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Photochemical Generation of Radical Cations of Dithienothiophenes, Condensed Thiophene Trimers, Studied by Laser Flash Photolysis

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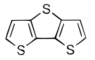
Photoinduced electron-transfer reactions between dithienothiophene (DTT) and the electron acceptors, *p*-dinitrobenzene (DNB) and CCl_4, have been investigated using nanosecond laser flash photolysis and time-resolved fluoresence spectroscopy. Generation of the radical cations of DTTs and radical anion of DNB in acetonitrile solution was confirmed by transient absorption spectra in the visible and near-IR regions. Observed transient absorption bands corresponded to those of radical ions generated by γ irradiation in a frozen matrix. Electron transfer occurred both from the singlet and triplet excited states of DTT to DNB at the diffusion-controlled rate, $\sim 10^{10}$ M^{-1} s^{-1}. When CCl_4 was used as an acceptor, electron transfer from the singlet excited state occurred at the diffusion-controlled rate, while the reaction from the triplet excited state occurred at $<10^9$ M^{-1} s^{-1} due to small ΔG_0 for this reaction. For both acceptors, the singlet route tended to dominate the triplet route when concentration of the acceptor was increased. The radical ions decayed with second-order kinetics by back-electron transfer at a rate closed to the diffusion-controlled limit. In cyclohexane, generation of radical ions was completely suppressed and the triplet excited state of DTT was deactivated by energy transfer to DNB.

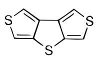
Introduction

Radical cations and dications of oligothiophenes have been investigated by many research groups[1−3] to help understand the nature of polarons and bipolarons in polythiophenes which are responsible for the electrical and optical properties of these π-conjugated polymers. These oxidized states have been well characterized by absorption spectra in the visible and near-IR regions and by ESR.[1−3] Studies on radical cations of oligothiophenes of lower polymerization degree, such as bithiophene and terthiophene, have been carried out mainly with end-capped oligomers, in which α-protons are substituted with unreactive groups such as methyl group.[2,3] This is because radical cations of small oligomers with α-protons are unstable and couple easily to form dimers. From detailed studies on the end-capped oligomers, the existence of a π-dimer of radical cations has been suggested.[3] Oxidation of oligomers has been carried out not only chemically and electrochemically but also photochemically.

Photochemical generation processes of radical cations of oligothiophenes have been studied by several groups.[4−7] Studies of the photochemical oxidation processes of terthiophene derivatives were reported by Evans and Scaiano using laser flash photolysis in the context of phototoxicity in vivo.[4] Wintgens et al. reported photoinduced electron-transfer reactions of terthiophene, quarterthiophene, and sexithiophene in dichloromethane.[5] They concluded that these radical cations were generated by electron transfer from lowest energy singlet excited state of oligothiophenes rather than from the triplet excited state. Poplawski et al. observed a transient absorption band ascribable to the dication in addition to those of the radical cation.[6] Buckminsterfullerene, C_{60}, has been also used as an electron acceptor for an electron-transfer reaction from oligothiophenes.[7] C_{60}-doped π-conjugated polymers, such as derivatives of poly(*p*-phenylenevinylene) and polythiophene, showed enhanced photoconductivity which resulted from charge generation due to photoinduced electron transfer between the polymers and C_{60}.[8] The electron-transfer processes between oligothiophene and C_{60} in solution and in composite film have been investigated by Sariciftci et al. using photoinduced absorption spectroscopy and light-induced electron spin resonance method.[7] They observed electron-transfer reaction from the oligothiophene to the triplet excited state of C_{60} in mixture solution.[7c] As for the composite film, they observed electron transfer from singlet excited state of oligothiophene to C_{60}.[7d] The investigations of radical cations and dications of thiophene derivatives have been mainly carried out with oligomers bonded at the α-position of the thiophene ring.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene has an interesting molecular structure in which 3- and 3′-positions of 2,2′-bithiophene are linked by sulfur that forces the two thiophene-rings in plane increasing π-conjugation. The compound has been investigated as a monomer for a conducting polymer or a donor for a conducting charge-transfer complex.[9,10] Furthermore, dithieno[3,4-*b*:3′,4′-*d*]thiophene has been known as a monomer for a small bandgap polymer.[11] However, there has been no spectroscopic characterization of the radical cations of dithienothiophenes. In previous papers, we reported that poly(dithienothiophene)s were obtained by photoirradiation of solutions which contained dithienothiophenes (DTT) and an adequate electron acceptor such as *p*-dinitrobenzene.[12] It was concluded that in the initial stage of the polymerization, radical cations of DTTs were generated by photoinduced electron transfer from excited DTTs to the electron acceptor. In this paper we present kinetic data and propose mechanisms for the generation of the radical cations of DTTs.


2,3-DTT


3,4-DTT

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Experimental Section

Materials. Dithieno[3,2-*b*:2′,3′-*d*]thiophene (2,3-DTT) and dithieno[3,4-*b*:3′,4′-*d*]thiophene (3,4-DTT) were synthesized following the procedure reported by De Jong and Janssen.[13] *p*-Dinitrobenzene (DNB) was purchased from Wako Pure Chemicals and purified by crystallization from ethyl acetate several times. Other chemicals were of the best commercial grade available.

Apparatus. Time-resolved transient-absorption spectra in the visible region (350−650 nm) were measured using a XeCl excimer laser (Lambda Physik, EMG101MSC, 308 nm, fwhm 20 ns) as the excitation source and a pulsed xenon flash lamp (Tokyo Instruments, XF 150) as the monitoring light. The monitoring light transmitted by the sample was detected with a MCP detector (Princeton Instrument, IRY-700G) equipped with a polychromator (McPHERSON Model 2035) and a gate pulser (Princeton, FG-100). The output signal was stored and analyzed using a personal computer. The transient-absorption spectra in the visible and near-IR regions (350−1000 nm) were measured using FHG (266 nm) of a Nd:YAG laser (Quanta-Ray, GCR-130, fwhm 6 ns) as the excitation source. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60) was used as the monitoring light. A Si-PIN photodiode (Hamamatsu Photonics, S1722-02) attached to a monochromator (Ritsu MC-10N) was employed as the detector. The output signal from the detector was recorded with a digitizing oscilloscope (Hewlett-Packerd 55410B) and analyzed using a personal computer.[14] Triplet lifetimes of DTTs were estimated using a xenon lamp and a photomultiplier as the monitoring light and the detector of above laser flash photolysis system. All the samples were contained in a 1 cm quartz cell and were deaerated by 15 min of argon bubbling. Since both DTT and DNB absorb at 266 nm, laser flash photolysis experiments were carried out with solutions containing excess DTT. This condition means that almost all the excitation light is absorbed by DTT. In order to avoid the effect of the polymerization of resulted radical cations on the kinetic studies, the concentrations of DTTs were adjusted to be <1 mM in most of the experiments.

Fluorescence spectra of the sample were measured on a Shimadzu RF-503A fluorospectrometer. Fluorescence lifetimes were measured by a single-photon counting method using an argon ion laser (Spectra-Physics, BeamLok 2060-10-SA), a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) with a pulse selector (Spectra-Physics, Model 3980), a third harmonic generator (GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334-01). In the present study, samples were excited at 282 nm.

Absorption spectra of radical ions, which were generated by γ irradiation in frozen glassy solutions (77 K), were recorded on a Hitachi U-3400 spectrophotometer.

Results and Discussion

Oxidation Potentials of DTT. Table 1 shows oxidation potentials of the ground and excited states of the DTTs. The oxidation potentials of the ground states were estimated from onset potentials of electrochemical oxidation in current−potential curves and singlet and triplet energies were estimated from 0−0 bands of fluorescence and phosphorescence spectra, respectively. Since reduction potentials of DNB and CCl_4 are −0.69 and −1.4 V vs SCE,[15] respectively, they are considered to be adequate acceptors for an electron-transfer reaction from the excited DTTs based on ΔG_0 values calculated via the Rehm−Weller relation.[16] Absorption spectra of mixtures of DTT and the acceptors (5−500 μM each) were identical to the superposition of those of DTT and the acceptors, proving that ground state complexes were not formed or negligible under the present experimental conditions.

TABLE 1: Oxidation Potentials of Ground and Excited States of 2,3-DTT and 3,4-DTT in Acetonitrile Solution

	oxidation potentials/V vs SCE		
compd	ground state[a]	S_1[b]	T_1[b]
2,3-DTT	1.07	−2.60 (338)	−1.51 (481)
3,4-DTT	1.04	−2.29 (372)	−1.62 (467)

[a] Data were onset potentials of electrochemical oxidation. [b] Data were estimated from oxidation potentials of the ground states and emission (fluorescence and phosphorescence) spectra. Numbers in parentheses show the peak positions of fluorescence and phosphorescence spectra (in nm).

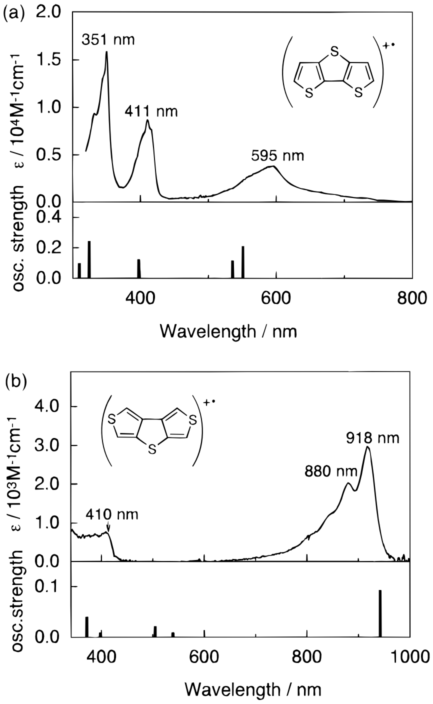

Figure 1. Absorption spectra of radical cations of (a) 2,3-DTT and (b) 3,4-DTT generated by γ irradiation in freon solution at 77 K. Lower: Transition energies and oscillator strengths calculated by the ZINDO method.

Absorption Spectra of Radical Cations of DTT. Figure 1 shows absorption spectra of the radical cations of DTTs that are generated by γ irradiation in frozen (77 K) freon solutions (equivolume solution of $CFCl_3$ and CF_2BrCF_2Br).[17] Mobile holes on the freon molecules, which were generated by γ irradiation, react with DTT and then generate the radical cation of DTT. In the case of 2,3-DTT, characteristic and intense absorption bands appeared in the visible region at 595, 411, and 351 nm. For 3,4-DTT, absorption bands appear both in the near-IR and visible regions at 918, 880, and 410 nm. In the lower parts of Figure 1, transition energies and oscillator strengths calculated by the ZINDO method[18] are shown by sticks. They show favorable correspondences with the experimental results. According to the calculations on radical cation of 2,3-DTT ($(2,3\text{-DTT})^{\bullet+}$), the absorption band at 595 nm is attributed mainly to HOMO-1 → SOMO and HOMO-2 → SOMO, the 411 nm band to HOMO → LUMO, and the 351 nm band to HOMO-3 → SOMO. In the case of radical cation of 3,4-DTT ($(3,4\text{-DTT})^{\bullet+}$), the absorption band at 918 nm is attributed mainly to HOMO-1 → SOMO.

Laser Flash Photolysis Study. In the laser flash photolysis of deaerated acetonitrile solutions containing 200 μM 2,3-DTT, a transient absorption band appeared at 384 nm immediately

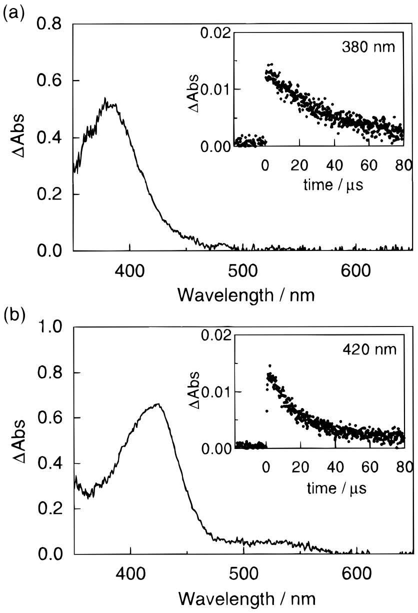

Figure 2. Transient absorption spectra of acetonitrile solutions containing 200 μM of (a) 2,3-DTT and (b) 3,4-DTT at 100 ns after laser excitation by XeCl excimer laser (308 nm). Insert: Absorption−time profile at (a) 380 nm and (b) 420 nm excited by Nd:YAG laser (266 nm).

after laser pulse excitation (Figure 2a). In the case of 3,4-DTT, an absorption band appeared at 422 nm accompanied by a weak broad band at 470−570 nm (Figure 2b). Since the absorption bands were readily quenched by oxygen, these absorptions could be assigned to the triplet excited states of 2,3-DTT and 3,4-DTT (^{T}(2,3-DTT)* and ^{T}(3,4-DTT)*), respectively. Absorption−time profiles of the absorption bands showed second-order decay indicating triplet−triplet annihilation when the concentration of DTT was higher than 200 μM and also at higher laser intensity. At low concentrations, first-order decays were observed (Figure 2 inserts) and their triplet lifetimes were estimated to be 45 and 30 μs for 2,3-DTT and 3,4-DTT, respectively. These lifetimes are longer than the reported value for 2,2′-bithiophene.[4b]

The transient absorption bands assigned to triplet excited states were readily quenched in the presence of the electron acceptor, DNB. In the laser flash photolysis of solutions containing 2,3-DTT and DNB, the absorption band of ^{T}(2,3-DTT)* (384 nm) disappeared within a few hundred nanoseconds, and new absorption bands appeared at 586, 406, and <350 nm (Figure 3a). These new absorption bands are attributed to (2,3-DTT)$^{\bullet+}$; their peak positions correspond well to those of (2,3-DTT)$^{\bullet+}$ generated by γ irradiation (Figure 1a). Furthermore, in the near-IR region, absorption bands appeared at 910, 820, and 780 nm with a rising absorption−time profile over about 500 ns (Figure 3b). These are assigned to radical anion of DNB (DNB$^{\bullet-}$).[19] The rate constant of a rising absorption−time profile was estimated by fitting to

$$\Delta\text{Abs} = C(1 - \exp(-k_{\text{obs}}t)) \qquad (1)$$

Here, C is a constant corresponding to the final absorbance of DNB$^{\bullet-}$ and k_{obs} is the pseudo-first-order rate constant for electron transfer. In this equation, it is assumed that the rate constant for generation of the radical ions is much larger than the rate constant for decay of the radical ions. The rate constant for generation of DNB$^{\bullet-}$ (910 nm) was estimated to be 9.1 × 10^{6} s^{-1} when the solution contained 1 mM 2,3-DTT and 400 μM DNB. As seen in Figure 3a, an absorption−time profile at 410 nm includes decay of ^{T}(2,3-DTT)* and generation of (2,3-DTT)$^{\bullet+}$. The observed time profile at 410 nm was resolved with curves of 8.9 × 10^{6} s^{-1} of the decay rate constant and 9.1 × 10^{6} s^{-1} of the rate constant for (2,3-DTT)$^{\bullet+}$ growth. Good correspondence of these rate constants indicates that the radical ions are generated by electron-transfer reaction from ^{T}(2,3-DTT)* to DNB.

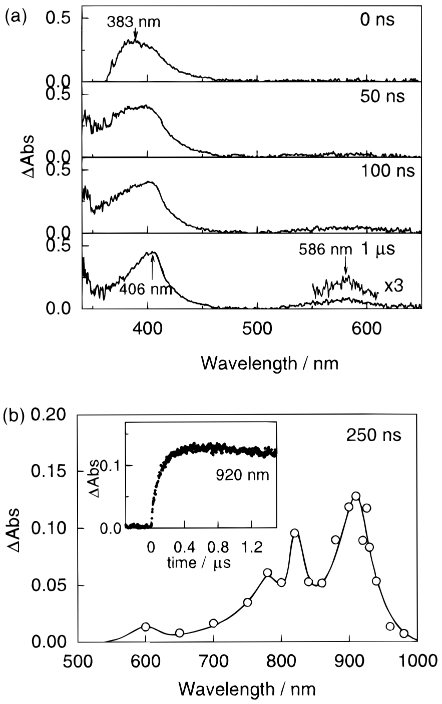

Figure 3. Transient absorption spectra of acetonitrile solutions containing 1 mM 2,3-DTT and 500 μM DNB in (a) the UV-visible region excited by a XeCl excimer laser and (b) the near-IR region excited by a Nd:YAG laser.

In a solution containing 3,4-DTT and DNB, new absorption bands appeared at 910, 880, 820, 780, and 396 nm (Figure 4, a and b), after the decay of ^{T}(3,4-DTT)* (422 nm). From comparison with the absorption spectra of (3,4-DTT)$^{\bullet+}$ and DNB$^{\bullet-}$ generated by γ irradiation, the absorption bands at 880, 820, and 396 nm can be attributed to (3,4-DTT)$^{\bullet+}$ and the 910, 820, and 780 nm bands to DNB$^{\bullet-}$. When the solution contained 1 mM 3,4-DTT and 400 μM DNB, the rate constant for the growth of (3,4-DTT)$^{\bullet+}$ and DNB$^{\bullet-}$ was estimated to be 1.4 × 10^{7} s^{-1} from the profile at 910 nm. The time profile at 430 nm, in which both the decay of ^{T}(3,4-DTT)* and the growth of (3,4-DTT)$^{\bullet+}$ were included, can be well analyzed by curve fitting assuming 1 × 10^{7} and 1.4 × 10^{7} s^{-1} of the rate constants, respectively. From the good correspondence of these rate constants, it can be concluded that the radical ions are generated by electron-transfer reaction from ^{T}(3,4-DTT)* to DNB.

Figure 5, a and b, shows the dependence of the absorption−time profiles of the radical ions on the concentration of DNB. A bimolecular rate constant for generation of the radical ions ($k_{\text{et}}{}^{\text{T}}$) can be estimated from the following equation,

$$k_{\text{obs}} = k_0 + k_{\text{et}}{}^{\text{T}}[\text{DNB}] \qquad (2)$$

In both cases, k_{obs} show good linearity on concentration of DNB as seen in the inserts of Figure 5a,b. The $k_{\text{et}}{}^{\text{T}}$ were estimated to be 2.4 × 10^{10} and 2.9 × 10^{10} M^{-1} s^{-1} for the electron-transfer reactions of 2,3-DTT and 3,4-DTT, respectively, indicating diffusion-controlled reaction. From the Rehm−Weller relation ΔG_0 for the electron-transfer reactions from ^{T}(2,3-DTT)* and ^{T}(3,4-DTT)* to DNB were estimated to be −85 and −96 kJ

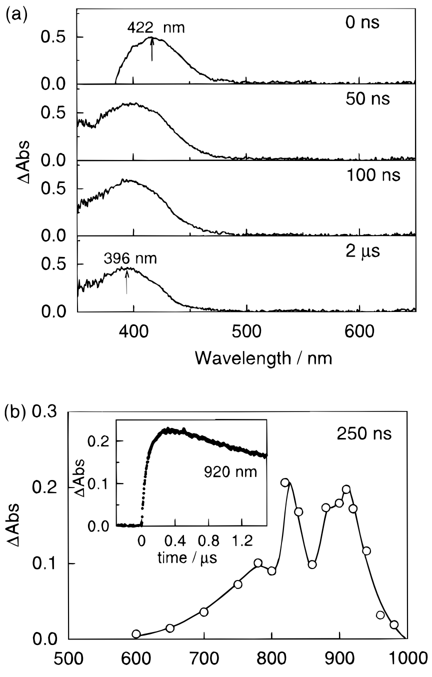

Figure 4. Transient absorption spectra of acetonitrile solutions containing 1 mM 3,4-DTT and 500 μM DNB in (a) the UV-visible region excited by a XeCl excimer laser and (b) the near-IR region excited by a Nd:YAG laser.

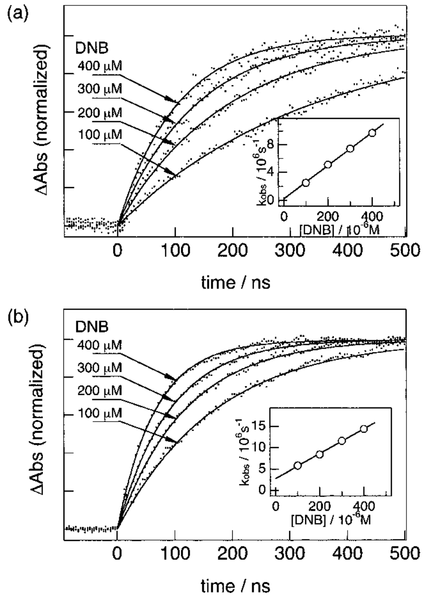

Figure 5. Absorption−time profiles of radical ions at 910 nm in acetonitrile solutions containing DNB and (a) 2,3-DTT and (b) 3,4-DTT. The concentrations of DNB are 400, 300, 200, and 100 μM. Solid lines are obtained by fitting to eq 1 in the text. Insert: Dependence of pseudo-first-order rate constant (k_{obs}) on concentration of DNB.

mol^{-1} by employing the oxidation potentials in Table 1 and 0.06 eV as the Coulombic energy term for acetonitrile. The large negative value of ΔG_0 are consistent with diffusion-controlled rate constants.

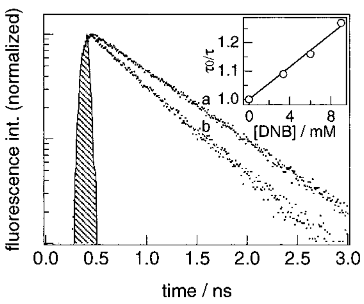

Figure 6. Fluorescence decay profiles of 5 mM 3,4-DTT in (a) the absence and (b) the presence of 9 mM DNB in acetonitrile. The insert shows a Stern−Volmer plot of fluorescence lifetime of 3,4-DTT.

In light of the large negative values of ΔG_0, electron-transfer reactions from the singlet excited states of DTTs (^{S}(2,3-DTT)* and ^{S}(3,4-DTT)*) to DNB are also anticipated. Fluoresence lifetimes of 2,3-DTT and 3,4-DTT were estimated from fluorescence decay profiles obtained by a single-photon counting method using a streakscope. The fluorescence decay profiles of 3,4-DTT are shown in Figure 6. The fluorescence lifetime of 3,4-DTT was estimated to be 6.5 × 10^2 ps when the solution contained 5 mM of 3,4-DTT. The fluorescence lifetime and peak position were independent of DTT's concentration in acetonitrile within the examined range, 50 μM-5 mM. In the presence of DNB, fluorescence lifetime became shorter; when the solution contained 5 mM 3,4-DTT and 9 mM DNB, the fluorescence lifetime was estimated to be 5.1 × 10^2 ps (part b in Figure 6). A clear linear relationship was confirmed between τ_0/τ and the concentration of DNB (Figure 6 insert), where τ_0 and τ are fluorescence lifetimes in the absence and the presence of DNB, respectively. From the Stern−Volmer equation, a rate constant for quenching of fluorescence of 3,4-DTT was estimated to be 4.4 × 10^{10} M^{-1} s^{-1}. As a mechanism of the fluorescence quenching electron-transfer reaction from ^{S}(3,4-DTT)* can be proposed. This mechanism is supported by the fact that in nanosecond laser flash photolysis of the solution containing 5 mM 3,4-DTT and 9 mM DNB substantial amounts of radical ions are generated within laser duration. Since the proposed electron-transfer reaction from the singlet state competes with intersystem crossing process, the reaction from the singlet will become evident in solutions containing much electron acceptor. In the present case electron-transfer rate from ^{S}DTT* (k_{et}^{S} × [acceptor]) becomes comparable to k_{isc} (∼10^8 s^{-1}) when the concentration of acceptor is larger than 10^{-2} M. When the solution contained <1 mM of DNB, the absorption−time profile of the radical ions showed only a gradual increase over about 500 ns with no abrupt increase within laser duration (Figure 5b). This indicates that almost the radical ions are generated by rather slow electron-transfer process, i.e., from triplet excited state.

In the case of 2,3-DTT, the fluorescence peak position and lifetime are strongly dependent on its concentration probably due to formation of some kind of aggregate. When the solution contained 5 mM 2,3-DTT, the fluorescence decay profile was multicomponent of which the fast component was estimated to be about 20 ps, on the same order as resolution of the instrument. For this reason fluorescence quenching experiments on 2,3-DTT were not conducted.

As shown in Figure 7, the absorption ascribable to the radical ions decays after reaching a maximum. The decay of absorption can be attributed to the back-electron-transfer reaction and radical coupling of DTT$^{\bullet+}$ yielding dimers. The decay will be mainly caused by back-electron-transfer reaction, because the concentration of the radical cation is expected to be low under the present experimental conditions. From the second-order plot shown in Figure 7b, the back-electron-transfer rate (k_{bet}) was estimated to be 1.1 × 10^{10} M^{-1} s^{-1} using an evaluated ϵ for DNB$^{\bullet+}$ at 910 nm (5.9 × 10^3 M^{-1} cm^{-1}).[20] In the case of Figure 7d, the decay time profile at 910 nm does not obey second-order plot, perhaps because the absorption−time profile at 910 nm is a summation of absorptions of DNB$^{\bullet-}$ and (3,4-DTT)$^{\bullet+}$.

TABLE 2: Estimated Rate Constants for Electron-Transfer Reaction between DTT and Acceptors (DNB and CCl_4) in Acetonitrile

	DNB			CCl_4	
DTT	$k_{et}^T/M^{-1}\ s^{-1}$	$k_{et}^S/M^{-1}\ s^{-1}$ [a]	$k_{bet}/M^{-1}\ s^{-1}$	$k_{et}^T/M^{-1}\ s^{-1}$ [a]	$k_{et}^S/M^{-1}\ s^{-1}$
2,3-DTT	2.4×10^{10}	*b*	1.1×10^{10}	*d*	$\sim 10^{10}$ [b]
3,4-DTT	2.9×10^{10}	4.4×10^{10}	9.9×10^{9} [c]	8×10^{8}	2.7×10^{10}

[a] In this table, the rate constants for fluorescence quenching were regarded as electron-transfer rates from singlet excited state (k_{et}^S). [b] The rate constant was not obtained because of the difficulty in estimation of fluorescence lifetime of 2,3-DTT (see text). [c] The rate constant was estimated by applying second-order plot to 0−5 μs region in absorption−time profile. [d] The rate constant was not obtained. Since absorption band of (2,3-DTT)$^{\bullet+}$ appeared at close position to ^{T}(2,3-DTT)* (see Figure 3a), estimation of growth rate constant for (2,3-DTT)$^{\bullet+}$ was difficult.

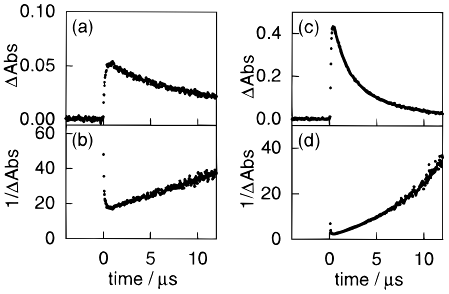

Figure 7. Absorption−time profiles and second-order plots for radical ions at 910 nm generated via electron transfer in acetonitrile solution containing (a, b) 1 mM 2,3-DTT and 400 μM DNB and (c, d) 1 mM 3,4-DTT and 400 μM DNB.

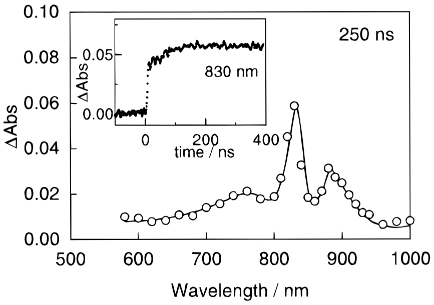

Figure 8. Transient absorption spectrum of an acetonitrile solution containing 1 mM 3,4-DTT and 20 mM CCl_4 at 250 ns after laser excitation by a Nd:YAG laser. Insert shows an absorption−time profile of the DTT radical cation at 830 nm.

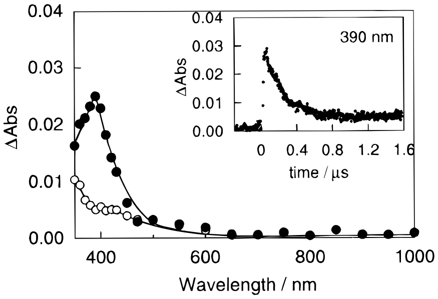

Figure 9. Transient absorption spectra of a cyclohexane solution containing 1 mM of 2,3-DTT and 400 μM of DNB at 100 ns (filled circles) and 1 μs (open circles) after laser excitation by a Nd:YAG laser. Insert shows an absorption−time profile at 390 nm.

The latter can be consumed not only by back electron transfer but also radical coupling reactions.

When laser flash photolysis was carried out in acetonitrile solution containing DTT and CCl_4, absorption bands ascribable to DTT$^{\bullet+}$ were observed immediately after laser excitation. Figure 8 shows the transient absorption spectrum of an acetonitrile solution which contains 1 mM 3,4-DTT and 20 mM CCl_4. Absorption bands at 880 and 830 nm can be attributed to (3,4-DTT)$^{\bullet+}$. As seen in the insert of Figure 8, absorption−time profile at 830 nm shows both steeply and gradually rising components indicating the existence of fast and slow electron-transfer processes, respectively. Fast generation of the radical ions can be attributed to electron-transfer reaction from the singlet excited state and slow radical generation to that from triplet excited state. Fluorescence of both 2,3-DTT and 3,4-DTT was quenched in the presence of CCl_4 according to the Stern−Volmer equation. The Stern−Volmer constants were estimated to be 1.55 and 17.7 M^{-1} for 2,3-DTT and 3,4-DTT, respectively, and quenching rate constants were estimated to be $\sim 10^{10}$ and $2.7 \times 10^{10}\ M^{-1}\ s^{-1}$. The estimated rate constant for 2,3-DTT includes some ambiguity because the fluorescence lifetime varies with concentration of 2,3-DTT. Since the ΔG_0 for electron-transfer reactions from ^{S}(2,3-DTT)* or ^{S}(3,4-DTT)* to CCl_4 were estimated to be −122 or −92 kJ mol^{-1}, respectively, diffusion-controlled rate constants are reasonable.

As for the slow component in insert of Figure 8, the growth rate constant was estimated to be $1.7 \times 10^7\ s^{-1}$ by fitting to

$$\Delta Abs = C_1(1 - \exp(-k_{obs}t)) + C_2 \tag{3}$$

Here, C_1 and C_2 are constants corresponding to absorbance of (3,4-DTT)$^{\bullet+}$ generated by the slow and the fast electron-transfer processes, respectively. From k_{obs}, k_{et}^T for electron-transfer reaction was estimated to be $8 \times 10^8\ M^{-1}\ s^{-1}$. The small k_{et}^T results from the relating small ΔG_0 for electron transfer from ^{T}(3,4-DTT)* to CCl_4, −27 kJ mol^{-1}. According to eq 3, the ratio of C_1 and C_2 can be regarded as the ratio of amount of the products generated via ^{T}(3,4-DTT)* and ^{S}(3,4-DTT)*. In the case of reaction in the solution containing 1 mM 3,4-DTT and 20 mM CCl_4 (Figure 8), the ratio of C_1 and C_2 was estimated to be 1:1.8, indicating that about 2/3 of the radical ions were generated by electron transfer from ^{S}(3,4-DTT)*. In the case of solution containing 1 mM 3,4-DTT and 400 μM DNB, almost radical ions were generated from ^{T}(3,4-DTT)*. The different reactivity of the excited state toward these acceptors can be attributed to differences in ΔG_0 for the electron-transfer reaction and in concentrations of the electron acceptor. From the ratio of C_1 and C_2 and the rate constants estimated in above, k_{isc} of 3,4-DTT was estimated to be $3 \times 10^8\ s^{-1}$. The rate constants for the electron-transfer reactions between DTT and electron acceptors are summarized in Table 2.

It is known that $CCl_4^{\bullet-}$ decomposes yielding chloride anion and $CCl_3^{\bullet}$.[14] $CCl_3^{\bullet}$ and/or its decomposition products will react via addition to the generated polymers. From elemental analysis of polymers which were generated by steady state photolysis in a solution containing CCl_4 as an acceptor, incorporation of chlorine into the polymer was confirmed.[21]

Upon laser flash photolysis of a cyclohexane solution containing DTT and DNB, no transient absorption band ascribable to the products of electron-transfer reactions was observed (Figure 9). In nonpolar solvents stabilization of ion pairs by the solvent is weak and electron transfer is unfavorable. In the case of cyclohexane containing 1 mM 2,3-DTT and 400 μM DNB, the transient absorption due to ^{T}(2,3-DTT)* disappeared within 500 ns after laser excitation, and a new absorption band appeared at wavelengths less than 350 nm. The new band can be attributed to the triplet excited state of DNB.[22] The result indicates that ^{T}(2,3-DTT)* is quenched by energy transfer to DNB. From the dependence of the decay rate constant of ^{T}(2,3-DTT)* on DNB concentration, the bimolecular rate constant for the energy transfer was estimated to be 8.8×10^{9} M^{-1} s^{-1}. As for cyclohexane solution of 3,4-DTT and DNB, quenching of ^{T}(3,4-DTT)* by energy transfer was also observed and the rate constants was 1.1×10^{10} M^{-1} s^{-1}.

Conclusion

In the present study, we showed that the radical cations of DTTs were generated efficiently by photoirradiation in the presence of appropriate electron acceptors in polar solvent. The reactions occurred at the diffusion-controlled rate from both the singlet and triplet excited states of DTT when DNB was used as an acceptor (ΔG_0 for the reaction <-80 kJ mol^{-1}). Since electron transfer from the singlet excited state competes with intersystem crossing, it only becomes evident when the concentration of DNB is higher than 10^{-2} M. The contribution of electron transfer from the singlet excited state also became large than for DNB when CCl_4 was used as an acceptor. In this case ΔG_0 for the reaction from the triplet excited state was also less negative. In cyclohexane, the triplet excited state of DTT was deactivated by energy transfer to DNB rather than electron transfer.

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