Laser flash photolysis study on the photoinduced reactions of 3,3'-bridged bithiophenes

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Photophysical properties and photoinduced reactions of 3,3'-bridged-2,2'-bithiophenes {dithieno[3,2-b:2',3'-d]-thiophene, 4H-cyclopenta[2,1-b:3,4-b']dithiophene, and 4H-dithieno[3,2-b;2',3'-d]pyrrole (DTP)} and 2,2'-bithiophene (BT) were investigated by observing the transient absorption spectra in the visible and near-IR regions using nanosecond laser flash photolysis. Fluorescence quantum yields for the bridged bithiophenes were low compared with that for BT. An especially low quantum yield for DTP in acetonitrile was attributed to an addition reaction with the solvent. The triplet energy of BT was the lowest amongst the examined bithiophenes, indicating some conformational change in the triplet state. Triplet-energy-transfer reactions at diffusion limited rates were confirmed between bithiophenes was confirmed by the transient absorption spectra, which show good correspondence with those observed in γ -ray radiolysis. It was found that the triplet quenching rates of the electron-transfer reactions were small when the Gibbs energy change for the reaction was ≥ -25 kJ mol⁻¹. The observed tendency agreed with the semi-empirical equation of Rehm–Weller. The generated radical cations decay according to a second-order function, indicating deactivation by a back electron-transfer reaction.

Introduction

Over the past decade, oligomers of conjugated polymers have attracted considerable attention because of their importance in understanding the interesting physical and chemical properties of conjugated polymers.1 In particular, radical cations and dications of oligomers have been investigated widely, since they are responsible for electrical and optical properties.²⁻¹¹ The studies on oligomers have been carried out not only to gain understanding of the electrical and optical properties but also for their practical applications. Sexithiophenes and larger oligomers have been examined as materials for non-linear optics12 and field-effect transistors.13,14 Photochemical processes of small αoligothiophenes, such as bithiophene and terthiophene, have been studied also in the context of biophotosensitizers¹⁵ and singlet oxygen sensitizers.16,17

While large oligomers are stable in their oxidized forms, oxidation of smaller oligomers often results in a coupling reaction to form longer oligomers and polymers.^{18–20} Recently, Guyard *et al.* reported investigations on the generation and coupling reactions of radical cations and neutral radicals of bipyrrole derivatives.²¹ They concluded from the kinetic data that only the cation radicals, and not the neutral radicals, produce higher oligomers *via* a coupling reaction followed by a deprotonation process.

The investigations on the oligothiophenes have been carried out mainly with linear oligomers bonded at the α -positions of the thiophene ring. Previously, we reported photochemical generation of radical cations and polymerization of dithieno[3,2-b:2',3'-d]thiophene and dithieno[3,4-b:3',4'-d] thiophene.^{20,22} In these dithienothiophenes, sulfur forces the two thiophene rings to lie in a plane, thus increasing the π conjugation. The well defined structure excludes cis-trans conformational change due to S-C(α)-C(α)-S twisting, which is expected for a-linked oligothiophenes such as 2,2'-bithiophene.²³⁻²⁵ Dithieno[3,2-b:2',3'-d]thiophene has been investigated as a donor for a conducting charge-transfer complex or as a monomer for a conducting polymer.²⁶⁻²⁹ A thin film of dithienothiophene dimer was reported to show high mobility and a high on/off ratio, comparable to that of amorphous silicon, resulting from the closely packed face-to-face stacking and wide HOMO-LUMO gap of the material.²⁸ Several bithiophene derivatives of which the 3,3-positions are bridged have already been reported and used as the starting monomer in chemical or electrochemical polymerization.³⁰ Properties of the bridged bithiophenes, such as the oxidation potential, largely depend on the electronic nature of the bridging group. For application of these oligomers to opto- and electro-functional materials, systematic studies on their excited states and charge generation process are indispensable. These are key processes of many useful and interesting properties such as photoconductivity of organic semiconductors.

In the present report, we describe a study of the photophysical and photochemical properties of 2,2'-bithiophene (BT) and three bridged bithiophenes (Scheme 1), dithieno[3,2b:2',3'-d]thiophene (DTT), 4H-cyclopenta[2,1-b:3,4-b'] dithiophene (CPDT), and 4H-dithieno[3,2-b;2',3'-d]pyrrole (DTP) by a laser flash photolysis method. Their properties in the excited states and the photoinduced reactions are discussed, based on the kinetic data.



Experimental

Materials

DTT,³¹ CPDT,³² and DTP³³ were synthesized according to the literature procedures. BT (Aldrich) and *p*-dinitrobenzene (*p*-DNB, Wako Pure Chemicals) were purified by several recrystallizations from methanol and ethyl acetate, respectively. Solvents for the measurements were of spectroscopic grade. Other chemicals were of the best commercial grade available.

Measurements

The transient absorption spectra in the visible and near-IR regions (350–1000 nm) were measured using an Si-PIN photodiode (Hamamatsu Photonics, S1722-02) as the detector and fourth harmonic generation (FHG, 266 nm) or third harmonic generation (THG, 355 nm) of a Nd:YAG laser (Quanta-Ray, GCR-130, fwhm 6 ns) as the excitation source.³⁴ Long-timescale phenomena were observed by using a photomultiplier as the detector. All the samples were contained in a 1 cm quartz cell and were deaerated by argon bubbling. In order to avoid the effect of polymerization of the resultant radical cations on the kinetic studies, the concentration of the bithiophenes was adjusted to be $\leq 1 \times 10^{-3}$ mol dm⁻³ in most of the experiments.

Steady-state fluorescence spectra of the samples were measured on a Shimadzu RF-5300PC 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, fwhm 1.5 ps) 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.

Phosphorescence spectra were recorded with a Hitachi 850 fluorescence spectrometer equipped with a phosphorescence unit.

Steady-state absorption spectra in the UV, visible, and near-IR regions were measured with a JASCO V-570DS spectrophotometer. Radical cations of bithiophenes at 77 K were generated by γ -ray irradiation of butyl chloride solutions containing 5×10^{-3} mol dm⁻³ of bithiophenes at 2.4×10^{4} R h⁻¹ for *ca*. 6 or 22 h. Butyl chloride was purified according to a published procedure.³⁵

The products of the photochemical reactions were analysed with a gas chromatograph mass spectrometer (GC–MS, Shi-madzu GCMS-QP5000).

Results and discussion

Ground-state absorption spectra of bithiophenes

Fig. 1 shows the absorption spectra of bithiophene derivatives. While their peaks appeared at similar positions, the molar



Fig. 1 Absorption and fluorescence spectra of bithiophenes in AN.

absorption coefficients of the bridged bithiophenes at the peak at *ca.* 300 nm are larger than that of BT. The absorption spectrum of a mixed solution of bithiophenes and dinitrobenzenes (DNB), which act as electron acceptors in the present electron-transfer studies, was the same with the superposition of the components. This finding indicates that, in the ground state, charge-transfer complex formation between them is negligible under the experimental conditions (bithiophenes 1.0×10^{-3} mol dm⁻³, DNB < 5×10^{-4} mol dm⁻³). In the laser flash photolysis experiments on the electron-transfer reactions, the concentration of DNB or triplet energy acceptors was adjusted so that the excitation light (266 nm) was absorbed predominantly by the bithiophenes.

Fluorescence spectra of bithiophenes

Steady-state fluorescence spectra, fluorescence quantum yields $(\Phi_{\rm F})$, and lifetimes $(\tau_{\rm F})$ are estimated as shown in Fig. 1 and Table 1. It has been reported that $\Phi_{\rm F}$ for the α -linked oligothiophenes tends to increase with the number of repeating units and becomes constant for larger oligomers than the pentamer: $\Phi_{\rm F}$ for BT was estimated to be 0.013, while that for sexithiophene is reported to be $0.40.1 \tau_F$ also increases with the size of the oligomer. Small $\Phi_{\rm F}$ can be attributed to effective spin-orbit coupling caused by the internal heavy atom effect of sulfur. For BT, the intersystem crossing process is reported to be the dominant deactivation process of the singlet excited state; the quantum yield for the triplet generation ($\Phi_{\rm T}$) is reported to be ca. 0.9.1 $\Phi_{\rm F}$ for the bridged bithiophenes is very small compared with that for BT (Table 1). In particular, that for DTP is very small: it was difficult to estimate an accurate fluorescence lifetime by the photon counting method because of the weak fluorescence. It is noteworthy that the $\Phi_{\rm F}$ for DTP

Table 1 Peak positions (λ_F) , lifetimes (τ_F) , and quantum yields (Φ_F) of fluorescence of bithiophene derivatives

	$\lambda_{\rm F}/{\rm nm}$	$ au_{ m F}/{ m ns}$	$\Phi_{\rm F}$ (in AN) ^a
BT	362	0.04	1.3×10^{-2}
CPDT	365	0.03	3.7×10^{-3}
DTT	333	b	1.0×10^{-3}
DTP	337	c	7.7×10^{-5}

^{*a*} $\Phi_{\rm F}$ values were estimated by using quinine sulfate in 1 mol dm⁻³ H₂SO₄ aq. as a reference. ^{*b*} $\tau_{\rm F}$ depends on the concentration of DTT (ref. 22). ^{*c*} $\tau_{\rm F}$ was difficult to estimate because of weak fluorescence.

depends largely on the solvent; 7.7×10^{-5} in acetonitrile (AN) compared with an estimated value of 2.7×10^{-4} in cyclohexane. The large difference between them indicates the existence of some photochemical reaction, which is discussed in the next section.

Triplet excited state of bithiophenes

Phosphorescence spectra of the bithiophenes were measured in MeOH/EtOH glass at 77 K (Fig. 2). While DTT, CPDT, and DTP show phosphorescence with clear vibrational structures, BT does not. This finding can be attributed to the rigid structure caused by the bridging group at the 3,3'-positions. The triplet energy of BT will be consumed by a non-radiative deactivation process, due to its flexible molecular structure. Triplet energies estimated from the 0–0 bands of the phosphorescence spectra are summarized in Table 2.

Fig. 3 shows a transient absorption spectrum of CPDT in AN obtained by the FHG laser irradiation. The absorption band at 380 nm can be attributed to the triplet excited state of CPDT (³CPDT*), because the transient absodrption band was quenched in the presence of triplet energy acceptors such as oxygen and β -carotene. The peak position and lifetime ($\tau_{\rm T}$) of ³CPDT* are similar to those of BT and DTT (Table 2).²²

In the case of DTP in AN, the solution was quite sensitive to the laser irradiation. The colourless solution became yellow after a few shots of the FHG laser pulse. Transient absorption was obtained as in Fig. 4. The absorption band at 440 nm appeared within the laser duration and did not decay. The solution after the photolysis experiment showed the same steady-state absorption as the transient spectrum (insert of Fig. 4), indicating generation of a photoproduct. From the GC-MS analysis of the coloured solution, the generation of an adduct of DTP with AN was confirmed.³⁶ As mentioned above, the $\Phi_{\rm F}$ for DTP is much smaller in AN than that in cyclohexane. The large difference in $\Phi_{\rm F}$ can be attributed to



Fig. 2 Phosphorescence spectra of bithiophenes in MeOH/EtOH at 77 K.



Fig. 3 Transient absorption spectrum of 1.0×10^{-3} mol dm⁻³ CPDT in AN at 100 ns after FHG laser irradiation. Insert: Absorption-time profile at 380 nm.

the addition reaction between DTP and AN, which occurred in the singlet excited state of DTP.

In order to observe an absorption band of ³DTP*, an energy-transfer reaction from a triplet energy donor to DTP was attempted. Here, benzophenone (BP) was adopted as the triplet energy donor because it has a sufficiently high triplet energy (2.97 eV) and $\Phi_{\rm T}$ (1.0).³⁷ Fig. 5 shows the transient absorption spectra of solutions containing DTP and BP in AN, obtained by the THG laser excitation which excites BP selectively. With decrease in the absorption band at 510 nm of ³BP*, a new absorption band appears at 400 nm with an increasing absorption-time profile (Insert of Fig. 5). The new absorption band can be attributed to ³DTP* generated by an energy-transfer reaction [eqn. (1)], while an absorption band at 520 nm, at 1 µs after the laser excitation, can be attributed to the BP ketyl radical.

$$BP \xrightarrow{h\nu(355 \text{ nm})} {}^{1}BP^{*} \xrightarrow{\text{isc}} {}^{3}BP^{*}$$

$$(1)$$

$${}^{3}BP^{*} + DTP \xrightarrow{k_{\text{ent}}(BP)} BP + {}^{3}DTP^{*}$$

The bimolecular rate constant of this reaction $[k_{ent}(BP)]$ was estimated to be $1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, from the relation



Fig. 4 Transient absorption spectrum of 1.0×10^{-3} mol dm⁻³ DTP in AN at 100 ns after FHG laser irradiation. Insert: Absorption spectra of DTP in AN before (· · ·) and after (—) laser irradiation.

Table 2 Properties of T-T absorption bands and reaction rates of bithiophene derivatives in triplet excited state

	Triplet energy ^a /eV	$\lambda_{\rm T}^{\ b}/{\rm nm}$	$\epsilon_{\rm T}^{\ b,c}/{\rm dm^3\ mol^{-1}\ cm^{-1}}$	$ au_{\mathrm{T}}{}^{b}/\mu\mathrm{s}$	$\frac{k_{\rm ent}(\beta c)^d}{/{\rm dm}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1}}$	$k_{ent}(BP)^b$ /dm ³ mol ⁻¹ s ⁻¹	$\frac{k_{\rm TT}}{\rm /dm^3 \ mol^{-1} \ s^{-1}}$
BT	2.1 ^e	374	2.1×10^{4}	26	9.5×10^{9}	1.2×10^{10}	1.2×10^{10}
CPDT	2.23	375	2.3×10^4	27	7.4×10^{9}	1.2×10^{10}	1.5×10^{10}
DTT	2.57	384	2.2×10^4	45	5.5×10^{9}	1.3×10^{10}	2.7×10^{10}
DTP	2.58	400	1.4×10^{4}	f	6.4×10^{9}	1.5×10^{10}	f

^{*a*} Estimated from 0–0 band of phosphorescence. ^{*b*} In acetonitrile. ^{*c*} Assuming ε of T–T absorption band of benzophenone to be 6.5 × 10³ dm³ mol⁻¹ cm⁻¹ at 520 nm (ref. 38). ^{*d*} In cyclohexane. ^{*e*} Estimated from energy-transfer reactions (Table 3). ^{*f*} The value was not obtained because of the photoinduced chemical reaction with the solvent (see text).

Fig. 5 Transient absorption spectra of AN solution containing 2×10^{-4} mol dm⁻³ DTP and 1.0×10^{-3} mol dm⁻³ BP at 100 ns (•) and 1.0 μ s (•) after THG laser irradiation. Insert: Absorption-time profiles at 400 and 510 nm.

between a pseudo-first order decay rate constant and the concentration of DTP. The population of the triplet energy of the other bithiophenes by the energy-transfer reaction from ³BP* [eqn. (1)] have been confirmed similarly. The estimated bimolecular rate constants are summarized in Table 2. The rate constants were quite similar to that of DTP, reflecting the diffusion-limited rate of the solvent, AN. The molar absorption coefficients (ε_T) of bithiophenes at the peak positions (λ_T) were estimated by using the ε_T of BP (6.5 × 10³ dm³ mol⁻¹ cm⁻¹ at 510 nm)³⁸ as a reference (Table 2). The estimated ε_T are ca. 2 × 10⁴ dm³ mol⁻¹ cm⁻¹, which are similar to the reported values for oligothiophenes.⁹

The T–T absorption bands of bithiophenes were quenched in the presence of triplet energy acceptors such as oxygen and β -carotene. Fig. 6 shows the transient absorption spectra observed in the reaction between ³CPDT* and β -carotene. In the case of the triplet energy transfer reaction from CPDT to β -carotene, generation of an absorption band of ³(β -carotene)* at 520 nm was confirmed, with decrease in ³CPDT* at 380 nm (Insert of Fig. 6). The rate constants of the present energytransfer reactions [$k_{ent}(\beta c)$] were also estimated as listed in Table 2. The diffusion-limited rate in cyclohexane is calculated to be 7×10^9 dm³ mol⁻¹ s⁻¹, which shows good correspondence with the estimated energy transfer rates.

As mentioned above, phosphorescence of BT was not observed. Here, in order to evaluate the triplet energy of BT, energy transfer from ³BT* to triplet energy acceptors was examined in cyclohexane. Table 3 summarizes the triplet energies of the acceptors and the observed reaction rates (k_{ent}). From the results in the Table, the triplet energy is considered to be 2.1 eV.

The triplet energy of BT is the smallest amongst the bithiophenes examined in this study. Recently, Di Césare *et al.* reported, in their theoretical study based on a semi-empirical MO method, that the triplet excited state of BT, which pos-



Fig. 6 Transient absorption spectra of cyclohexane solution containing 1.0×10^{-3} mol dm⁻³ CPDT and 3.0×10^{-5} mol dm⁻³ β -carotene at 250 ns (\bullet) and 2.5 μ s (\bigcirc) after FHG laser irradiation. Insert: Absorption-time profiles at 380 and 525 nm.

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 Table 3
 Energy transfer rates from ³BT* to energy acceptors

Energy acceptor	$E_{\rm T}$ of energy acceptor ^{<i>a</i>} /eV	$k_{\text{ent}}^{\ b}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
β-Carotene 1,4-Diphenylbutadiene Benz[a]anthracene Pyrene 9-Fluorenone Benzophenone ^d	0.91 1.83 2.04 2.10 2.19 2.97	$\begin{array}{l} 9.5 \times 10^9 \\ 5.1 \times 10^9 \\ 7.3 \times 10^9 \\ 3.9 \times 10^9 \\ \text{n.r.}^c \\ 1.2 \times 10^{10} \end{array}$

^{*a*} From ref. 37. ^{*b*} In cyclohexane. ^{*c*} No reaction. ^{*d*} Energy transfer from ³BP* to BT in AN.

sesses a biradical nature, has energy minima when the thiophene rings are in a perpendicular arrangement as well as when they are in a planar arrangement.²⁴ The flexible structure of BT will be favourable for lowering its triplet energy, while the other bridged bithiophenes cannot take more stable arrangements because of the rigid structures due to the bridging group.

The absorption-time profiles of the T-T absorption band of oligothiophenes deviated somewhat from a first-order decay function when the excitation laser power became high (Fig. 7 and insert). This deviation can be attributed to a T-T annihilation process [eqn. (2)].

$${}^{3}\mathrm{Th}^{*} + {}^{3}\mathrm{Th}^{*} \xrightarrow{k_{\mathrm{TT}}} {}^{1}\mathrm{Th}^{*} + \mathrm{Th}$$
(2)

where Th represents a bithiophene. Assuming that absorption of ${}^{3}Th^{*}$ regenerated *via* ${}^{1}Th^{*}$ in eqn. (2) is negligible, then the absorption-time profile of the T-T absorption can be analysed by the following equation:

$$\Delta A = \left\{ \left(\frac{1}{A_0} + \frac{k_{\rm TT}}{\varepsilon_{\rm T} k_{\rm T}} \right) \exp\left(k_{\rm T} t\right) - \frac{k_{\rm TT}}{\varepsilon_{\rm T} k_{\rm T}} \right\}^{-1}$$
(3)

where A_0 is the initial absorbance of the T–T absorption, k_T and k_{TT} are the first- and second-order decay rate constants, respectively. The rate constants for the T–T annihilation process indicate that the present deactivation process is diffusion controlled (Table 2).

Absorption spectra of radical cations

The generation of radical cations by γ -ray irradiation in a frozen matrix is a well established process whose reaction mechanism is shown below.³⁵

$$RX + \gamma \rightarrow RX^{+} + e^{-}$$

$$RX^{+} + Th \rightarrow RX + Th^{+}$$
(4)

where RX represents butyl chloride, used as a solvent in this study. In the previous report we applied this method to DTT and dithieno[3,4-b:3',4'-d]thiophene and confirmed the good correspondence with the absorption of radical cations observed in the photoinduced electron-transfer reaction.²²



Fig. 7 Absorption-time profiles at 380 nm of an AN solution containing 1.0×10^{-3} mol dm⁻³ CPDT. Insert: First-order plot.



Fig. 8 Absorption spectra of γ -irradiated butyl chloride solutions containing bithiophenes at 77 K.

The absorption spectra of radical cations of the bridged bithiophenes are shown in Fig. 8. The absorption spectra of these radical cations are quite similar to each other with a weak broad band at 550-600 nm and a sharp well structured band at 380-430 nm.

Electron-transfer reaction of bridged bithiophenes

Photo-illumination of the solution containing thiophene derivatives and an appropriate electron acceptor results in an electron-transfer reaction which generates the radical cation of the thiophene derivatives.^{9–11,18–20,22} In the present report, *o*-, *m*-, and *p*-DNB have been used as electron acceptors. Based on their reduction potentials (-0.81, -0.90, -0.69 V vs. SCE for *o*-, *m*-, *p*-DNB, respectively),³⁹ Gibbs energy changes for the electron-transfer reactions (ΔG) were estimated using the Rehm–Weller equation [eqn. (5), Table 4]:⁴⁰

$$\Delta G(\text{kJ mol}^{-1}) = 96.49[E(\text{D}^{+}/\text{D}) - E(\text{A}/\text{A}^{-}) - \Delta E_{0.0} - e_0^2/ae]$$
(5)

where $E(D^{+}/D)$ is the oxidation potential of the bithiophene derivative,⁴¹ $E(A/A^{-})$ is the reduction potential of the acceptor, $\Delta E_{0,0}$ is the excitation energy of the bithiophene, and e_0^2/ae is the Coulombic term (0.06 eV for AN).⁴⁰ A wide variety of negative ΔG were expected by combining dinitrobenzenes and bithiophenes, for which $E(D^{+}/D)$ depends on the electronic nature of a bridging group.

In the transient absorption spectra of an AN solution containing CPDT and p-DNB (Fig. 9), the generation of new

 Table 4
 Oxidation potentials of bithiophene derivatives and Gibbs

 energy changes for the electron-transfer reactions with dinitrobenzenes
 benzenes

	E(D):+/D)/	$\Delta G^b/\mathrm{kJ}~\mathrm{mol}^{-1}$			
	/V vs. SCE	p-DNB	o-DNB	m-DNB	
BT	1.09	-39.7	-25.1	-16.4	
CPDT	0.98	- 59.8	-48.3	-39.6	
DTT	1.07	-83.9	-72.4	-63.7	
DTP	0.75	-115.8	-104.2	-95.5	

^{*a*} Onset potential of electropolymerizations. ^{*b*} 0.06 eV of Coulombic term was employed.



Fig. 9 Transient absorption spectra of AN solution containing 1.0×10^{-3} mol dm⁻³ CPDT and 1×10^{-4} mol dm⁻³ *p*-DNB at 250 ns (\bullet) and 2.5 μ s (\bigcirc) after FHG laser irradiation. Insert: Absorption-time profiles at 930, 400 and 380 nm.

absorption bands at 930, 550, and 400 nm was confirmed with a decrease in the band at 380 nm due to ³CPDT*. The absorption band at 930 nm can be attributed to the radical anion of p-DNB (p-DNB^{•-}).³⁵ The bands at 550 and 400 nm are assigned to the radical cation of CPDT (CPDT⁺), which show good correspondence with those observed in the γ -ray radiolysis experiment (Fig. 8). Absorption-time profiles at 930, 400, and 380 nm are shown in the insert of Fig. 9. The time profile at 930 nm does not show fast radical generation within the laser duration, indicating that any contribution of ¹CPDT* to the electron-transfer reaction will be negligible under the present experimental conditions, p-DNB $< 5 \times 10^{-4}$ mol dm⁻³. The rising absorption-time profile at 930 nm shows good correspondence with the decay of the ³CPDT*. These findings indicate the generation of radical ions by an electron-transfer reaction via ³CPDT*, i.e.

³CPDT* + *p*-DNB
$$\xrightarrow{k_q}$$
 CPDT'+ + *p*-DNB'⁻ (6)

The absorption–time profile at 930 nm can be analysed by a first-order rise function [eqn. (7)],

$$\Delta A = A_0 [1 - \exp\left(-k_{\text{obs}} t\right)] \tag{7}$$

where it is assumed that the generation rate of radical ions (k_{obs}) is much larger than the decay rate of the generated radical ions. From the dependence of k_{obs} on the concentration of *p*-DNB, the bimolecular rate constant for the quenching of ³CPDT* (k_q^T) was estimated to be 2.0×10^{10} dm³ mol⁻¹ s⁻¹. The quenching rate constant at the diffusion limit of the solvent is reasonable for a reaction where the Gibbs energy change is estimated from eqn. (5) to be -59.8 kJ mol⁻¹. The molar absorption coefficient for CPDT⁺ at 400 nm was estimated to be 1.2×10^4 dm³ mol⁻¹ cm⁻¹, from comparison with the absorbance of *p*DNB⁻ at 930 nm. The estimated molar absorption coefficient of CPDT⁺⁺ was similar to those of BT⁺⁺ and DTT⁺⁺ (Table 5).

Upon 266 nm laser irradiation of a cyclohexane solution containig CPDT and *p*-DNB, the absorption bands which indicate electron-transfer reactions were not observed, while the decay of ³CPDT* was accelerated. After decay of ³CPDT*, an absorption band due to ³(*p*-DNB)* was observed at a shorter wavelength than 350 nm. Thus, the decay of ³CPDT* can be attributed to triplet-energy transfer to *p*-DNB; radical ion formation is not preferential in a nonpolar solvent. Similar energy transfer was observed in a cyclohexane solution containing DTT and *p*-DNB.²² The bimolecular rate constant for the present energy transfer reaction was estimated to be 8.6×10^9 dm³ mol⁻¹ s⁻¹, indicating a diffusion-controlled process.

When an AN solution containing DTP and *p*-DNB was irradiated with the FHG laser, generation of p-DNB⁻⁻ was observed in the transient absorption spectra, in addition to an

Table 5 Peak positions (λ_{max}) and molar absorption coefficients (ε) of cation radicals of bithiophene derivatives and reaction rates $(k_q^T \text{ and } k_{bet})$ with *o*-, *m*-, and *p*-DNB

			$k_{\mathbf{q}}^{\mathrm{T}}/\mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$			$k_{\text{bet}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		
	$\lambda_{\rm max}/{\rm nm}$	$\epsilon^a/dm^3 mol^{-1} cm^{-1}$	p-DNB	o-DNB	<i>m</i> -DNB	p-DNB	o-DNB	<i>m</i> -DNB
BT CPDT DDT DTP	417, 600 395, 560 406, 586 – ^c	$8.8 \times 10^{3} \\ 1.2 \times 10^{4} \\ 6.5 \times 10^{3} \\ - c$	$\begin{array}{c} 1.5 \times 10^{10} \\ 2.0 \times 10^{10} \\ 2.4 \times 10^{10} \\ ca. \ 10^{10} \ d \end{array}$	2.6×10^9 1.6×10^{10} 9.2×10^9 _ c	$\begin{array}{c} 2.5 \times 10^{9} \\ 1.5 \times 10^{10} \\ 9.3 \times 10^{9} \\ - \begin{array}{c} c \end{array}$	$\begin{array}{c} 8.4 \times 10^9 \\ 1.3 \times 10^{10} \\ 1.1 \times 10^{10} \\ - c \end{array}$	$3.8 \times 10^{10} \\ 2.4 \times 10^{10} \\ 3.3 \times 10^{10} \\ - c$	$\frac{_^{b}}{3.2 \times 10^{10}}$ 8.5 × 10 ⁹ $_^{c}$

^{*a*} ε values at peaks around 400 nm were estimated from ε of *p*-DNB⁻⁻ (5.9 × 10³ dm³ mol⁻¹ s⁻¹ at 930 nm, see ref. 22). ^{*b*} k_{bet} was difficult to estimate because of small ΔA . ^{*c*} Radical cation and reaction rates were not obtained from transient spectra because of large ΔA of photoreaction product of DTP and AN. ^{*d*} The rate was estimated from the absorption band of *p*-DNB⁻⁻ at 930 nm.

addition reaction between excited DTP and AN, which shows an absorption band at 450 nm (Fig. 10). The rate for the quenching of ³DTP* by *p*-DNB can be estimated to be *ca*. 10^{10} dm³ mol⁻¹ s⁻¹ from the absorption-time profile at 930 nm (insert of Fig. 10).

When o-DNB or *m*-DNB was used as an acceptor for the electron-transfer reaction, generation of radical cations of bithiophenes was similarly confirmed in the transient absorption spectra (Fig. 11). The rate constants for reaction between bithiophenes in the triplet state and an electron acceptor are summarized in Table 5. While k_q^T for CPDT and DTT were close to the diffusion-limited rate, those of BT were *ca.* (2–3) × 10⁹ dm³ mol⁻¹ s⁻¹ (Table 5). In the case of *m*-DNB, the quantum yield for the generation of BT⁺ was *ca.* 1/20 of that for *p*-DNB. Therefore, the rate constant for the electron-transfer reaction (k_{el}) between ³BT* and *m*-DNB will be *ca.* 10⁸ dm³ mol⁻¹ s⁻¹. Similarly, k_{et} for the reaction between ³BT* and *o*-DNB was *ca.* 1 × 10⁹ dm³ mol⁻¹ s⁻¹. The small k_q^T and k_{et} can be attributed to the small Gibbs energy changes for the reactions (Table 4). The observed ΔG dependence of k_{et} is in accord with the semi-empirical equation of Rehm–Weller.⁴⁰

The absorption bands of the generated radical ions decay after reaching a maximum (Insert of Fig. 12). For the decay mechanism of the radical cation, a back electron-transfer reaction [eqn. (8)], a coupling reaction between cation radicals [CR-CR, eqn. (9)], and that of cation radical and neutral substrate [CR-S, eqn. (10)] are expected.

$$CPDT^{+} + p\text{-}DNB^{-} \xrightarrow{k_{bet}} CPDT + p\text{-}DNB \quad (8)$$

$$CPDT^{+} + CPDT^{+} \xrightarrow{k_{dim}(CR-CR)} (CPDT)_2^{2+}$$
(9)

$$CPDT^{+} + CPDT \xrightarrow{k_{dim}(CR-S)} (CPDT)_2^{+}$$
(10)

The first two processes obey a second-order decay function while the third is of first order. As shown in Fig. 12, the time profile of CPDT⁺⁺ obeys a second-order decay function over the examined timescale and does not depend on the concentration of CPDT, indicating a negligible contribution from



Fig. 10 Transient absorption spectra of AN solution containing 1.0×10^{-3} mol dm⁻³ DTP and 2×10^{-4} mol dm⁻³ *p*-DNB at 100 ns (\bullet) and 1.0 µs (\bigcirc) after FHG laser irradiation. Insert: Absorption-time profiles at 920 and 460 nm.

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eqn. (10); the upper limit of $k_{dim}(CR-S)$ will be *ca*. 10⁶ dm³ mol⁻¹ s⁻¹. Since the absorption band which can be attributed to the products of radical coupling reaction was not observed in either the transient or steady-state absorption spectra after laser experiments, the contribution of eqn. (9) will also be



Fig. 11 Transient absorption spectra of AN solutions containing BT and (a) *p*-DNB, (b) *o*-DNB, and (c) *m*-DNB at 250 ns (\bigcirc) and 2.5 µs (\bigcirc) after FHG laser irradiation. Concentrations of BT and DNB are 1.0×10^{-3} and 1.0×10^{-4} mol dm⁻³, respectively.



Fig. 12 Second-order plot of an absorption-time profile at 410 nm of AN solution containing 1.0×10^{-3} mol dm⁻³ CPDT and 1.0×10^{-4} mol dm⁻³ *p*-DNB. Insert: Absorption-time profile at 410 nm.

minor under the present experimental conditions. Thus, the generated radical ions are considered to decay mainly according to a back electron-transfer reaction. From the slope of the second-order plot of the absorption-time profile at 400 nm, $k_{\rm bet}/\epsilon$ was estimated to be 1.1×10^6 cm s⁻¹. Employing the molar absorption coefficient of CPDT⁺ (Table 5), $k_{\rm bet}$ was estimated to be 1.3×10^{10} dm³ mol⁻¹ s⁻¹. The back-electron-transfer reaction rates were estimated for other bithiophenes, as summarized in Table 5. In each case, the generated radical ions return to the neutral form at the diffusion limited rate.

Conclusion

The photophysical properties and photoinduced reactions of bridged bithiophenes were investigated using nanosecond laser flash photolysis. Photoinduced electron-transfer reactions proceed *via* triplet states of bithiophenes under the present experimental conditions (bithiophenes 1.0×10^{-3} mol dm⁻³, acceptors $< 5 \times 10^{-4}$ mol dm⁻³). The reaction rates depend on the Gibbs energy changes estimated by the Rehm–Weller equation. The different reactivities of the bithiophenes reflect the electron-donor ability at each, which is an important characteristic in their application in conducting charge-transfer complexes and as monomers for conducting polymers. The generated radical ions decay mainly by back electron-transfer reactions.

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