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Photoinduced electron transfer reactions of highly twisted 1-donor-substituted 2,4,6-triphenylpyridinium cations

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Abstract

Primary processes of photoelectron transfer reactions of highly twisted 1-mesityl- (**1a**), 1-(2,5-dimethoxyphenyl)- (**1b**), and 1-(2,3,5,6-tetramethoxyphenyl)- 2,4,6-triphenylpyridinium (**1c**) tetrafluoroborates in butyronitrile were investigated. The charge-shift states were observed in all cases. Irradiation of **1a** generated the charge-shift state (360, 475, and 550 nm), which was converted with a lifetime of 21 ns into the long-lived triplet state ($\tau = 2.2\ \mu s$) localized on the pyridinium moiety. On the other hand, compounds **1b** and **1c** generated the charge-shift states ($\lambda_{max} = 440$ and 540 and $\lambda_{max} =$ ca. 550 nm as a broad absorption) of short lifetimes, 35 and 16 ps, respectively, decaying exclusively to the singlet ground states.

Keywords: Photochemistry; Electron transfer; Triphenylpyridinium

1. Introduction

There has been considerable attention paid to the photoinduced electron transfer reactions of short-linked D–A systems, especially on the time-scale of the charge-separated or charge-shift states [1]. Most successful approach is based on the utilization of the spin-forbidden process in charge recombination, which places the radical ion pairs in different spin-multiplicity (e.g., triplet) from the ground state (usually singlet). There are a few such molecular systems that show charge-separated states with relatively long lifetime of a microsecond order [1,2].

However, surprisingly simple approach using Marcus inverted region effect in a highly twisted D–A system has recently reported by Fukuzumi and coworkers. They reported a remarkably long-lived charge-shift state (98% yield with $\tau > 1000$ s at 223 K in frozen PhCN) of 9-mesityl-10-methylacridinium [3]. Shortly after this report, Harriman and coworkers reported that the lifetime of the charge-shift state of the same species in the same solvent is as short as 6 ns and that there is no spectroscopic evidence to indicate the presence of an unusually long-lived charge-shift state [4].

In related studies, it has been established that 9-aryl-10-methylacridinium derivatives have a low-lying locally excited (LE) triplet state ($E_T = 1.9$ eV) due to the acridinium chromophore. The charge-shift state decays to this LE triplet state, which has a lifetime of 30 μs for 9-mesityl-10-methylacridinium [4,5].

In principle, the lowest triplet charge-shift state for such a highly twisted D–A system, if generated, may have a lifetime of the order of microsecond or longer. Accepting 6 ns as a lifetime of the charge-shift state of 9-mesityl-10-methylacridinium, an important question remains; how the lifetime is expanded when the low-lying LE triplet state is eliminated. Hitherto, reports on the photoelectron-transfer reactions of highly twisted (directly combined) D–A systems are sparse [6]. We envisioned that replacing acridinium by a pyridinium chromophore should place the local triplet state at a higher energy level than the charge-shift state for suitable donors. The orthogonal relationship between D and A chromophores in 9-mesityl-10-methylacridinium is important and must be retained, because the S–T energy gap [7] as well as the rate of intersystem crossing [8] in such a highly

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twisted charge-shift states are likely to be strongly affected by this torsion angle. We report photoinduced electron transfer reactions of 2,4,6-triphenylpyridinium derivatives **1a**–**1c**.

2. Experimental

2.1. Materials

Compounds **1a** and **1d** were prepared according to the Katritzky procedure using 2,4,6-triphenylpyrylium salt [9]. Synthesis of **1b** and **1c** were carried out with slight modification as described below. 2,3,5,6-Tetramethoxyaniline **3**, a key intermediate for the synthesis of **1c**, was prepared through azide **2** according to Scheme 1.

2.1.1. Synthesis of 1b

A solution of 2,4,6-triphenylpyrylium tetrafluoroborate (**4**) (570 mg) and 2,5-dimethoxyaniline (306 mg) in dichloroethane was refluxed with stirring overnight under nitrogen. After cooling the reaction mixture, a small amount of ethanol and an excess amount of ether were added. By cooling the reaction mixture at 0 °C, precipitates appeared. The precipitates were collected by filtration and recrystallized by methanol–ether, to give pale cream-colored needles (550 mg, 72%). **1b**: mp 215 °C, ^{1}H NMR (400 MHz, DMSO–d_6) δ 8.69 (s, 2H), 8.36 (d, $J = 8.8$ Hz, 2H), 7.72–7.64 (m, 3H), 7.46–7.40 (m, 10H), 7.22 (s, 1H) 6.80 (s-like, 2H), 3.54 (s, 3H), 3.50 (s, 3H), MS (FAB$^+$) *m/z* 444.0, IR (KBr) 3061, 2841, 1624, 1555, 1510, 1447, 1416, 1283, 1236, 1040, 897, 764, 698 cm^{-1}. Anal. Calcd for $C_{31}H_{26}BF_4NO_2$: C 70.07, H 4.93, N 2.64, found: C 70.12, H 4.89, N 2.63.

2.1.2. Synthesis of azide 2

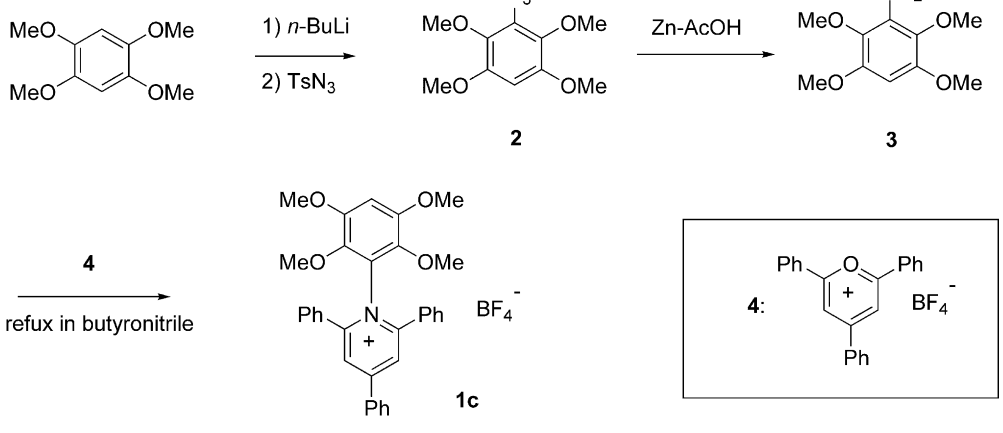
To a stirred solution of 1,2,4,5-tetramethoxy benzene (2.75 g) in dry THF (50 mL) was slowly added *n*-butyllithium in hexane (9.3 mL, 1.57 M) via a syringe at 0 °C. The mixture was stirred for 30 min at room temperature. To this solution, a solution of tosylazide (4.65 g) in 40 mL dry THF was slowly added at 0 °C and the mixture was stirred at room temperature for 1 h. The solvent was removed to the half volume under reduced pressure and diluted by adding water (100 mL). The mixture was extracted by toluene and the organic layer was dried over sodium sulfate. After filtration and evaporation of the solvent, the crude products were subjected to the silica gel chromatography (benzene:ethyl acetate = 30:1, v/v) to give almost pure **2**, which was recrystallized from hexane to give pale yellow crystals (2.10 g, 63% yield), **2**: mp 53 °C, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.32 (s, 1H), 3.85 (s, 6H), 3.82 (s, 6H), MS (FAB$^+$) *m/z* 239.07, IR 2999, 2941, 2844, 2104, 1589, 1502, 1472, 1423, 1361, 1225, 1203, 1063, 966, 877 cm^{-1}. Anal. Calcd for $C_{10}H_{13}N_3O_4$: C 50.21, H 5.48, N 17.56, found: C 50.28, H 5.53, N 17.54.

2.1.3. Synthesis of 3

Zinc dust (7.02 g) was added in five portions into the stirred solution containing **2** (2.06 g) in acetic acid (15 mL) at 10 °C. The mixture was stirred for further 10 min at 10 °C. Then, the zinc dust was removed by filtration. The filtrate was neutralized by adding sodium hydroxide solution (5 M) under cooling and extracted by toluene. The toluene layer was washed by water and dried over sodium sulfate. After evaporation of the solvent, the mixture was subjected to silica gel chromatography (eluent, toluene:ethyl acetate = 5:1) to give almost pure **3**, which was recrystallized from hexane to give colorless crystals (1.70 g, 93%), **3**: mp 82 °C, ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.95 (s, 1H), 4.00 (brs, 2H), 3.83 (s, 6H), 3.79 (s, 6H), MS (FAB$^+$) *m/z* 213.09, IR (KBr) 3443, 3348, 2970, 2937, 2825, 1616, 1506, 1473, 1429, 1350, 1224, 1120, 1030, 841 cm^{-1}. Anal. Calcd for $C_{10}H_{15}NO_4$: C 56.33, H 7.09, N 6.57, found: C 56.36, H 7.12, N 6.50.

2.1.4. Synthesis of 1c

A mixture of **3** (370 mg) and 2,4,6-triphenylpyrylium tetrafluoroborate (**4**) (453 mg) in butyronitrile (30 mL) was refluxed for 2 days under nitrogen. After cooling, a small amount of ethanol and an excess amount of ether were added into the mixture. By cooling the reaction mixture and scratching the inner wall of the reaction flask by a spatula at 0 °C, precipitates formed. The precipitates were collected by filtration and recrystallized by methanol–ether, to give pale yellow needles (580 mg, 86%). **1c**: mp 291 °C, ^{1}H NMR (400 MHz, DMSO–d_6) δ 8.72 (s, 2H), 8.37



Scheme 1.

(d, $J = 7.1$ Hz, 2H), 7.74–7.65 (m, 3H), 7.55–7.44 (m, 10H), 6.84 (s, 1H), 3.71 (s, 6H), 3.54 (s, 6H), MS (FAB$^+$) *m*/*z* 504, IR (KBr) 2989, 2945, 2360, 1618, 1545, 1508, 1445, 1413, 1354, 1238, 1155, 1062, 959, 760 cm^{-1}. Anal. Cacld for $C_{33}H_{30}BF_4NO_4$: C 67.02, H 5.11, N 2.37, found: C 67.05, H 5.09, N 2.41.

2.2. *Crystal structure analysis of* ***1c***

Colorless crystals suitable for X-ray analysis were obtained by slow recrystallization from methanol–ether. Crystallographic data for **1c** ($C_{33}H_{30}BF_4NO_4$); FW = 591.41, monoclinic, space group *C*2/*c* (#15), $a = 10.940(3)$, $b = 23.090(7)$, $c = 11.703(3)$ Å, $\beta = 89.754(6)°$, $V = 2956.4(15)$ Å^3, $Z = 4$, $T = 113$ K, unique reflections 3331, observation 2101 ($I > 2.0\sigma(I)$), $R_1 = 0.071$, $R_W = 0.080$ ($I > 2\sigma(I)$), CCDC 633716. The observed torsion angle (83° for **1c**) was in good agreement with the calculated torsion angles (76.0°, 73.1°, and 84.8° using TURBOMOLE (RI-DFT) [10] for **1a**, **1b** and **1c**, respectively).

2.3. *Molecular orbital calculation of* ***1a–1c***

The molecular orbital calculations (TD-DFT/6-31G*) for the excited state **1a–1c** were carried out using Gaussian 03 program package at their ground state geometries. The geometry optimization was carried out using TURBOMOLE (RI-DFT) [10].

2.4. *Laser-flash photolysis of* ***1a–1d***

Nanosecond time-resolved difference spectra were obtained by using the third harmonic of a Q-switched Nd^{3+}:YAG laser (Continuum Surelite I-10, $\lambda = 355$ nm) [11]. A sample solution in a 1 cm-quartz cell were deaerated by bubbling with argon for 5 min. White light from a Xe-arc lamp was used for acquisition of absorption spectra of species. For measurements of picosecond time-resolved difference spectra, a sample solution in a quartz cell (2 mm length) was excited with the third harmonic pulses of a mode-locked Nd^{3+}:YAG laser (Continuum PY61C-10) [12]. The transient absorption spectra in the time range from 10 ps to 6 ns were acquired by using continuum pulses generated by focusing the fundamental laser pulse into a flowing H_2O/D_2O mixture (1:1, v/v).

3. Results and discussion

3.1. *Ground state structure*

Fig. 1 shows a molecular structure of **1c** determined by X-ray structure analysis. The torsion angle between the tetramethoxy benzene and pyridinium rings was determined as 83°. The observed torsion angle was in good agreement with the calculated torsion angle (76.0°, 73.1°, and 84.8° for **1a**, **1b** and **1c**, respectively). These nearly perpendicular geometries minimize the electronic interaction between the donor (mesityl or methoxy phenyl rings) and the acceptor (pyridinium ring) in the ground states.

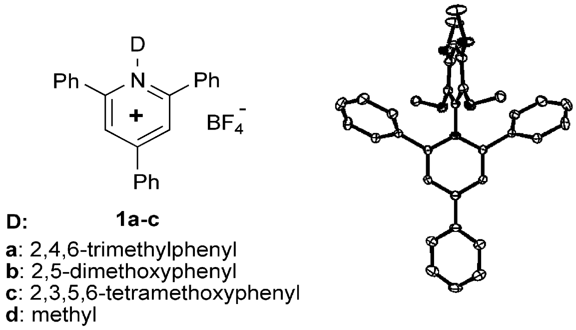


Fig. 1. Structure of **1a**–**1d** and ORTEP drawing at 50% ellipsoids level for **1c**; the dihedral angle between tetramethoxy benzene and pyridinium ring is 83°. The counter anion BF_4^- is omitted for clarity.

3.2. *Spectral properties of* ***1a–1d***

Because of the large torsion angles between the donor (mesityl and methoxyphenyl) and the acceptor (pyridinium) rings, the charge-transfer bands from the donor to the acceptor orbitals should appear in low intensities. In fact, compounds **1a–1c** and reference compound **1d** showed a similar absorption maximum around 310 nm with a molar absorptivity of ca. 30,000 in butyronitrile (SI), which can be assigned to π–π* absorptions [13]. Interestingly, a weak absorption extending to 440 nm was observed as a tail of the π–π* absorption for **1b** (Fig. 2), although such an absorption was not observed for 1-(di-*ortho*-substituted phenyl) derivatives, **1a** and **1c**. The observed weak and broad absorption for **1b** can be assigned as an intramolecular CT-band due to the transition from the donor part to the pyridinium moiety. The observation of the CT-band for **1b** suggests that similar but much weaker CT-bands for **1a** and **1c** are hidden in the tail of the strong π–π* absorption of the pyridinium moiety. This consideration is supported by the TD-DFT calculation for these compounds (SI), where the lowest singlet excited states include mainly HOMO (donor orbital) → LUMO (acceptor orbital) transition. It should be noted that the CT-band for **1b** allows rough estimation of the reorganization energy λ of the back charge-shift process for the present system by applying Hush's relation that the CT-band (E_{opt}) is expressed as a summation of the reorganization energy and the 0–0 transition energy [14]. The latter corresponds to the driving force of the

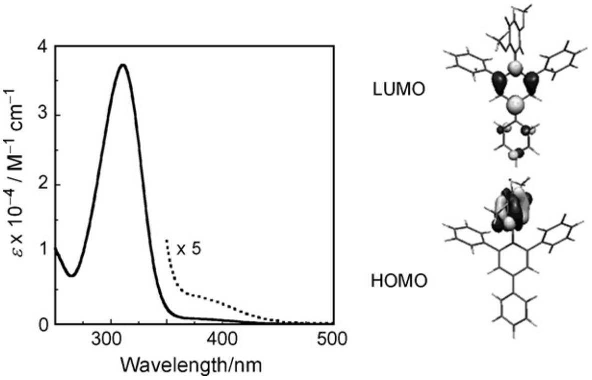


Fig. 2. UV–vis absorption of **1b** in butyronitrile and the frontier molecular orbitals.

Table 1
Photophysical properties of **1a**–**1d** in butyronitrile

Compound	Abs (λ_{max})[a] (nm)	Flu (λ_{max})[b] (nm)	Phos (0–0 band)[c] (nm)	E_S[d] (eV)	E_T[e] (eV)
1a	314	470	448	3.52	2.77
1b	310	–	–	3.58	–
1c	310	–	–	3.54	–
1d	304	433	445	3.64	2.79

[a] Absorption maximum.
[b] Fluorescence maximum.
[c] Phosphorescence 0–0 band.
[d] Singlet energy estimated by the absorption edge at the 1/10 height of the maximal height of the π–π* absorption.
[e] Triplet energy of the local pyridinium cation moiety estimated from the 0–0 band of the phosphorescence measured at 77 K.

Table 2
Redox potentials and free energy changes for the charge-shift (ΔG_{CS}) and back charge-shift (ΔG_{BCS}) processes of **1a**–**1d** in butyronitrile

Compound	E_{red}[a] (V)	E_{ox}[a] (V)	ΔG_{CS}[b] (eV)	ΔG_{BCS}[c] (eV)
1a	−1.39	>+2.0	>−0.13	<−3.39
1b	−1.42	+1.24	−0.92	−2.66
1c	−1.41	+0.85	−1.28	−2.26
1d	−1.45	>+2.0	–	–

[a] vs. Fc/Fc$^+$ using a glassy carbon as a working electrode with sweep rate 100 mV/s in the presence of tetrabutylammonium hexafluorophosphate.
[b] Free energy change for the photoinduced electron transfer (singlet state) calculated using the Rehm-Weller equation with neglect of the coulombic term.
[c] Free energy change for the back charge-shift reaction of the charge-shift state.

back electron transfer process and can be estimated from the electrochemical data [$-\Delta G_{BCS} = (E_{ox} - E_{red}) = 2.66$ eV for **1b**, see Table 2]. Then, the reorganization energy can be estimated as 0.78 eV from the charge-transfer band (E_{opt} = ca. 360 nm (3.44 eV) for **1b**).

The singlet energies (E_S) of the LE singlet states for these compounds are estimated from the absorption edge (Table 1). The model compound **1d** and the mesityl derivative **1a** showed fluorescence at $\lambda_{max} = 433$ and 470 nm, respectively, with a large Stokes-shift due to the conformational relaxation in the excited state of 2,4,6-triphenylpyridinium structure [13]. The methoxy-substituted derivatives **1b** and **1c** showed virtually no fluorescence, probably because of the efficient intramolecular electron transfer in the singlet states. Furthermore, compounds **1d** and **1a** showed similar phosphorescence in butyronitrile glass at 77 K, whose 0–0 band was located at 445 nm ($E_T = 2.79$ eV) with a vibronic structure spacing of 1420 cm^{-1} for **1d**, and 448 nm ($E_T = 2.77$ eV) with a spacing of 1400 cm^{-1} for **1a** (SI). The similarity of the phosphorescence spectra between these compounds indicates that the phosphorescence is originated from the LE triplet on the pyridinium chromophore. On the other hand, **1b** and **1c** did not show appreciable phosphorescence, suggesting that the triplet charge-shift states are lower in energy than the LE triplet states. Photophysical properties including LE singlet and triplet energies of these compounds are summarized in Table 1.

3.3. Redox potentials and free energy change in photoelectron transfer and back electron transfer reactions of *1a–1c*

Compounds **1a**–**1d** showed reversible reduction waves at ca. −1.4 V vs. Fc/Fc$^+$, which are attributed to the reduction of pyridinium cations [15]. The reversible oxidation waves were observed for **1b** and **1c**. The oxidation potential of **1a** could not be precisely determined because of the competing oxidations of the other phenyl groups. The redox potentials are summarized in Table 2 along with the free energy change for the formation of charge-shift states from the LE singlet states (ΔG_{CS}) and that for the back charge-shift process resulting in the singlet ground state (ΔG_{BCS}).

From these tables, the following energy-profile is apparent: (1) the free energy change from the LE singlet state to the charge-shift state is small for **1a**, and exothermic for **1b** and **1c**, (2) the process of the back charge-shift giving the singlet ground state is highly exothermic for **1a**–**1c**, and (3) the charge-shift state for **1a** has enough energy to produce the LE triplet state on the pyridinium chromophore, but the process is endothermic for **1b** and **1c**.

3.4. Laser-flash photolysis of *1a–1c*

Irradiation of a deaerated butyronitrile solution of **1a** with a picosecond laser pulse (355 nm, FWHM: 17 ps) and a nanosecond pulse (355 nm, FWHM: 4 ns) gave the transient spectra shown in Fig. 3.[1] After the picosecond pulse excitation, weak absorptions appeared around 475 and 550 nm with a time constant of ca. 15 ps (Fig. 3A).[2] They were slowly converted to the species with a 460 nm absorption (Fig. 3B) within 100 ns ($\tau = 21$ ns). The 460 nm species decayed much slowly with a lifetime of 2.2 μs.

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[1] During the laser-photolysis, appreciable decomposition of the starting materials **1a**–**1c** was not observed as confirmed by measurement of the absorption spectra and TLC of the photolysates.

[2] The time constant was determined by numerical simulation with the convolution of the instrumental function.

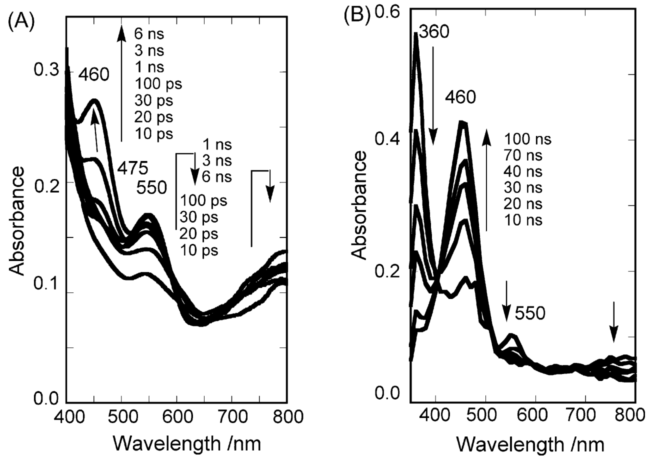

Fig. 3. Transient absorption spectra of **1a** ([**1a**] = 5.89 × 10^{-4} M and 2.45 × 10^{-4} M for A and B, respectively) in deaerated butyronitrile at 298 K taken 10, 20, 30, 100 ps, 1, 3, 6 ns after a 355 nm laser pulse (FWHM: 17 ps, A) and 10, 20, 30, 40, 70, 100 ns after a 355 nm laser pulse (FWHM: 4 ns, B).

In control experiments, similar excitation of the model compound **1d** afforded a relatively long-lived excited singlet state with a strong induced emission around 485 nm (SI). The excited singlet state decayed with a time constant of $\tau = 1.3$ ns to the LE triplet (460 nm with $\tau = 1.8$ μs, SI), that has an identical spectral pattern with that observed for the photolysis of **1a**, demonstrating that the 460 nm species generated from **1a** (Fig. 3) is due to the LE triplet state on the pyridinium moiety.

The initial species (360 nm in Fig. 3B, 475 and 550 nm in Fig. 3A, 20 ps to 3 ns) is thought to be a precursor of the LE triplet (460 nm). The absorptions at 360 and 550 nm can be assigned to those of a pyridinyl radical (λ_{max} 357 nm and 585 nm in CH_2Cl_2, electrochemically generated from **1a**, SI). The weak 475 nm absorption shows good agreement with the reported value of the mesitylene radical cation (λ_{max} 470 nm in CH_2Cl_2 [16], 475 nm in CH_3CN [4b]). The origin of broad absorption around 800 nm (Fig. 3) is not clear. Neither mesityl radical cation nor the pyridinyl radical exhibit the strong absorptions, although pyridinyl radicals show a weak absorption in this region (SI). The absorption may be ascribed to the electronic interaction within the radical ion pair.

The rate constant for the formation of the LE triplet (460 nm) was identical with the decay of the 360 nm species within experimental error ($\tau = 20$–25 ns). Furthermore, the lifetime of the charge-shift state was identical with that of the fluorescence ($\tau = 20$ ns) of **1a**, indicating that the singlet charge-shift state is an emissive state [4b].

These results are consistent with the following mechanisms for the formation of the LE triplet: (1) a pathway involving the intersystem crossing within the charge-shift state followed by rapid back electron transfer to give the LE triplet state ($^1CS \rightarrow {}^3CS \rightarrow {}^3LE$) [5], (2) direct electron transfer from the singlet charge-shift state to the LE triplet state ($^1CS \rightarrow {}^3LE$), by the spin–orbit coupling of the nitrogen *p*-orbitals involved in the orbitals of the pyridinium and phenyl moieties with perpendicular orientation [5,17], and (3) another route involving the intersystem crossing of the thermally populated LE singlet state, which is formed from the singlet charge-shift state, is operative because of the small energy gap of ΔG_{CS} for **1a** ($^1CS \rightleftharpoons {}^1LE \rightarrow {}^3LE$). Differentiation of these mechanisms is difficult at present.

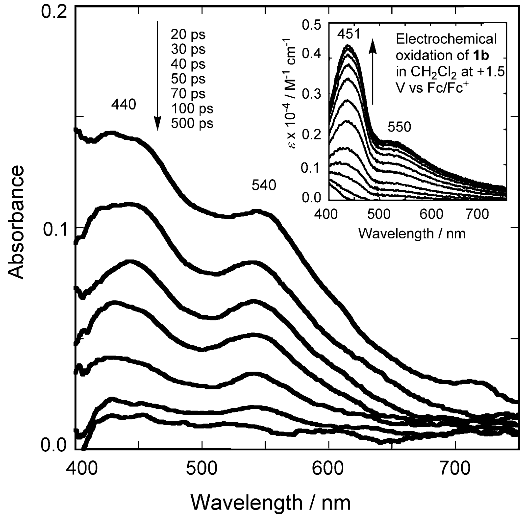

Fig. 4. Transient absorption spectra of **1b** ([**1b**] = 8.15 × 10^{-4} M) in deaerated butyronitrile at 298 K taken 20, 30, 40, 50, 70, 100, 500 ps after a 355 nm laser pulse (FWHM: 17 ps). Inset is a spectral change with rough estimation of the molar absorptivity during the electrochemical oxidation of **1b** in CH_2Cl_2.

Excitation of **1b** with a picosecond pulse showed broad absorptions with maxima at 440 and 540 nm (Fig. 4) (see footnote 1). They decayed with $\tau = 35$ ps. The observed absorptions are assigned to the charge-shift state by comparing them with the absorption of **1b** radical cation generated by the electrochemical method (451, 550 nm (sh) in CH_2Cl_2, inset in Fig. 4) and the pyridinyl radical (λ_{max}: 550 nm in Fig. 3).

Similar results were obtained in the photolysis of **1c** (Fig. 5) (see footnote 1). The transient species had a broad absorption

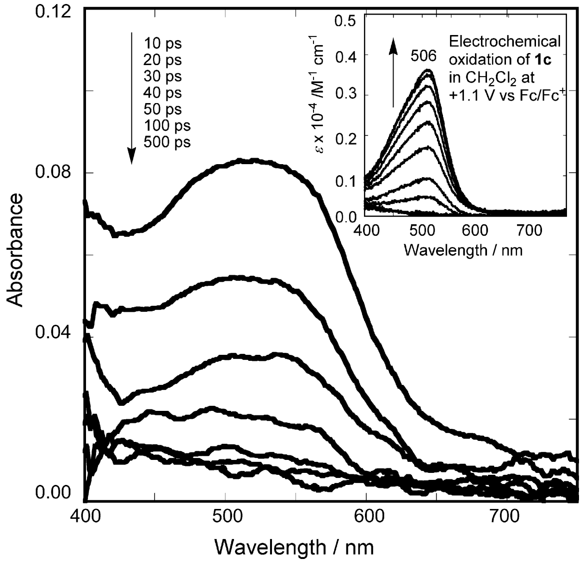

Fig. 5. Transient absorption spectra of **1c** ([**1c**] = 6.70 × 10^{-4} M) in deaerated butyronitrile at 298 K taken 10, 20, 30, 40, 50, 100, 500 ps after a 355 nm laser pulse (FWHM: 17 ps). Inset is a spectral change with rough estimation of the molar absorptivity during the electrochemical oxidation of **1c** in CH_2Cl_2.

around 520 nm (τ = ca. 16 ps) (see footnote 2), which is reasonable as a summation of the absorptions of the **1c** radical cation (506 nm in CH_2Cl_2, inset in Fig. 5) and the pyridinyl radical (λ_{max}: 550 nm in Fig. 3).

In both cases (**1b** and **1c**), the absorptions in the 400–750 nm region had almost vanished within 100 ps, indicating a minor contribution of long-lived triplet charge-shift states, if they are generated. These results can be explained by the rapid back charge-shift to the singlet ground state, i.e., the expected intersystem crossing of the singlet charge-shift state is too slow to compete with the fast back charge-shift process for **1b** and **1c**.

It is of interest to compare the lifetimes of the charge-shift states for **1a**–**1c**. The lifetimes increase in the order of **1c** < **1b** ≪ **1a**. This sequence is independent from of the torsion angle between the donor and pyridinium rings (**1b** < **1a** < **1c** in the ground state) but related to the sequence of $-\Delta G_{BCS}$ values (**1c** < **1b** ≪ **1a**), indicating that the back charge-shift processes are in Marcus inverted region [18]: the large free energy gain, ΔG_{BCS}, for **1a** slows the back charge-shift to the singlet ground state to allow intersystem crossing to the LE triplet state on the pyridinium moiety. On the other hand, very rapid back charge-shift reactions were observed for **1b** ($\tau = 35$ ps) and **1c** ($\tau = 16$ ps). The observed lifetimes are much shorter than those predicted from the classical Marcus theory [18]: applying the classical Marcus theory predicts the time constant of the decay of the charge-shift state for **1b** to be $\tau = 2.4 \times 10^6$ s[3]; the remarkable difference (10^{17} order) between the experiment and the theory. Thus, the short lifetime of the present system is in sharp contrast to the report by Fukuzumi and coworkers [3a], who reported that the observed lifetime is in accord with the classical Marcus theory. Although the presence of the inverted region has been experimentally demonstrated in many systems, the effect is known to be much less than that predicted based on the classical Marcus theory, indicating the importance of nuclear tunneling quantum effects [19] in the Marcus inverted region. Our results are totally consistent with those reported by Verhoeven, Harriman, and coworkers [1,4].

4. Conclusion

The pyridinium cations with the donor of mesityl (**1a**, $\Delta G_{BCS} < -3.4$ eV) and 2,5-dimethoxyphenyl (**1b**, $\Delta G_{BCS} = -2.7$ eV) and 2,3,4,5-tetramethoxypheny (**1c**, $\Delta G_{BCS} = -2.3$ eV) were investigated. In all cases, the singlet charge-shift states were observed. The mesityl charge-shift state was converted to the LE-pyridinium triplet state with a time constant of 20–25 ns. The methoxy charge-shift states decayed to the singlet ground states very rapidly with lifetimes of 35 ps (**1b**), and 16 ps (**1c**). These results clearly show that the perpendicular approach for the directly linked D–A system does not lead to a long-lived triplet charge-shift state. The rate of the back charge-shift reactions for **1b** and **1c** are extremely fast, contrary to the expectation from the classical Marcus theory in the inverted region ($\Delta G_{BCS} < -2$ eV, $\lambda = 0.78$ eV). The expected intersystem crossing of the singlet charge-shift state cannot be operative for **1b** and **1c** because of their fast back charge-shift processes,

Further exploration of long-lived (>∼μs) triplet radical ion pair states by fast intersystem crossing in D–A-linked systems are in progress.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.08.019.

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[3] The electronic coupling for the charge-shift state of **2b** was estimated from the CT absorption ($\varepsilon_{max} = 753\ M^{-1}\ cm^{-1}$, $\nu_{max} = 27{,}800\ cm^{-1}$ (360 nm), $\Delta\nu_{1/2} = 4500\ cm^{-1}$, and $R_c = 4.3$ Å) [14] as $V = 1.5 \times 10^2\ cm^{-1}$, which resulted in a higher value of the pre-exponential factor than the nuclear vibration limit ($10^{13}\ s^{-1}$). Thus, the estimation of the rate constant of the back charge-shift state using the semi-classical Marcus theory [18] governed by the vibrational limit gave also the very long lifetime of $\tau = 1.5 \times 10^6$ s.

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