

Properties of Excited Radical Cations of Substituted Oligothiophenes

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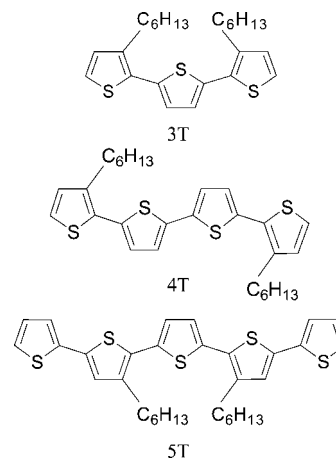
Excited-state properties of radical cations of substituted oligothiophenes ($nT^{+\bullet}$, n denotes the number of thiophene rings, $n = 3, 4, 5$) in solution were investigated by using various laser flash photolysis techniques including two-color two-laser flash photolysis. $nT^{+\bullet}$ generated by photoinduced electron transfer to *p*-chloranil or resonant two-photon ionization (RTPI) by using the first 355-nm ns laser irradiation was selectively excited with the second picosecond laser (532 nm). Bleaching of the absorption of $nT^{+\bullet}$ together with growth of a new absorption was observed during the second laser irradiation, indicating the generation of $nT^{+\bullet}$ in the excited state ($nT^{+\bullet*}$). The D_1 state lifetime was estimated to be 34 ± 4 , 24 ± 2 , and 18 ± 1 ps for $3T^{+\bullet}$, $4T^{+\bullet}$, and $5T^{+\bullet}$, respectively. In the presence of hole acceptor (Q), bleaching of $nT^{+\bullet}$ and growth of $Q^{+\bullet}$ were observed upon selective excitation of $nT^{+\bullet}$ during the nanosecond–nanosecond two-color two-laser flash photolysis, indicating the hole transfer from $nT^{+\bullet}(D_1)$ to Q. Recovery of $nT^{+\bullet}$ was also observed together with decay of $Q^{+\bullet}$ because of regeneration of $nT^{+\bullet}$ by hole transfer from $Q^{+\bullet}$ to nT at the diffusion-limiting rate. It was suggested that the hole transfer rate (k_{HT}) from $nT^{+\bullet}(D_1)$ to Q depended on the free-energy change for hole transfer ($-\Delta G = 1.41$ – 0.46 eV). The estimated k_{HT} faster than the diffusion-limiting rate can be explained by the contribution of the static quenching for the excited species in the presence of high concentration of Q (0.1–1.0 M).

Introduction

Radical cation of organic molecule can be produced by various methods such as resonant two-photon ionization (RTPI), photoinduced electron transfer, pulse radiolysis, γ -radiolysis, electrochemical reaction, and chemical reaction. Properties and reactions of radical cations have been extensively investigated.¹ However, properties of excited radical cations have not been well investigated. It is noteworthy that various reactions are expected to occur from radical cation in the excited state even when those from the ground (D_0) state are energetically impossible. The radical cations are usually nonemissive in solution, although a few exceptions such as thianthrene,^{2a} perylene,^{2b} and so on^{2c,d} have been reported. Therefore, the lifetime of excited radical cation has been estimated by using either direct or indirect methods. As the indirect method, kinetic analysis of bimolecular hole transfer from excited radical cations can be pointed out, although the lifetime estimated by this method includes some ambiguity due to several assumptions in the analysis.³ As the direct method, picosecond transient grating^{4a} and femtosecond pump–probe transient absorption measurements^{4b} have been reported, whereas examples of these studies are rather limited.^{4c,d}

For the direct clarification of properties of radical cations in the excited state, transient absorption measurements during two-color two-laser flash photolysis by using ultrashort pulse laser should be useful, because it can detect photogenerated transient species even when the generated species are nonemissive and/or short-lived one. During the first laser flash photolysis, the radical cation can be generated by photoinduced electron transfer or RTPI. With a short-time delay after the first laser flash, the radical cation can be selectively excited by the second laser

SCHEME 1



flash with the wavelength tuned to absorption of the radical cation. Transient absorption spectra and kinetic traces of the excited radical cations with short lifetimes can be obtained. Recently, we have applied two-color two-laser flash photolysis to the studies on the higher triplet excited states^{5a–i} and excited ketyl radicals,^{5j} indicating the wide utility of the present method.

In this paper, we investigated properties of radical cations of substituted oligothiophenes ($nT^{+\bullet}$, n denotes the number of thiophene rings, $n = 3, 4, 5$, Scheme 1) in the excited states such as the transient absorption spectra, lifetimes (τ), and reactivities by using various laser flash photolysis techniques including two-color two-laser flash photolysis. Owing to their unique electronic and optical properties, polythiophenes and their derivatives are one of the most intensively investigated organic materials which can be used to various applications, such as field-effect transistors (FET) and light-emitting diodes (LED).⁶

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Because the properties of conjugated polymers are often difficult to interpret because of structural ambiguity, well-defined oligothiophenes and their derivatives have been used to investigate polythiophene properties.⁷ Oxidized state of oligothiophene often plays an important role in their properties such as photoabsorption and conductivity.⁸ Thus, its excited state is an interesting subject to be cleared. The lifetimes and transient phenomena of nT^{+*} in the excited state (nT^{+*}) were evaluated. This is the first report on direct observation of short-lived excited radical cations having lifetime shorter than 1 ns based on the transient absorption measurement.

Experimental Section

Materials. Synthesis of nT was described in the previous papers.⁹ Other compounds were of the best commercial grade available. Acetonitrile (AN) and 1,2-dichloroethane ($C_2H_4Cl_2$) were spectral grade and used as a solvent without further purification.

Apparatus. The nanosecond-picosecond two-color two-laser flash photolysis was carried out by using the first laser flash at 355 nm (Continuum, Surelite, 5-ns fwhm, 10 Hz) and the second laser flash at 532 nm (Continuum, RGA69-10, 30-ps fwhm, 10 Hz). Two laser flashes were synchronized by a pulse generator with a delay time of 1 μ s. Transient absorption spectra in the picosecond region were measured by the pump and probe method. A spectral continuum, providing the wavelengths for probing, was generated by focusing the fundamental pulse of the picosecond laser on a D_2O/H_2O cell. Then, the probe pulse was detected with an MOS linear image sensor (Hamamatsu Photonics, M2493-40) equipped with a polychromator (Hamamatsu Photonics, C5094) after passing through the sample. The total system was controlled with a personal computer via GP-IB interface. A rectangular Suprasil flow cell (optical path length of 0.5 cm) was used to make sure that each laser shot was irradiated on the fresh sample.

The lifetime of nT^{+*} was measured by subpicosecond-laser flash photolysis.¹⁰ In the present paper, the samples were excited with 550, 650, and 690 nm laser pulse.

For investigation of the hole transfer from nT^{+*} to hole acceptor (Q), nanosecond–nanosecond two-color two-laser flash photolysis was carried out by using THG (355 nm) of a Nd^{3+} :YAG laser and SHG (532 nm) of a Nd^{3+} :YAG laser (Quantel, Brilliant, 5 ns-fwhm, 10 Hz) as the first and second lasers, respectively. The second laser was irradiated at 2–5 μ s after the first laser.^{3,5a–f,h,i}

Results and Discussion

Transient Absorption Spectrum of $4T^{+*}$ in the Excited State. $4T^{+*}$ was generated by photoinduced electron transfer. The 355 nm laser flash irradiation (5 nanosecond fwhm, 2.3 mJ pulse⁻¹) to a mixture of 4T (3.8×10^{-5} M) and *p*-chloranil (Chl) (5.0×10^{-3} M) in air-saturated AN generates Chl in the triplet excited state ($^3Chl^*$) almost quantitatively, which causes electron transfer with 4T to give $4T^{+*}$ and $Chl^{\cdot-}$ as shown in Figure 1.¹¹ The transient absorption peak around 650 nm (Figure 1a, black line) can be assigned to the $D_0 \rightarrow D_2$ transition of $4T^{+*}$.^{8a} A part of $Chl^{\cdot-}$ was quenched by oxygen to give $O_2^{\cdot-}$. $4T^{+*}$ decayed with a time constant of several microseconds through the back electron transfer from $Chl^{\cdot-}$ or $O_2^{\cdot-}$.³

Because $4T^{+*}$ shows an absorption band at 500–680 nm with a lifetime on microsecond order, it can be excited with second 532 nm laser flash with a delay time of 1 μ s after the first 355 nm laser flash. When the second 532 nm laser flash (30 ps fwhm, 21 mJ pulse⁻¹) was irradiated after the first laser flash, the rapid

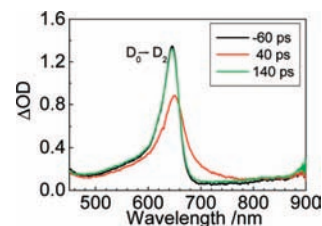


Figure 1. Transient absorption spectra observed at 60 ps (black line) before and 40 (red line) and 140 ps (green line) after the first 355 nm laser flash during the nanosecond–picosecond two-color two-laser flash photolysis of 4T in air-saturated AN in the presence of *p*-chloranil. The bleaching of D_0 state absorption at 650 nm together with the generation of new absorption band at 670 nm was observed upon second 532 nm laser irradiation.

TABLE 1: Oxidation Potentials (E^{OX}), Transient Absorption Peaks, Energies of the $D_0 \rightarrow D_2$, $D_0 \rightarrow D_1$, and $D_1 \rightarrow D_2$ in AN, and D_1 State Lifetimes (τ) of nT^{+*} in $C_2H_4Cl_2$

nT	E^{OX} V vs Ag/AgCl	$D_0 \rightarrow D_2$		$D_0 \rightarrow D_1$		$D_1 \rightarrow D_2$		τ ($D_1 \rightarrow D_0$) ps
		nm	eV	nm	eV	nm	eV	
3T	1.1	550	2.3	840	1.5	580	0.77	34 ± 4
4T	1.0	650	1.9	1070 ^a	1.2	670	0.75	24 ± 2
5T	0.9	700	1.8	1250 ^b	1.0	740	0.78	18 ± 1

^a Reference 8a. ^b Figures S3 in the Supporting Information.

bleaching of the absorption band around 650 nm together with the rapid generation of new absorption band around 660–780 nm was observed as shown in Figure 1 (red line). At 140 ps after the second laser flash, the absorption band around 650 nm was recovered completely together with the decay of new absorption band (Figure 1 green line). Because only $4T^{+*}$ has absorption at 532 nm, $4T^{+*}$ should be selectively excited to generate $4T^{+*}$ in the excited state ($4T^{+*}$). New absorption band can be attributed to $4T^{+*}$.

For $3T^{+*}$ and $5T^{+*}$, the nanosecond-picosecond two-color two-laser flash photolysis was carried out (Figures S1 in the Supporting Information). For $3T^{+*}$, two absorption peaks at 550 and 840 nm assigned to $D_0 \rightarrow D_2$ and $D_0 \rightarrow D_1$ transitions of $3T^{+*}$, respectively (Table 1), were observed after the first laser irradiation. These bands were bleached, and a new absorption band was generated at around 580 nm immediately after the second laser flash. For $5T^{+*}$, the bleaching of absorption peak at 700 nm due to the D_0 state together with the generation of new absorption band at around 740 nm due to the excited state was observed.

Lifetime of $4T^{+*}$ in the Excited State. Although the absorption change was observed during the nanosecond–picosecond two-color two-laser flash photolysis, determination of the lifetimes of nT^{+*} was difficult, because the spectral changes were observed almost during the pulse duration (30 ps fwhm). Therefore, the lifetimes of nT^{+*} were measured by using femtosecond-laser flash photolysis (130 fs fwhm) of nT^{+*} , generated by chemical oxidation by Iron (III) chloride ($FeCl_3$) in air-saturated $C_2H_4Cl_2$. Complete replacement of neutral nT by nT^{+*} was achieved by stepwise addition of $FeCl_3$ as reported in the literature.^{8a} The formation of $4T^{+*}$ was confirmed by the evolution of characteristic absorption spectrum of $4T^{+*}$ that remained unchanged for a hour. When the $4T^{+*}$ was irradiated with a 650 nm laser flash, the rapid bleaching and recovery of the absorption band at 660 nm was observed (Figure 2). This absorption change is the same as that observed in nanosecond–picosecond two-laser flash photolysis. From the fitting to the recovery at 660 nm, lifetime of $4T^{+*}$ was estimated to be 24 ± 2 ps.

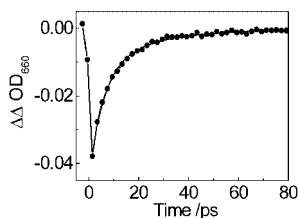
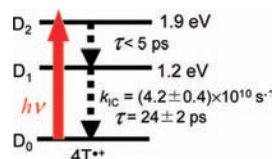


Figure 2. Time profile of the absorption change at 660 nm ($\Delta\Delta\text{OD}_{660}$) during femtosecond-laser flash photolysis (130 fs fwhm) of $4\text{T}^{+\bullet}$. The red line is the fitting curve.

SCHEME 2



Because the recovery of the transient absorption of $4\text{T}^{+\bullet}$ was completed in 100% yield, the chemical reactions such as hole injection from $4\text{T}^{+\bullet}$ to solvent¹² is not involved in the decay of $4\text{T}^{+\bullet}$. Furthermore, fluorescence was not observed. Therefore, the recovery of $4\text{T}^{+\bullet}$ can be attributed to the internal conversion from $4\text{T}^{+\bullet}$ to $4\text{T}^{+\bullet}(\text{D}_0)$. The rate constant of the internal conversion (IC) (k_{IC}) can be related to the energy gap between two electronic states (ΔE) by the energy gap law,¹³ $k_{\text{IC}}^{-1} \approx 10^{-13} \exp(\alpha \Delta E)$, where α is a constant of 3–5 eV⁻¹ depending on aromatic hydrocarbons.¹⁴ The energy gaps of $\text{D}_0\text{--D}_1$, $\text{D}_0\text{--D}_2$, and $\text{D}_1\text{--D}_2$ were calculated from the absorption peaks to be 1.2, 1.9, and 0.75 eV, respectively. The k_{IC} values for the $\text{D}_1 \rightarrow \text{D}_0$ (k_{IC}^{0-1}), $\text{D}_2 \rightarrow \text{D}_0$ (k_{IC}^{0-2}), and $\text{D}_2 \rightarrow \text{D}_1$ (k_{IC}^{1-2}) of $4\text{T}^{+\bullet}$ transitions were calculated on the basis of $\alpha = 3\text{--}5$ eV⁻¹ to be $(3.1\text{--}31) \times 10^{10}$, $(0.71\text{--}33) \times 10^9$, and $(2.4\text{--}11) \times 10^{11}$ s⁻¹, respectively. In the absence of the emission process and other processes, the corresponding lifetimes, $\tau_{\text{IC}} = k_{\text{IC}}^{-1}$, were calculated to be 3.2–33 ps, 0.030–1.4 ns, and 0.95–4.3 ps for the $\text{D}_1 \rightarrow \text{D}_0$, $\text{D}_2 \rightarrow \text{D}_0$, and $\text{D}_2 \rightarrow \text{D}_1$, respectively. Therefore, the observed $\tau_{4\text{T}^{+\bullet}} = 24 \pm 2$ ps can be attributed to the $\text{D}_1 \rightarrow \text{D}_0$ transition. In other words, observed absorption band around 660–670 nm is assigned to $4\text{T}^{+\bullet}$ in the D_1 state ($4\text{T}^{+\bullet}(\text{D}_1)$) with 24 ± 2 ps of lifetime. The 650 nm excitation of $4\text{T}^{+\bullet}$ generates initially $4\text{T}^{+\bullet}$ in the D_2 state ($4\text{T}^{+\bullet}(\text{D}_2)$) which decays rapidly to $4\text{T}^{+\bullet}(\text{D}_1)$ (Scheme 2). The lifetime of $4\text{T}^{+\bullet}(\text{D}_2)$ seems to be shorter than 5 ps as expected from the energy gap law.

In the cases of $3\text{T}^{+\bullet}$ and $5\text{T}^{+\bullet}$, the rapid bleaching and recovery of D_0 absorption were also observed at 600 and 700 nm, respectively, upon the femtosecond-laser flash. From the time profiles of the absorption change, the τ values of $3\text{T}^{+\bullet}(\text{D}_1)$ and $5\text{T}^{+\bullet}(\text{D}_1)$ were estimated to be 34 ± 4 and 18 ± 1 ps, respectively (Figure S2 in the Supporting Information). Because the $\text{D}_0\text{--D}_1$ energy gaps for $3\text{T}^{+\bullet}$ and $5\text{T}^{+\bullet}$ were estimated to be 1.5 and 1.0 eV, respectively (Table 1),^{8a} the k_{IC} values for the $\text{D}_1 \rightarrow \text{D}_0$ transitions of $3\text{T}^{+\bullet}$ and $5\text{T}^{+\bullet}$ were calculated to be $(6.2\text{--}120) \times 10^9$ and $(7.0\text{--}51) \times 10^{10}$ s⁻¹, respectively, indicating that τ_{IC} values were 8.4–160 and 2.0–14 ps, respectively. Thus, the observed $\tau_{3\text{T}^{+\bullet}} = 34 \pm 4$ and $\tau_{5\text{T}^{+\bullet}} = 18 \pm 1$ ps are attributed to the D_1 lifetime of $3\text{T}^{+\bullet}$ and $5\text{T}^{+\bullet}$, respectively. From the k_{IC}^{-1} values of $n\text{T}^{+\bullet}$ ($n = 3, 4, 5$) and $\text{D}_0\text{--D}_1$ energy gaps, α value of $n\text{T}^{+\bullet}$ was estimated to be 3.3 eV⁻¹ as expected for rigid aromatic hydrocarbons.¹⁴

Hole-Transfer Quenching of $n\text{T}^{+\bullet}(\text{D}_1)$ by Q. In order to examine the reactivities of $n\text{T}^{+\bullet}$, hole-transfer quenching of $n\text{T}^{+\bullet}(\text{D}_1)$ by Qs (diphenylsulfide (DPS), 1-methoxynaphthalene

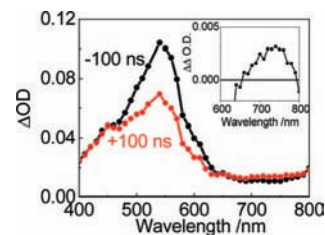


Figure 3. Transient absorption spectra of 3T in the presence of DPS (1.0 M) in air-saturated AN observed at 100 ns before (black line) and 100 ns after (red line) the second laser flash during nanosecond–nanosecond two-color two-laser flash photolysis (355 nm, fwhm 5 ns, 30 mJ pulse⁻¹ and 532 nm, fwhm 5 ns, 50 mJ pulse⁻¹). Inset: difference spectrum between the transient absorption spectra observed at 100 ns before and at 100 ns after the second laser flash.

(1-MeONp), 1,2-dimethoxybenzene (1,2-DMeOBz), 1,3-dimethoxybenzene (1,3-DMeOBz), and 1-methylnaphthalene (1-MeNp)), which cover 1.09–1.34 V (vs Ag/Ag^+) of oxidation potentials,^{5e,15} was studied by using the nanosecond–nanosecond two-color two-laser flash photolysis. These Qs have negligible absorption at the excitation wavelengths (355 and 532 nm). $n\text{T}$ s are known to exhibit lower oxidation potentials ($E^{\text{OX}} = 0.9\text{--}1.1$ V (vs Ag/Ag^+)).^{8a,16} Therefore, the hole-transfer process from $n\text{T}^{+\bullet}$ to Qs is expected to be energetically possible even though that from $n\text{T}^{+\bullet}(\text{D}_0)$ is impossible.

3T was irradiated with the 355 nm laser in the absence of other solute. Then, the $3\text{T}^{+\bullet}$ was confirmed in the transient absorption spectrum. The log–log plots of ΔOD due to $3\text{T}^{+\bullet}$ versus laser intensity (I) gave a linear line with a slope of 1.5 (Figure S4 in the Supporting Information), suggesting that $3\text{T}^{+\bullet}$ was generated through RTPI. In the present hole-transfer study, $n\text{T}^{+\bullet}$ was generated by RTPI, in order to make the reaction system simple.

Figure 3 shows the transient absorption spectra observed during the nanosecond–nanosecond two-color two-laser flash photolysis of 3T (5.0×10^{-5} M) in the presence of DPS (1.0 M) in air-saturated AN. The transient absorption spectrum observed at 1.9 μs after the first 355-nm laser flash (5 ns fwhm, 30 mJ pulse⁻¹) can be assigned to $3\text{T}^{+\bullet}$.^{8a} Contribution of the triplet excited 3T can be neglected because of the absence of the absorption due to the triplet (470 nm).^{5g,8a} It should be noted that at 100 ns after the second 532 nm laser flash (5 ns fwhm, 50 mJ pulse⁻¹), the absorption peak of $3\text{T}^{+\bullet}$ became weaker, and a new band appeared at 650–800 nm (Figure 3 inset), which can be assigned to $\text{DPS}^{+\bullet}$, because it is known that $\text{DPS}^{+\bullet}$ has an absorption band at around 750 nm but not in 400–600 nm.¹⁷ At 750 nm, the molar absorption coefficient (ϵ) of $\text{DPS}^{+\bullet}$ ($\epsilon_{750} = 5.6 \times 10^3$ M⁻¹ cm⁻¹ in HClO_4)^{17a} is larger than that of $3\text{T}^{+\bullet}$ ($\epsilon_{750} = 1.5 \times 10^3$ M⁻¹ cm⁻¹ in $\text{C}_2\text{H}_4\text{Cl}_2$).^{8a,18} As a result, it is suggested that the hole transfer from $3\text{T}^{+\bullet}(\text{D}_1)$ to DPS occurred to give $\text{DPS}^{+\bullet}$ immediately after the second laser irradiation as expressed by the following eq 1.



Figure 4a,b show the kinetic traces of ΔOD at 540 and 750 nm, respectively. The kinetic trace of ΔOD at 540 nm shows the second laser-induced rapid bleaching and slow recovery of $3\text{T}^{+\bullet}$, whereas the trace at 750 nm shows the rapid growth and decay. At 750 nm, the decay of newly formed $\text{DPS}^{+\bullet}$ was completed in 100% yield, indicating the back hole transfer regenerating $3\text{T}^{+\bullet}$ (Figure 4d). It was found that $\text{DPS}^{+\bullet}$ decayed with a time constant of 0.98 ± 0.05 μs , indicating that the rate

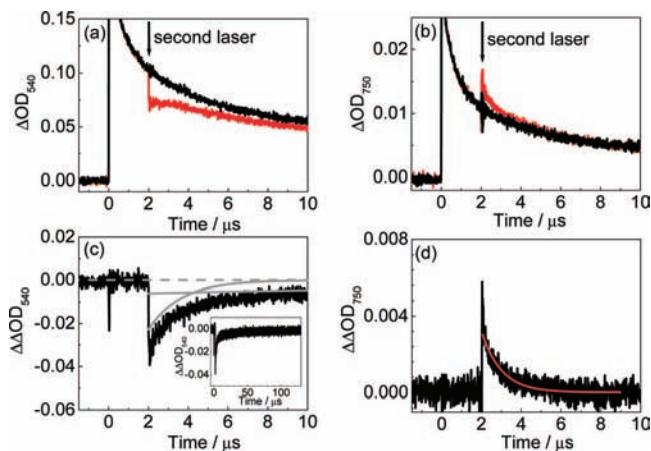


Figure 4. Kinetic traces of transient absorption spectra at 540 (a) and 750 nm (b) during nanosecond-nanosecond two-color two-laser flash photolysis of 3T in the presence of DPS (1.0 M) in air-saturated AN and absorption changes at 540 nm (c) and 750 nm (d) during the 532 nm laser irradiation obtained by subtraction of the red line from the black line. The gray lines in panel c show that the bleaching at 540 nm was recovered by two components with $\tau = 1.7$ and $45 \pm 1 \mu\text{s}$ of time constants. Panel c, inset shows the time profile in the time scale of 120 μs . The red line in Panel d was the fitting curve as the first-order exponential function.

constant of back hole transfer from $\text{DPS}^{+\cdot}$ to 3T ($5.0 \times 10^{-5} \text{ M}$) was $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The rate constant of this back hole transfer (k_{BHT}) was equivalent to the diffusion-limiting rate constant in AN ($k_{\text{diff}} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).¹⁹

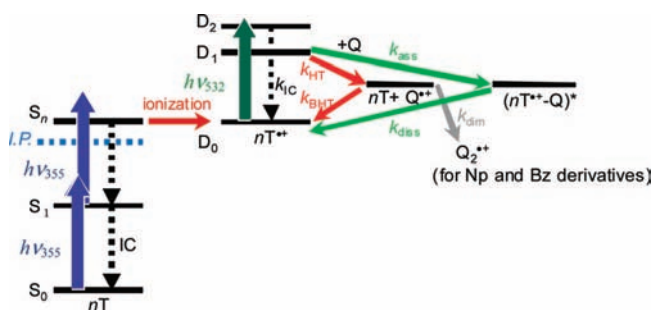


At 540 nm, the bleaching of $3\text{T}^{+\cdot}$ was completed to 100% in the time scale of several tens microseconds (Figure 4c). The bleached absorption of $3\text{T}^{+\cdot}$ can be expressed by the following eq 3,

$$\Delta\Delta\text{OD}_0 = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (3)$$

where τ_1 and τ_2 are time constants of the short- and long-lived components, respectively. $\Delta\Delta\text{OD}_0$ shows the bleached optical density of $n\text{T}^{+\cdot}$. As a result, it is found that the bleaching at 540 nm was recovered by two components with $\tau_1 = 1.7$ and $\tau_2 = 45 \pm 1 \mu\text{s}$ of time constants (Figure 4c, gray lines). Thus, the short-lived component attributes to the regeneration of $3\text{T}^{+\cdot}$ by the back hole transfer from $\text{DPS}^{+\cdot}$ to 3T. On the other hand, the long-lived component indicates that $3\text{T}^{+\cdot}$ partly reacted with other species to form the intermediate with no absorption at 540 nm and dissociated to regenerate $3\text{T}^{+\cdot}$ in the time scale of several tens microseconds. For electrochemical or photochemical generation of $n\text{T}^{+\cdot}$, it has been reported that a π -dimerization occurs between these species.²⁰ Because the concentration of $3\text{T}^{+\cdot}$ at 2 μs is estimated to be $3.4 \times 10^{-6} \text{ M}$ based on ϵ value of $3\text{T}^{+\cdot}$ ($\epsilon_{\text{max}} \sim 2.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),^{8a,18} the ratio of concentration ($\text{DPS}:3\text{T}^{+\cdot}$) is $10^6:1$. Thus, the dimerization of $3\text{T}^{+\cdot}$ with $3\text{T}^{+\cdot}$ generating the π -complex dimer ($3\text{T}^{+\cdot}$)₂ is negligible. As another conceivable process, the dimerization of $3\text{T}^{+\cdot}$ with 3T ($5.0 \times 10^{-5} \text{ M}$) to give dimer radical cation ($3\text{T}_2^{+\cdot}$) seems to be assumed although the formation of $n\text{T}_2^{+\cdot}$ has not been reported. However, the ratio of concentration ($\text{DPS}:3\text{T}$) is $10^5:1$, indicating that the dimerization of $3\text{T}_2^{+\cdot}$ is also negligible. Consequently, the formation of ($3\text{T}^{+\cdot}$ -DPS)* exciplex, generated by the association of $3\text{T}^{+\cdot}$ with DPS, is assumed to be the most conceivable process. Because the

SCHEME 3



concentration of DPS is high (1.0 M), the rapid formation of ($3\text{T}^{+\cdot}$ -DPS)* exciplex is possible if the association rate constant of $3\text{T}^{+\cdot}$ with DPS (k_{ass}) was equivalent to k_{diff} . The formation of a complex between $3\text{T}^{+\cdot}$ and DPS (0.1–1.0 M) in the ground state ($3\text{T}^{+\cdot}$ -DPS) was not confirmed by the absorption measurement. Thus, ($3\text{T}^{+\cdot}$ -DPS)* is assumed to undergo the dissociation to regenerate $3\text{T}^{+\cdot}$ and DPS with the dissociation rate constant (k_{diss}) of $(2.2 \pm 0.5) \times 10^4 \text{ s}^{-1}$ (Scheme 3).

The hole transfer from $3\text{T}^{+\cdot}(\text{D}_1)$ to other Qs was also observed. Similarly, $4\text{T}^{+\cdot}$ and $5\text{T}^{+\cdot}$ were generated by the RTP1 of 4T and 5T, respectively, and the hole transfers from $4\text{T}^{+\cdot}(\text{D}_1)$ and $5\text{T}^{+\cdot}(\text{D}_1)$ to Qs, back hole transfer, association of $n\text{T}^{+\cdot}$ with Q to give ($n\text{T}^{+\cdot}$ -Q)*, and dissociation of ($n\text{T}^{+\cdot}$ -Q)* to regenerate $n\text{T}^{+\cdot}$ and Q were also observed during the second 532 nm laser irradiation. For 5T-DPS, no bleaching was observed. The absence of the bleaching of $5\text{T}^{+\cdot}$ can be attributed to similar absorption coefficients of $5\text{T}^{+\cdot}$ ($\epsilon_{700} \approx 8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in dichloromethane)^{8a,16} and $\text{DPS}^{+\cdot}$ ($\epsilon_{750} = 5.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in HClO_4).^{17a}

For some of the bimolecular hole transfer systems from $n\text{T}^{+\cdot}$ to 1,2-DMeOBz, 1-MeNp, 1,3-DMeOBz, and 1-MeNp, the transient absorption of $n\text{T}^{+\cdot}$ recovered incompletely after the second laser irradiation. This result indicates that the back hole transfer to regenerate $n\text{T}^{+\cdot}$ did not occur completely after the initial hole transfer. In our previous paper, the incomplete recovery of the transient absorption of 1,3,5-trimethoxybenzene radical cation ($\text{TMB}^{+\cdot}$) has been observed after the irradiation of $\text{TMB}^{+\cdot}$ in the presence of Q such as benzene and naphthalene because of the formation of the dimer radical cation of Q ($\text{Q}_2^{+\cdot}$).³ For Qs such as naphthalene and benzene derivatives, the formation of $\text{Q}_2^{+\cdot}$ is assumed to occur competitively with the back hole transfer from $\text{Q}^{+\cdot}$ to $n\text{T}$, which resulted in the incomplete recovery of the transient absorption of $n\text{T}^{+\cdot}$. By assuming that $\text{Q}^{+\cdot}$ dimerized at Q with the diffusion-limiting rate, $\text{Q}_2^{+\cdot}$ should be formed within the pulse duration because of the high concentration of Q (0.1–1.0 M). Although dimer radical cations of unsubstituted naphthalene^{21a-c} and benzene^{21c,d} have a weak absorption around 550 and 580 nm, respectively, the formation of new absorption bands of $\text{Q}_2^{+\cdot}$ were not observed in this study. The ratio of bleaching due to $\text{Q}_2^{+\cdot}$ formation to the total one was less than 6.6%, suggesting that this dimerization process was a minor process.

The optical density due to the formation of $\text{Q}_2^{+\cdot}$, $\Delta\text{OD}_{\text{Q}_2^{+\cdot}}$, was subtracted from $\Delta\Delta\text{OD}_0$, and then, A_1 , A_2 , τ_1 , and τ_2 values in eq 3 were estimated by curve-fitting technique. It is found that the bleached absorption of $n\text{T}^{+\cdot}$ was found to be composed of short-lived main component (71–100%) and long-lived small component (0–22%). In the presence of 1.0 M Qs, the time constants of short-lived components (τ_1) were calculated to be 0.98–2.3, 1.5–2.5, and 1.7–2.3 μs for $3\text{T}^{+\cdot}$ -Q, $4\text{T}^{+\cdot}$ -Q, and $5\text{T}^{+\cdot}$ -Q systems, respectively. Thus, the k_{BHT} from $\text{Q}^{+\cdot}$ to 3T ($5.0 \times 10^{-5} \text{ M}$), 4T ($3.8 \times 10^{-5} \text{ M}$), and 5T ($1.9 \times 10^{-5} \text{ M}$)

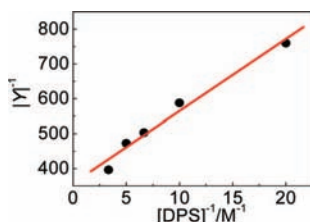


Figure 5. Plots of $|Y|^{-1}$ vs $[DPS]^{-1}$ during the irradiation of $3T^{*+}$ in the presence of DPS.

were estimated to be $(0.86-2.0) \times 10^{10}$, $(1.1-1.8) \times 10^{10}$, and $(2.3-3.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively, which were almost equivalent to the diffusion-limiting rate constant in AN ($k_{\text{diff}} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

Hole-Transfer Rate from $nT^{*+}(D_1)$ to Q Faster than Diffusion-Limiting Rate. The bleaching of $nT^{*+}(D_1)$ due to the hole transfer to Q increased with the increase in the concentration of Q ($[Q]$). The amount of bleaching shows the efficiency of the hole transfer from $nT^{*+}(D_1)$ to Q. Because the hole transfer from $nT^{*+}(D_1)$ to Q occurs competitively with the IC from $nT^{*+}(D_1)$ to $nT^{*+}(D_0)$ and association of nT^{*+*} with Q to give $(nT^{*+}-Q)^*$, the bleaching yield (Y) is represented by eq 4,^{4d}

$$Y = \frac{\Delta\Delta OD_0}{\Delta OD_0} = \frac{I_0(k_{\text{HT}} \times [Q])}{(k_{\text{IC}} + ((k_{\text{HT}} + k_{\text{ass}}) \times [Q]))} \quad (4)$$

where ΔOD_0 and $\Delta\Delta OD_0$ are the optical densities of nT^{*+} observed at just before the second laser flash and bleaching immediately after the second laser flash, respectively, and I_0 is the efficiency of formation of $nT^{*+}(D_1)$. $\Delta\Delta OD_0$ is composed of short-lived main component due to the hole transfer process from nT^{*+} to Q and long-lived small component due to the association of nT^{*+*} with Q. Consequently, the hole transfer yield (Y') is represented by eq 5,

$$Y' = \frac{\Delta\Delta OD_0 \times (A_1/(A_1 + A_2))}{\Delta OD_0} = \frac{I'_0(k_{\text{HT}} \times [Q])}{(k_{\text{IC}} + (k_{\text{HT}} \times [Q]))} \quad (5)$$

For the bimolecular hole-transfer process from $3T^{*+}$ to DPS, A_1 and A_2 values were estimated to be 0.078 and 0.0065, respectively. Thus, a linear relation was obtained when $|Y'|^{-1}$ was plotted against $[DPS]^{-1}$ according to eq 5 (Figure 5).

Because $k_{\text{IC}} = (2.9 \pm 0.3) \times 10^{10} \text{ s}^{-1}$ for IC from $3T^{*+}(D_1)$ to $3T^{*+}(D_0)$, k_{HT} was calculated to be $(5.1 \pm 0.6) \times 10^{11} \text{ s}^{-1}$ for $3T^{*+}$ -DPS system from the slope and intercept of the line (Figure 5). The k_{HT} values for other nT^{*+} -Q bimolecular hole-transfer systems were evaluated as summarized in Table 2. For all nT^{*+} -Q systems, the k_{HT} values are larger than k_{diff} in AN ($1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).¹⁹ Formation of a complex between nT^{*+} and Q in the ground state also can make the k_{HT} value larger than k_{diff} . However, this is not the case for the bimolecular hole transfer from $3T^{*+}(D_1)$ to Q, because no complex formation between $3T^{*+}$ and Q (0.1–1.0 M) was confirmed.

According to the classical electron (hole) transfer theory,²² the maximum value of k_{HT} is k_{diff} . Therefore, the bimolecular hole-transfer process becomes apparent when the τ value of $nT^{*+}(D_1)$ is longer than 53 ps ($1/k_{\text{diff}} [Q]$) in the presence of 1.0 M of Q in AN. However, bimolecular hole-transfer process were clearly observed in the presence of 1.0 M of Q during the hole quenching of $nT^{*+}(D_1)$ with τ value of 18–34 ps. These results indicate that the hole transfer reaction from nT^{*+*} to Q cannot be explained by the classical dynamic quenching limited by diffusion.

TABLE 2: Oxidation Potentials (E^{OX}) of Q, Free Energy Changes (ΔG), and Bimolecular Hole Transfer Rate Constants (k_{HT}) for the Hole Transfer from $3T^{*+}(D_1)$, $4T^{*+}(D_1)$, and $5T^{*+}(D_1)$ to Qs

Q	E^{OX} (V vs Ag/Ag ⁺) ^a	ΔG (eV)	k_{HT} ($10^{11} \text{ M}^{-1} \text{ s}^{-1}$)
3T^{*+}			
1-MeONp	1.09 ^b	-1.51	7.0 ± 0.8
1,2-DMeOBz	1.16 ^c	-1.44	6.2 ± 0.7
DPS	1.16 ^c	-1.44	5.1 ± 0.6
1,3-DMeOBz	1.20 ^c	-1.40	2.7 ± 0.3
1-MeNp	1.34 ^b	-1.26	1.7 ± 0.2
4T^{*+}			
1-MeONp	1.09	-1.11	7.1 ± 0.6
1,2-DMeOBz	1.16	-1.04	0.73 ± 0.1
DPS	1.16	-1.04	3.7 ± 0.3
1,3-DMeOBz	1.20	-1.00	1.2 ± 0.1
1-MeNp	1.34	-0.86	0.20 ± 0.02
5T^{*+}			
1-MeONp	1.09	-0.81	3.5 ± 0.1
1,2-DMeOBz	1.16	-0.74	0.91 ± 0.04
DPS	1.16	-0.74	^d
1,3-DMeOBz	1.20	-0.70	0.27 ± 0.01
1-MeNp	1.34	-0.56	0.27 ± 0.01

^a Calculated from E^{OX} (vs Ag/Ag⁺) = E^{OX} (vs SCE) - 0.29 V (in CH₃CN). ^b Reference 5e. ^c Reference 15. ^d Bleaching was not observed.

Hole-Transfer Mechanism from $nT^{*+}(D_1)$ with Short Lifetime to Q. When concentration of Q is sufficiently high, it is well-established that the quenching reaction occurs by both static and dynamic mechanisms.^{23,24} Therefore, k_{HT} value larger than diffusion-limiting rate can be attributed to the contribution of the static quenching in the presence of high concentration of Q. We have previously reported on the faster bimolecular energy transfer than the diffusion-limiting rate and explained it by the Ware's theoretical model.⁵ According to this model, the quenching rate constant k_{HT} is expressed by lifetime-independent and -dependent terms as in eq 6,

$$k_{\text{HT}} = k_{\text{diff}} [1 + \sigma' / (\pi D \tau)^{1/2}] \quad (6)$$

where σ' and D are the reaction distance and sum of the diffusion coefficients for the excited molecule (M^*) and Q, respectively and τ is the lifetime of M^* . By assuming the large contribution of the lifetime-dependent term ($\sigma' / (\pi D \tau)^{1/2}$) on k_{HT} , the larger k_{HT} than k_{diff} can be explained. Here, we discuss whether eq 6 can be applicable to the hole transfer from nT^{*+*} to Q by estimating the σ' and D values. Equation 6 can be transformed to eq 7,

$$\pi D \sigma'^{-2} = (k_{\text{HT}} / k_{\text{diff}} - 1)^{-2} \tau^{-1} \quad (7)$$

Then, the term $D\sigma'^{-2}$ is a function of k_{HT} , k_{diff} , and τ values and can be estimated to be $7.3 \times 10^6 - 1.5 \times 10^8$, $1.0 \times 10^7 - 4.8 \times 10^{12}$, and $5.8 \times 10^7 - 1.0 \times 10^{10} \text{ s}^{-1}$ for $3T^{*+}$ -Q, $4T^{*+}$ -Q, and $5T^{*+}$ -Q systems, respectively. It was found that the $D\sigma'^{-2}$ values for nT^{*+} -Q systems tended to increase with the increase of thiophene ring and E^{OX} value of Q.

In order to estimate the σ' values, at first, we tried to estimate the D values of nT^{*+} -Q systems by using Stokes-Einstein's equation (eq 8),

$$D = k_B T / 6\pi\eta r \quad (8)$$

where η is the viscosity of the solution (AN: 0.345 (cP))¹⁹ and r is the molecular radius of nT^{*+} or Q. For unsubstituted $3T$, the density $\rho = 1.509 \text{ g cm}^{-3}$ is reported from an X-ray

crystallographic study.²⁵ By assuming a spherical shape for simplification, the r value of $3T^{+}$ can be estimated from $r = (3 \times 10^{24} M / 4\pi\rho N_A)^{1/3}$ to be 4.8 Å. By assuming similar densities for $4T^{+}$ and $5T^{+}$, we estimated $r(4T^{+}) = 5.1$ Å and $r(5T^{+}) = 5.4$ Å. Similarly, r values of Qs were estimated to be 3.8–4.0 Å. As a result, the D values of nT^{+} –Q systems are estimated to be nearly constant $((2.8\text{--}3.0) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$. Then, the σ' values were estimated to be 45–200, 0.25–170, and 1.7–69 Å for $3T^{+}$ –Q, $4T^{+}$ –Q, and $5T^{+}$ –Q systems, respectively. This result indicates that the σ' values of nT^{+} –Q systems decreased with the increase of thiophene ring. This is unusual tendency, because the σ' value should increase with the number of thiophene ring.

When nT^{+} and Q were approximated to a linear shape, the r values of $3T^{+}$, $4T^{+}$, and $5T^{+}$ were estimated to be 6.0, 7.5, and 9.3 Å, respectively, on the basis of the MM calculation. Similarly, r values of Qs were estimated to be 3.6–5.1 Å. As a result, the D values of nT^{+} –Q systems are estimated to be $((1.9\text{--}2.9) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$. Then, the σ' values were estimated to be 43–200, 0.23–160, and 1.6–65 Å for $3T^{+}$ –Q, $4T^{+}$ –Q, and $5T^{+}$ –Q systems, respectively. Thus, this approximation also gave unusual tendency. In addition, it was found that the σ' values show small variations even when the r values were slightly varied by changing the approximation method. Therefore, eqs 7 and 8 cannot explain the present results. Consequently, Ware's theoretical model is not applicable to the hole transfer from nT^{+} to Q probably because of rod-like structure of oligothiophenes. For theoretical understanding, improvement of theories for quenching and diffusion seems to be needed.

Driving-Force Dependence of Hole Transfer from $nT^{+}(D_1)$. It should be noted that k_{HT} value varies depending on the kind of molecule. It was found that the k_{HT} value from $nT^{+}(D_1)$ to 1-MeONp was larger than that to 1-MeNp. It was also found that the k_{HT} value of $3T^{+}(D_1)$ tends to be larger than those of $4T^{+}(D_1)$ or $5T^{+}(D_1)$. Thus, it is suggested that k_{HT} depends not on the properties of $nT^{+}(D_1)$ but also on the Qs. In order to elucidate the effect of properties of Qs on k_{HT} , the free-energy changes for the hole transfer from $nT^{+}(D_1)$ to Qs were estimated on the basis of the redox potentials of nT^{+} and Q.

The free-energy change for the hole transfer (ΔG) from excited hole-donor radical cation to neutral hole acceptors is represented by eq 7,^{2a}

$$\Delta G(\text{eV}) = -E_{D^{+}/D} + E_{A^{+}/A} - \Delta E_{0,0} \quad (7a)$$

where $\Delta E_{0,0}$ is the excitation energy. For the hole transfer from $nT^{+}(D_1)$ to Q, $E_{D^{+}/D}$ and $E_{A^{+}/A}$ correspond to the oxidation potentials (E^{OX}) of nT and Q, respectively, and $\Delta E_{0,0}$ is the D_1 state energy of nT^{+} . The E^{OX} values for 3T, 4T, and 5T are 1.1, 1.0, and 0.9 V (vs Ag/AgCl), respectively (Table 1).^{8a,16} Calculated ΔG values for the hole transfer from $nT^{+}(D_1)$ to Q are also summarized in Table 2. The tendency that k_{HT} value decreased with a decrease of $-\Delta G$ was observed for $nT^{+}(D_1)$. These results strongly indicate that the rate of hole transfer depends on the driving force.

Conclusions

In the present study, the properties of nT^{+} ($n = 3, 4, 5$) were investigated by using various laser flash photolysis techniques including two-color two-laser flash photolysis. We have succeeded in the direct observation of the transient absorption spectra of nT^{+} , for the first time. The τ values of $3T^{+}$, $4T^{+}$, and $5T^{+}$ were estimated to be 34 ± 4 , 24 ± 2 , and 18 ± 1 ps, respectively, by using the femtosecond laser flash. Although

the $\tau_{nT^{+}}$ values are in the order of picoseconds, the hole transfer from $nT^{+}(D_1)$ to Q was observed. In the presence of high concentration of Q (0.1–1.0 M), the estimated k_{HT} faster than the diffusion-limiting rate could be explained because of the contribution of the static quenching. These results show that although the hole transfer from $nT^{+}(D_0)$ to Q is energetically impossible, that from $nT^{+}(D_1)$ to Q is possible. The direct observation of the D_n states allows us to study various reactions from the D_n states.

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Supporting Information Available: Transient absorption spectra observed during the nanosecond-picosecond two-color two-laser flash photolysis of 3T and 5T in air-saturated AN with *p*-chloranil. Time profiles of the absorption change during femtosecond-laser flash photolysis (130 fs fwhm) of $3T^{+}$ and $5T^{+}$ in the presence of FeCl_3 . Absorption spectrum of 5T in Ar-saturated *n*-BuCl after the γ -ray irradiation at 77K. Log–log plot of laser intensity (I) vs $\Delta O.D._{540}$ during the 355 nm laser flash photolysis of 3T in air-saturated AN. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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