2.59	4.0	1.4	1.63
1-isopropylnaphthalene	45 ± 2.7	2.58	4.2	1.6	1.63
1-methoxynaphthalene	61 ± 8.6	2.65	4.3	1.7	1.38
2-methylnaphthalene	34 ± 6.5	2.62	3.8	1.2	1.65
2-ethylnaphthalene	36 ± 9.2	2.62	4.2	1.5	1.64
2-isopropylnaphthalene	48 ± 10	2.58	4.2	1.5	1.65
2-methoxynaphthalene	63 ± 13	2.62	4.2	1.6	1.41
2,6-dimethylnaphthalene	51 ± 13	2.62	4.3	1.7	1.49

[a] Reference 10. [b] References 8 and 11.

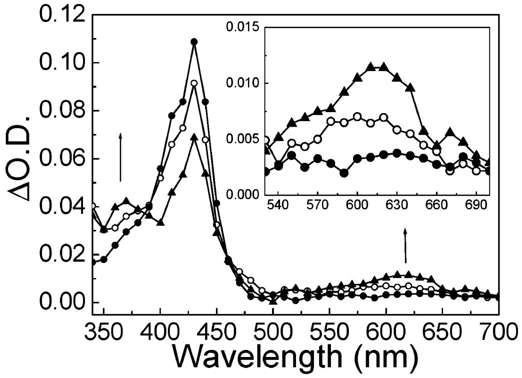


Figure 1. Transient absorption spectra obtained during the one-laser (355-nm) excitation (●) and two-laser (first 355- and second 425-nm) excitation of BP (7.0×10^{-3} M) with 2-methoxynaphthalene (7.0×10^{-3} M) in Ar-saturated acetonitrile in the presence of 1,4-dichlorobenzene (○) or 1,2,4-trichlorobenzene (▲) (1 M), respectively. The second laser was irradiated at 250 ns after the first laser pulse. These spectra were obtained at 300 ns after the first laser.

Parts A−C of Figure 2 show the kinetic traces of ΔOD at 440 and 630 nm in the presence of chlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene, respectively. Curves a, c, and e show the second laser-induced bleaching of the triplet−triplet (T−T) absorption at 440 nm within the second 425-nm laser flash (duration: 5 ns). Insets show the difference of the kinetic traces at 440 nm between with and without the second laser irradiation. Because the lowest triplet excited-state energies of the CBs (3.5, 3.4, and 3.4 eV for chlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene, respectively) were intermediates between NpD (T_2) and NpD (T_1) (Table 1, vide infra),[8,9] the recovery after the bleaching can be assigned to ENT from the CBs (T_1) to 2-methoxynaphthalene after ENT from 2-methoxynaphthalene (T_n) to the CBs (Scheme 1).[4a−d] The incomplete recovery indicates that processes that did not reproduce 2-methoxynaphthalene (T_1) such as ELT and decomposition of the CBs were involved in the deactivation processes of 2-methoxynaphthalene (T_n). Curves b, d, and f show the growth of the radical cation absorption at 630 nm within the second laser pulse. The bleaching and growth occurred concomitantly. From these results, it is indicated that the ELT from 2-methoxynaphthalene (T_n) to the CBs occurs competitively with the ENT and IC within the second laser duration of 5 ns (Scheme 1).

The ELT from the T_n state was inefficient in several NpD−CB pairs (Figure 3 and Table 2) where no NpD radical cation was detected, although bleaching and recovery of NpD (T_1) were observed upon the irradiation of the second laser (Figure 3). Figure 4 A shows the transient spectra obtained during the two-color two-laser experiment of the naphthalene−1,2,4-trichlorobenzene system. The absorption band around 350 nm is reasonably assigned to the corresponding Cl−CHD$^•$ and chlorine

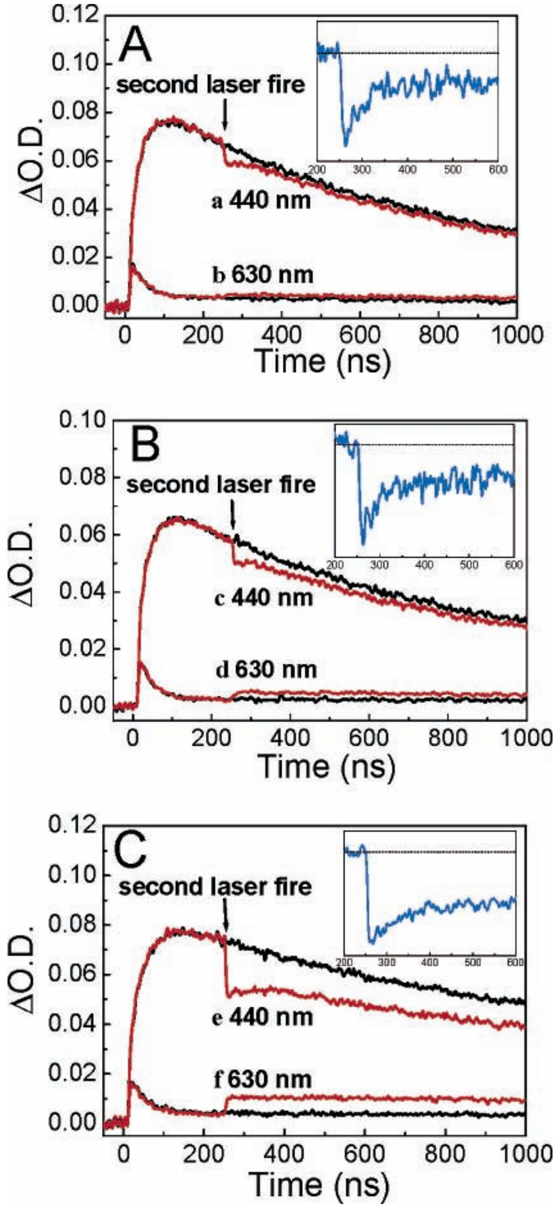


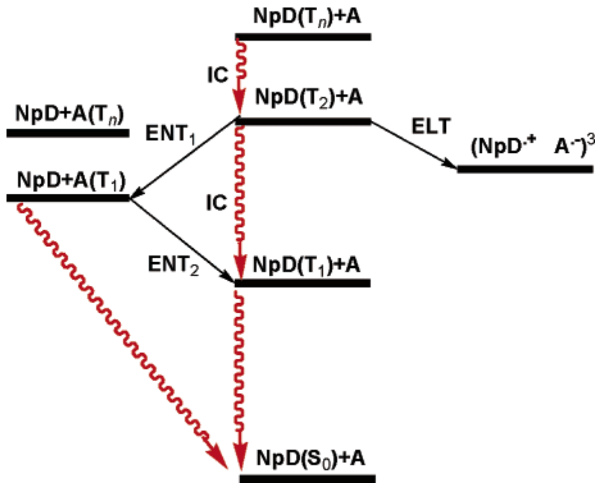
Figure 2. The kinetic traces of ΔOD at 440 (a, c, e) and 630 (b, d, f) nm during the two-laser (first 355- and second 425-nm, delay time of the second laser after the first laser was 250 ns, red line) and one-laser (355-nm, black line) excitation of 2-methoxynaphthalene (7.0×10^{-3} M) with BP (7.0×10^{-3} M) in Ar-saturated acetonitrile in the presence of chlorobenzene (A), 1,4-dichlorobenzene (B), or 1,2,4-trichlorobenzene (C) (1.0 M). Insets show the difference of the kinetic traces at 440 nm with and without the second laser irradiation.

TABLE 2: ELT Efficiency Estimated from the Experimental Result (f_{ELT}) and the Calculated ELT Efficiency (f_{ELT}(calcd))

	chlorobenzene		1,4-dichlorobenzene		1,2,4-trichlorobenzene	
NpD	f_{ELT}[a]	f_{ELT}(calcd)[c]	f_{ELT}[a]	f_{ELT}(calcd)[c]	f_{ELT}[a]	f_{ELT}(calcd)[c]
naphthalene	*b*	0	*b*	0	*b*	0
1-methylnaphthalene	*b*	0	*b*	0	*b*	0
1-ethylnaphthalene	*b*	0	0.07	0.01	0.11	0.02
1-isopropylnaphthalene	*b*	0	0.13	0.13	0.2	0.23
1-methoxynaphthalene	0.09	0.09	0.20	0.34	0.43	0.34
2-methylnaphthalene	*b*	0	0.07	0.07	0.14	0.17
2-ethylnaphthalene	*b*	0	0.09	0.10	0.2	0.19
2-isopropylnaphthalene	*b*	0	0.13	0.14	0.25	0.24
2-methoxynaphthalene	0.09	0.09	0.23	0.34	0.37	0.34
2,6-dimethylnaphthalene	0.08	0.07	0.13	0.18	0.18	0.19

[a] Error ± 15%, $\epsilon_{NpD^{\bullet+}}$ and ϵ_T of 1-methylnaphthalene, 1-ethylnaphthalene, 1-isopropylnaphthalene, 1-methoxynaphthalene, 2-methylnaphthalene, 2-ethylnaphthalene, 2-isopropylnaphthalene, 2-methoxylnaphthalene, and 2,6-dimethylnaphthalene in acetonitrile are $\epsilon_{690} = 3800$ and $\epsilon_{420} = 20000$, $\epsilon_{690} = 4200$ and $\epsilon_{420} = 21000$, $\epsilon_{690} = 2700$ and $\epsilon_{420} = 19000$, $\epsilon_{702} = 3080$ and $\epsilon_{440} = 9980$, $\epsilon_{690} = 2500$ and $\epsilon_{420} = 20000$, $\epsilon_{690} = 2800$ and $\epsilon_{420} = 19000$, $\epsilon_{690} = 2200$ and $\epsilon_{420} = 23000$, $\epsilon_{630} = 4500$ and $\epsilon_{440} = 18000$, and $\epsilon_{690} = 3300$ and $\epsilon_{420} = 21000$ M^{-1} cm^{-1}, respectively.[8,11,24,25] [b] No ELT was observed. [c] Error ±20%.

SCHEME 1: Energy Diagram for Relaxation and Reaction Processes of NpD (T_n) in the NpD−Chlorobenzene or NpD−1,4-Dichlorobenzene Pairs[a]



[a] A means the triplet energy or electron acceptor, i.e., chlorobenzene or 1,4-dichlorobenzene.

atom.[12−14] Figure 4B shows simultaneous growth of Cl−CHD$^\bullet$ at 350 nm. Thus, it is suggested that Cl−CHD$^\bullet$ was generated by the homolytic C−Cl bond cleavage after the ENT from NpD (T_n). It should be noted that homolytic C−Cl bond dissociation energies of 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, and chlorobenzene were reported to be 3.7, 3.8, and 3.8 eV, respectively, which are higher than energy levels of the CBs (T_1) (3.4−3.5 eV).[15] Thus, it is concluded that the C−Cl bond dissociation takes place from 1,2,4-trichlorobenzene (T_n) ($n > 1$) after the ENT from NpD (T_n) (Scheme 2). This is the first example of the intermolecular ENT from the molecules in the T_n state to quenchers giving the quenchers in the T_n state.

Discussion

Photoinduced Process of NpD (T_n). It should be noted that neither radical cations nor Cl−CHD$^\bullet$ was observed without the second laser irradiation even in the presence of CBs, indicating the contribution of the T_n state to the present ELT and ENT. However, in the absence of the CBs, no change of the transient absorption of the NpD (T_1) was observed during the second laser irradiation. These results exclude the photoionization during the two-color two-laser irradiation. Photoionization of the NpD can be also ruled out from the energetical consideration. Because 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).[16]

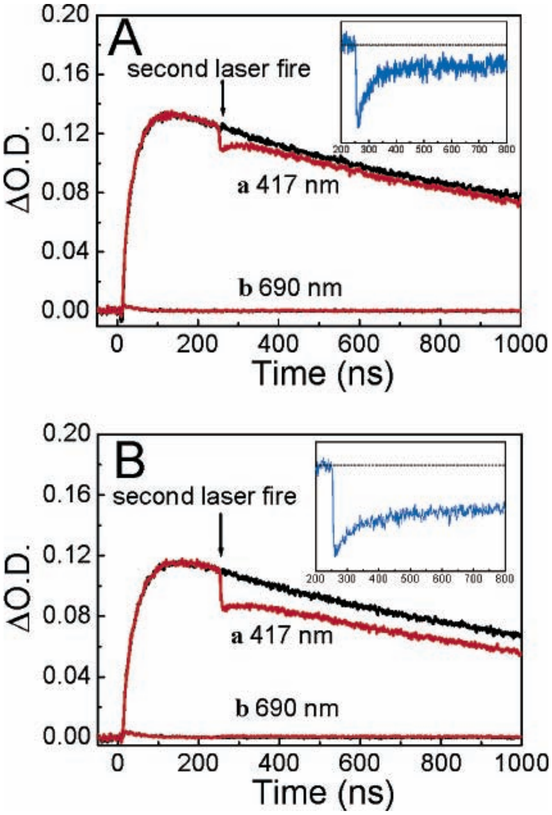
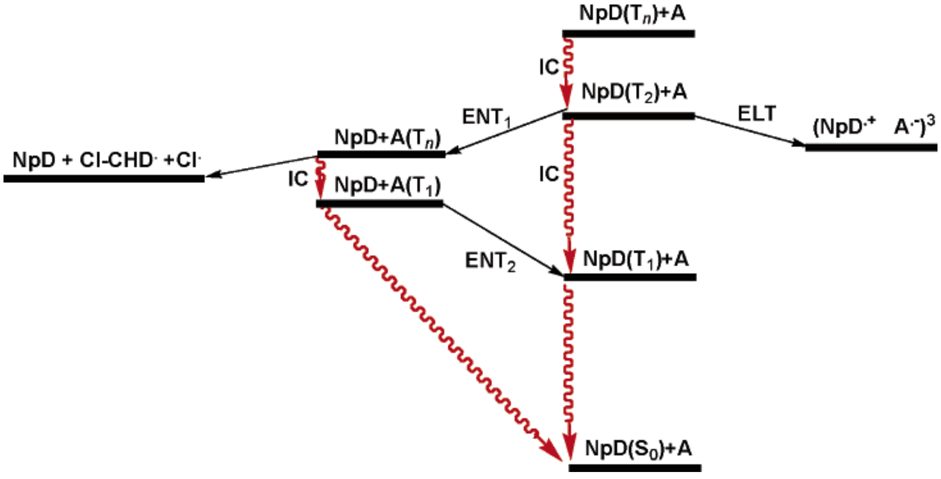


Figure 3. The kinetic traces of ΔOD at 417 nm during the two-laser (first 355- and second 425-nm, delay time of the second laser after the first laser was 250 ns, red line) and one-laser (355-nm, black line) excitation of naphthalene (7.0×10^{-3} M) with BP (7.0×10^{-3} M) in Ar-saturated acetonitrile in the presence of chlorobenzene (A) or 1,2,4-trichlorobenzene (B) (1.0 M). Insets show the difference of the kinetic traces at 417 nm between with and without the second laser irradiation.

Because no fluorescence from NpD (S_1) was observed after the second laser irradiation regardless of the presence of the CBs, back intersystem crossing ($T_n \rightarrow S_1$) can be neglected. Therefore, NpD (S_1) is not involved in the present two-color two-laser experiment although ELT from NpD (S_1) to CBs has been reported.[9] Although 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.[17] Contribution of the T_m ($m = 3−10$) states seems

SCHEME 2: Energy Diagram for Relaxation and Reaction Processes of NpD (T_n) in the NpD−1,2,4-Trichlorobenzene Pair[a]



[a] A means the triplet energy or electron acceptor, i.e., 1,2,4-trichlorobenzene.

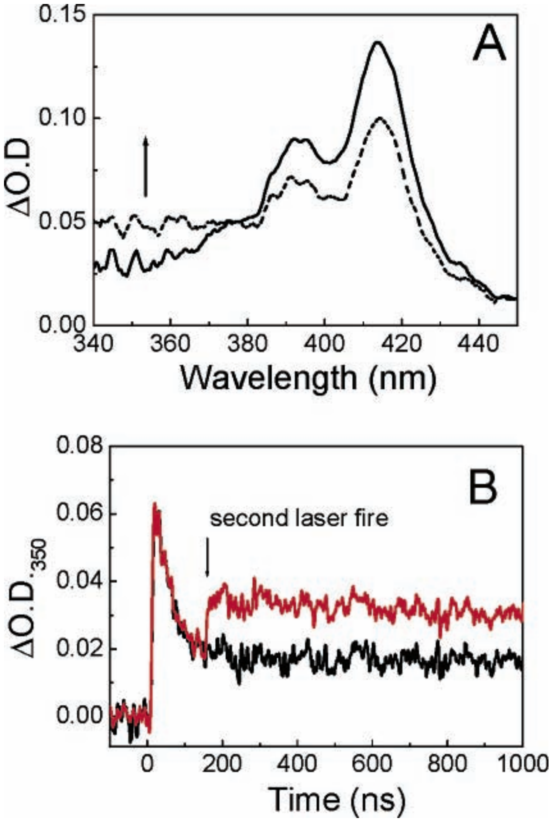


Figure 4. (A) Transient absorption spectra obtained during one-laser (355-nm) excitation (solid line) and two-laser (first 355- and second 425-nm) excitation (broken line) of BP (7.0×10^{-3} M) with naphthalene (7.0×10^{-3} M) in Ar-saturated acetonitrile in the presence of 1,2,4-trichlorobenzene (1 M). The second laser was irradiated at 150 ns after the first laser pulse. These spectra were obtained at 200 ns after the first laser. (B) The kinetic traces of ΔOD at 350 nm with (red line) and without (black line) the second laser irradiation.

to be less because the $T_{10} \rightarrow T_2$ IC is too fast for the bimolecular reaction due to a quite small energy gap between the T_n ($n = 2-10$) states.[17a] Therefore, ENT and ELT are expected to proceed mainly from NpD (T_2) with the longest lifetime among T_n ($n = 2-10$) as summarized in Schemes 1 and 2 although contribution of the T_n ($n = 3-10$) states may not be negligible.

Determination of Lifetime of NpD (T_n). The lifetimes of the NpD (T_2) were estimated by the same method as the previous papers.[4a−d,6b] In cyclohexane, only ENT occurred from NpD (T_2) to CCl_4. Figure 5 shows the kinetic traces of ΔOD at 420 nm for 2,6-dimethylnaphthalene (T_1) in which the second laser irradiation caused bleaching of the T−T absorption in the presence of various concentrations of CCl_4. Because the ENT quenching of NpD (T_2) occurs by the bimolecular process, the $\Delta\Delta OD_{420}$ can be represented as a function of the concentration of CCl_4 as shown in eq 1,[4a−d,5i,j,6b]

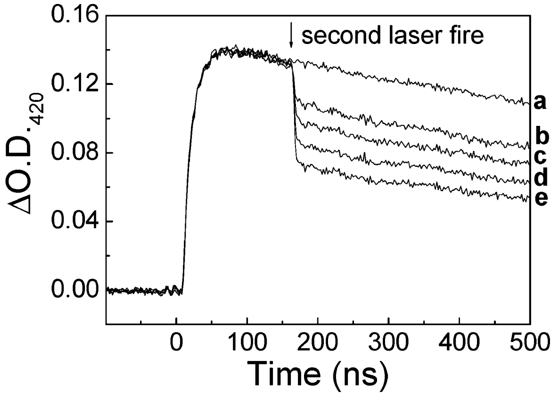


Figure 5. Kinetic traces of ΔOD at 420 nm during the two-color two-laser flash photolysis of a mixture of 2,6-dimethylnaphthalene (7.0×10^{-3} M) and BP (7.0×10^{-3} M) in Ar-saturated cyclohexane in the absence (a) and presence of CCl_4 (0.05 (b), 0.1 (c), 0.15 (d), and 0.20 M (e)) at room temperature.

$$\frac{1}{\Delta\Delta OD_{420}} = \beta\left(1 + \frac{1}{k_{ENT}\tau[CCl_4]}\right) \qquad (1)$$

where β is a constant which depends on reaction system,[4a−d,5i,j,6b] k_{ENT} is the ENT quenching rate constant of NpD (T_2) by CCl_4, and τ is the lifetime of NpD (T_2). According to eq 1, the plots of $(\Delta\Delta OD_{420})^{-1}$ vs $[CCl_4]^{-1}$ gave a linear relation as shown in Figure 6.

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 the high concentration of CCl_4. Because the lifetime-dependent quenching should be considered, k_{ENT} is represented as the sum of the lifetime-independent and dependent terms (eq 2),[4a−d,6b,18]

$$k_{ENT} = k_{diff}\left(1 + \frac{\sigma'}{(\pi D\tau)^{0.5}}\right) \qquad (2)$$

TABLE 3: Driving Force of ELT from the $T_1(-\Delta G\ (T_1))$ and $T_2(-\Delta G\ (T_2))$ States of the NpDs to the CBs

	chlorobenzene		1,4-dichlorobenzene		1,2,4-trichlorobenzene	
NpD	$-\Delta G\ (T_1)^a$ eV	$-\Delta G\ (T_2)$ eV	$-\Delta G\ (T_1)^a$ eV	$-\Delta G\ (T_2)$ eV	$-\Delta G\ (T_1)^a$ eV	$-\Delta G\ (T_2)$ eV
naphthalene	−1.6	−0.39 ± 0.03	−1.1	0.06 ± 0.03	−1.0	0.16 ± 0.03
1-methylnaphthalene	−1.4	−0.21 ± 0.01	−0.97	0.23 ± 0.01	−0.87	0.33 ± 0.01
1-ethylnaphthalene	−1.5	−0.12 ± 0.04	−1.0	0.32 ± 0.04	−0.94	0.42 ± 0.04
1-isopropylnaphthalene	−1.5	0.12 ± 0.01	−1.1	0.56 ± 0.01	−0.95	0.66 ± 0.01
1-methoxynaphthalene	−1.2	0.52 ± 0.02	−0.73	0.96 ± 0.02	−0.63	1.1 ± 0.02
2-methylnaphthalene	−1.5	0.06 ± 0.03	−1.0	0.51 ± 0.03	−0.93	0.61 ± 0.03
2-ethylnaphthalene	−1.5	0.09 ± 0.04	−1.0	0.53 ± 0.04	−0.92	0.63 ± 0.04
2-isopropylnaphthalene	−1.5	0.11 ± 0.03	−1.1	0.55 ± 0.03	−0.97	0.66 ± 0.03
2-methoxynaphthalene	−1.2	0.46 ± 0.03	−0.69	0.90 ± 0.03	−0.69	1.0 ± 0.03
2,6-dimethylnaphthalene	−1.3	0.32 ± 0.04	−0.87	0.76 ± 0.04	−0.77	0.86 ± 0.04

[a] $\Delta G\ (T_1)$ values were given by the following equation: $\Delta G_{ELT} = E_{OX} - E_{RED} - w_p - E\ (T_1)$.

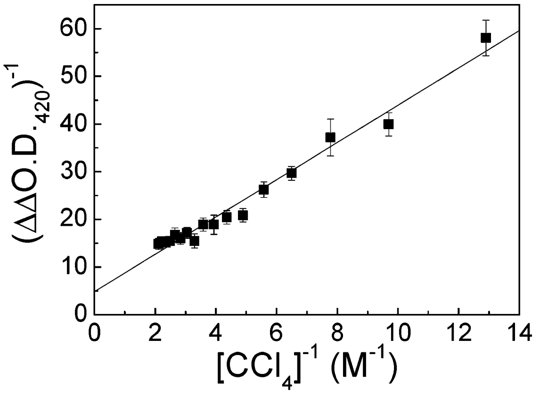


Figure 6. Plots of $(\Delta\Delta OD_{420})^{-1}$ versus $[CCl_4]^{-1}$ during the two-color two-laser photolysis of a mixture of 2,6-dimethylnaphthalene (7.0×10^{-3} M) and BP (7.0×10^{-3} M) in the presence of various concentrations of CCl_4.

where σ' is a collisional distance. k_{diff} is a diffusion-controlled rate constant given by eq 3,[4a−d,5i,j,6b,8]

$$k_{diff} = 4\pi N\sigma' D \tag{3}$$

where N is the Avogadro number and D is the mutual diffusion coefficient of the excited molecule and quencher. Here, $\sigma' = 0.6$ nm and $D = 0.8 \times 10^{-5}$ cm^2 s^{-1} were employed.[4a−d,6b] The τ value of naphthalene (T_2) is consistent with the value estimated by the theoretical and experimental methods.[6b]

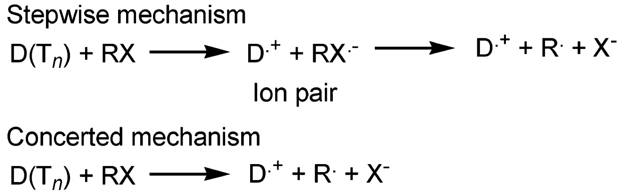
The energy gap (ΔE) between NpD (T_2) and NpD (T_1) was estimated from eq 4,

$$\tau\ (T_2)^{-1} = k_{IC} \sim 10^{13} \exp(-\alpha\Delta E) \tag{4}$$

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).[6b] Estimated τ and ΔE values were summarized in Table 1.

Electron-Transfer Mechanism. CBs radical anions are well-known to decompose rapidly to radical and chloride anion.[19] The absence of deactivation of NpD radical cation generated from the ELT from NpD (T_2) to the CBs was in accord with the instability of the radical anions of the CBs.[20] Because the C−Cl bond dissociation rate of chlorobenzene radical anion was reported to be 1.8×10^9 to $>2 \times 10^{10}$ s^{-1}, the radical ion pair should be formed after the ELT from NpD (T_2).[19a,d] For the stepwise mechanism (Scheme 3), the dissociative ELT theory for the concerted dissociation cannot be applied.[21] Marcus's theory is adequate for the present system.[22]

SCHEME 3: The Stepwise and Concerted Mechanisms for Electron Transfer from D (T_n) to RX



Driving Force Dependence of ELT from the T_2 State. According to Marcus's ELT theory, free energy change for ELT (ΔG_{ELT}) is represented by eq 5,[22]

$$\Delta G_{ELT} = E_{OX} - E_{RED} - w_p - E\ (T_2) \tag{5}$$

where E_{OX} is the oxidation potential of NpD, E_{RED} is the reduction potential of the CBs ($E_{RED} = -1.9$, -2.0, and -2.4 V versus SCE, for chlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene, respectively),[8,9] w_p is a Coulombic energy (−0.06 eV),[22a] 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 driving forces ($-\Delta G_{ELT}$) are summarized in Table 3. As shown in Table 3, the ELT from the triplet excited NpD to the CBs occurs only from the T_2 state.

It is found that ELT from NpD (T_2) efficiently occurred with 1,2,4-trichlorobenzene and 1,4-dichlorobenzene but not with chlorobenzene. Thus, the efficiency of ELT from NpD (T_2) to the CBs depends on not only the properties of NpD (T_2) but also the CBs. The efficiency of ELT (f_{ELT}) from NpD (T_2) to the CBs is represented by eq 6,

$$f_{ELT} = \frac{\Delta\Delta OD_{NpD\bullet+}}{\epsilon_{NpD\bullet+}[NpD\ (T_2)]_0} \tag{6}$$

where $\Delta\Delta OD_{NpD\bullet+}$ is the difference of ΔOD at 630 or 690 nm with and without the second laser irradiation in the presence of the CBs (1.0 M), $\epsilon_{NPD\bullet+}$ is the molar absorption coefficient of NpD radical cation, and $[NPD\ (T_2)]_0$ is the initial concentration of NpD (T_2). The $[NpD\ (T_2)]_0$ value can be estimated from the rate constant of IC and the bleaching of transient absorption of NpD (T_1) in CCl_4 upon the second laser irradiation.[23] The estimated f_{ELT} values for various NpD (T_2) are listed in Table 2.

As shown in Figure 7, the f_{ELT} value increases with an increase in the $-\Delta G_{ELT}$ value, indicating that the rate of ELT depends on the driving force. According to Marcus's theory, the fastest ELT rate is expected when $-\Delta G_{ELT}$ is the same as the reorganization energy. Thus, the present ELT of NpD (T_2) was positioned in the normal region. Because ELT from NpD (T_2) occurs competitively with other fast processes such as IC

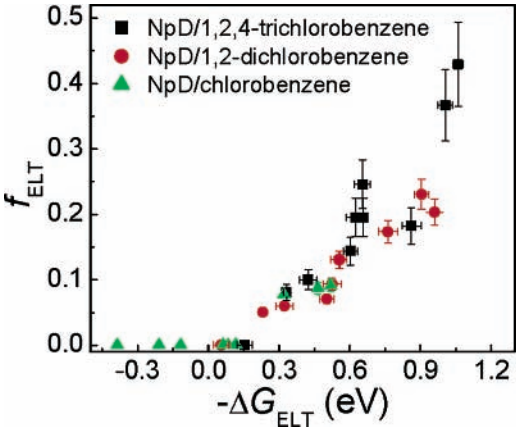


Figure 7. Plots of f_{ELT} versus $-\Delta G_{\mathrm{ELT}}$.

($T_2 \rightarrow T_1$) and ENT, the large $-\Delta G_{\mathrm{ELT}}$ value is necessary for the occurrence of the ELT.

According to the Marcus's ELT theory, the activation energy (ΔG^*) can be represented by eq 7,[22]

$$\Delta G^* = \frac{\lambda}{4}\left(1 + \frac{\Delta G}{\lambda}\right)^2 \tag{7}$$

where λ is an intrinsic barrier corresponding to the bond length change and solvent reorganization. According to the literature, we employed λ = 1.9 eV.[22b] In the simplified form, the activation-energy-controlled ELT rate constant can be expressed by eq 8,[22]

$$k_{\mathrm{ELT}} = \upsilon \exp\left(\frac{-\Delta G^*}{RT}\right) \tag{8}$$

where υ is the frequency factor. Here, υ is assumed to be 5.0×10^{13} M^{-1} s^{-1}.[21m] For the bimolecular reaction, the electron-transfer rate constant (k_{ELT}') can be given by eq 9, taking the formation of an encounter complex into account,[22a]

$$\frac{1}{k_{\mathrm{ELT}}'} = \frac{1}{k_{\mathrm{diff}}} + \frac{1}{k_{\mathrm{ELT}}} \tag{9}$$

where k_{diff} is the diffusion-controlled rate in acetonitrile. Because of the high concentration of the CBs and short lifetime of the T_2 state, the ELT quenching mechanism of NpD (T_2) by the CBs cannot be explained by the simple diffusion-controlled process. For the lifetime-dependent quenching, quenching rate constant k_{ELT}'' is represented as a sum of the lifetime-independent and -dependent terms. The classical theory leads to the expression of k_{ELT}'' as eq 10,[4a−e,18]

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

Here, $D = 2.0 \times 10^{-5}$ cm^2 s^{-1} were employed. From Schemes 1 and 2, the efficiency of ELT from NpD (T_2) (f_{ELT} (calcd)) can be calculated by eq 11,

$$f_{\mathrm{ELT}}\,(\mathrm{calcd}) = \frac{k_{\mathrm{ELT}}''[\mathrm{CBs}]}{(k_{\mathrm{ELT}}'' + k_{\mathrm{ENT}})[\mathrm{CBs}] + k_{\mathrm{IC}}} \tag{11}$$

where k_{IC} is the IC rate constant and given by the reciprocal of τ, [CBs] is the concentration of the CBs as a quencher ([CBs] = 1 M), and k_{ENT} is the rate constant of ENT from NpD (T_2) to the CBs and expressed by eq 2. The estimated f_{ELT} (calcd) values are summarized in Table 2. As shown in Figure 8, the plots of f_{ELT} versus f_{ELT} (calcd) showed a good correlation, indicating that the efficiency of ELT from NpD (T_2) to the CBs is explained qualitatively by Marcus's ELT theory.

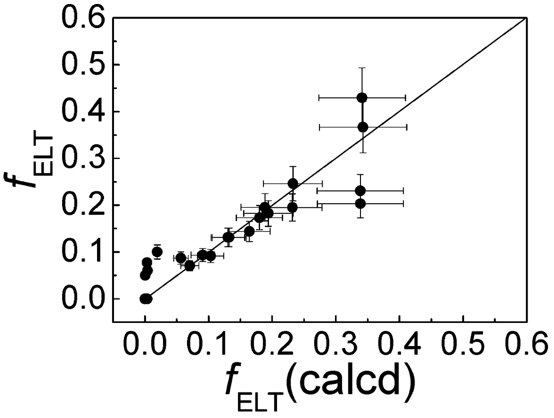


Figure 8. Plots of f_{ELT} versus f_{ELT}(calcd).

Energy Transfer from NpD (T_2) to the CBs. The deactivation of NpD (T_2) in the presence of the CBs involves two ENT processes as shown in Schemes 1 and 2. The ENT from CB (T_1) to NpD (S_0) was observed as the recovery of NpD (T_1). The recovery rate of NpD (T_1) (k_{REC}) corresponding to ENT_2 in Schemes 1 and 2 was estimated to be 3.3×10^7 s^{-1}. Because the ISC of 1,2,4-trichlorobenzene (T_1) is slow compared with the ENT from 1,2,4-trichlorobenzene (T_1) to NpD (S_0) (k_{ENT2}),[26] k_{REC} is expressed as the eq 12,

$$k_{\mathrm{REC}} = k_{\mathrm{ENT2}}[\mathrm{NpD}\ (S_0)]_0 \tag{12}$$

where $[\mathrm{NpD}(\ S_0)]_0$ is concentration of NpD (7 mM). From the large difference of the lowest triplet energies of CB (T_1) and NpD (T_1), the rate constant of the ENT from CB (T_1) to NpD (S_0) should be the diffusion-controlled rate.[1b] The k_{ENT2} value was estimated to be 4.8×10^9 $M^{-1}s^{-1}$ which is similar to the k_{diff} in acetonitrile.

One of the important findings of the present study is the ENT from NpD(T_2) to CB (S_0) giving CB (T_n) ($n > 1$) in which the homolytic C−Cl bond dissociation occurs. Ichimura et al. reported the photofragmentation of chlorobenzene in gas-phase upon excitation with 193 or 248 nm using a laser-molecular beam technique.[27] They suggested that the photodissociation of the C−Cl bond of chlorobenzene takes place through three different processes, i.e., (i) a direct dissociation through the electronic excited state (T_n ($n > 1$) or S_l ($l \geq 1$)) and dissociation from (ii) vibrationally excited triplet states and (iii) from a highly excited vibrational level of the ground state.[27a] In the present system, 1,2,4-trichlorobenzene (T_n) was generated by the triplet sensitization, (iii) can be eliminated. Because the lifetime of vibrationally excited states is the quite short in solution, (ii) can be also eliminated. Thus, it is suggested that the bond dissociation takes place via (i) indicating the T_n state. For the bond dissociation from the T_n state, 1,2,4-trichlorobenzene (T_n) should satisfy the following conditions. First, the triplet energy of 1,2,4-trichlorobenzene (T_n) should be between that of naphthalene (T_2) and the C−Cl bond dissociation energy. Second, the energy of 1,2,4-trichlorobenzene (T_n) should be sufficiently lower than naphthalene (T_2) because the ENT should proceed competitively with the quite rapid IC process. From these reasons, the energy of 1,2,4-trichlorobenzene (T_n) was estimated to be around 3.7 eV. Theoretical calculation indicated that chlorobenzene has the four low-lying triplet states, i.e., $^3(\pi,\pi^*)$ (2.86 eV), $^3(\pi,\pi^*)$ (3.23 eV), $^3(\pi,\sigma^*)$ (3.71 eV), and $^3(\pi,\sigma^*)$ (4.63 eV).[28a] Thus, the photodissociation of the

C−Cl bond seems to occur via $^3(\pi,\sigma^*)$.[28] From the comparison of the bond dissociation energies, the $^3(\pi,\sigma^*)$ state of 1,2,4-trichlorobenzene is lower than those of chlorobenzene and 1,2-dichlorobenzene. This consideration explains the more efficient bond dissociation of 1,2,4-trichlorobenzene than others as observed in Figures 3 and 4.

The bond dissociation rate from 1,2,4-trichlorobenzene (T_n) (k_C) was roughly estimated as follows. The naphthalene-1,2,4-trichlorobenzene system was selected as a representative. Because the ELT process is negligible in this system, the initial concentration of [1,2,4-trichlorobenzene (T_n)] ([1,2,4-trichlorobenzene (T_n)]$_0$) is given by eq 13,

$$[\text{1,2,4-trichlorobenzene } (T_n)]_0 = \frac{k_{\text{ENT}}[\text{PCB}]}{k_{\text{IC1}} + k_{\text{ENT}}[\text{PCB}]}[\text{NpD } (T_2)]_0 \quad (13)$$

where k_{IC1} is the rate constant of IC (naphthalene (T_2) → naphthalene (T_1)). The ratio of the recovered component to NpD (T_1) (f_{REC}) at 150 ns after the second laser pulse was given by eq 14,

$$f_{\text{REC}} = \frac{[\text{1,2,4-trichlorobenzene } (T_n)]_0 - [\text{NpD } (T_1)]_{\text{UNREC}}}{[\text{1,2,4-trichlorobenzene } (T_n)]_0} \quad (14)$$

where $[\text{NpD } (T_1)]_{\text{UNREC}}$ is the component that did not recover to NpD (T_1). From eq 14, f_{REC} was estimated to be 0.4. However, k_C has a relation with f_{REC} as eq 15,

$$\frac{k_{\text{IC2}}}{k_{\text{IC2}} + k_C} = f_{\text{REC}} \quad (15)$$

where k_{IC2} is the rate constant of IC (1,2,4-trichlorobenzene $^3(\pi,\sigma^*)$ → 1,2,4-trichlorobenzene $^3(\pi,\pi^*)$) and estimated from the energy gap law ($k_{\text{IC2}} \approx 10^{13} \exp(-\alpha\Delta E)$. Assuming $\alpha = 3.8$, the k_{IC2} was estimated to be 1.6×10^{12} s^{-1}).[1] From eqs 13, 14, and 15, k_c was calculated to be 2.4×10^{12} s^{-1}.

The present systematic study on the reactions from NpD (T_2) confirmed the occurrence of competitive reactions of ELT and ENT from the T_2 state. First, we found the ELT from NpD (T_2) to the CBs. The ELT from NpD to the CBs is energetically impossible from the T_1 state but possible from the T_2 state. The ELT from NpD (T_2) to the CBs was well explained by Marcus's ELT theory. Second, We found the intermolecular triplet energy transfer from NpD (T_2) to 1,2,4-trichlorobenzene giving 1,2,4-trichlorobenzene $^3(\pi,\sigma^*)$, which leads to the C−Cl bond dissociation of 1,2,4-trichlorobenzene. The molecules in the T_n states with the large excitation energy have interesting reactivates.

Conclusions

The occurrence of competitive reactions of ELT and ENT from NpD (T_2) was confirmed in acetonitrile solution. We found the intermolecular ELT occurred from a series of NpD (T_2) to CBs to give a NpD radical cation and a CB radical anion. The f_{ELT} value for ELT from NpD (T_2) to the CBs was well explained by Marcus's ELT theory. We also found the intermolecular ENT from NpD (T_2) to 1,2,4-trichlorobenzene occurred to give 1,2,4-trichlorobenzene (T_n), $^3(\pi,\sigma^*)$, leading to the C−Cl bond dissociation. Finally, we would like to remark that the present study will bring further work on reactions from various compounds in the higher 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 of the experiments were carried out at room temperature.

Transient Absorption Measurement Using Two-Color Two-Laser Flash Photolysis. The two-color two-laser flash photolysis experiment was carried out using the third harmonic oscillation (355 nm) of an 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 an 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 150 or 250 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 ($1.0 \times 1.0 \times 4.0$ cm^3).

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Supporting Information Available: The absorption spectrum of 2-methoxynaphthalene radical cation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) It is known that CCl_4 decomposes after the ENT from NpD (T_n).[4a−d] The bleaching rate without contribution of the recovery was determined by using CCl_4 as a higher triplet quencher. The second laser irradiation induced bleaching of the initial concentration of NpD (T_1) in 56% yield in Ar-saturated neat CCl_4 under the present experimental condition. Because the efficiency of the quenching of NpD (T_2) is expressed as $f_q = (k_{ENT}[CBs])/(k_{ENT}[CBs] + k_{IC})$, the initial concentration of NpD (T_2) ([NpD (T_2)]$_0$) was estimated from [NpD (T_2)]$_0$ = 0.56[NpD (T_1)]$_0$/f_q, where [NpD (T_1)]$_0$ is the concentration of NpD (T_1) before the second laser irradiation. The ratios of [NpD (T_2)]$_0$ to [naphthalene (T_1)]$_0$, [1-methylnaphthalene (T_1)]$_0$, [1-ethylnaphthalene (T_1)]$_0$, [1-isopropylnaphthalene (T_1)]$_0$, [1-methoxynaphthalene (T_1)]$_0$, [2-methylnaphthalene (T_1)]$_0$, [2-ethylnaphthalene (T_1)]$_0$, [2-isopropylnaphthalene (T_1)]$_0$, [2-methoxynaphthalene (T_1)]$_0$, and [2,6-dimethylnaphthalene (T_1)]$_0$ were estimated to be 90, 89, 78, 68, 66, 71, 70, 68, 66, and 67%, respectively.

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