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Direct observation and kinetic characterization of *o*-quinodimethane and its radical cation variant generated in a photoinduced electron-transfer reaction of 1,2-bis(α-styryl)benzene

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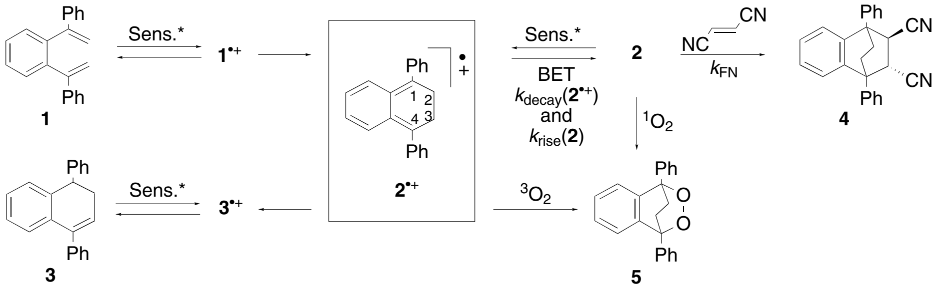
Abstract—Nanosecond time-resolved absorption spectroscopy on the laser flash photolysis of 1,2-bis(α-styryl)benzene (**1**) under *N*-methylquinolinium tetrafluoroborate–toluene-sensitized conditions in acetonitrile confirmed that an *o*-quinodimethane radical cation ($\mathbf{2}^{\cdot+}$, $\lambda_{max} = 569$ nm) decayed and the corresponding neutral prototype (**2**, $\lambda_{max} = 444$ nm) rose with rate constants of 5.6 and 5.9×10^5 s^{-1}, respectively, showing the first agreement in kinetics between a reactive radical cation intermediate intervening in chemical reaction and the corresponding neutral species formed by back electron transfer.

Previously, we reported on preliminary results of an electrocyclization reaction of 1,2-bis(α-styryl)benzene (**1**, Scheme 1, anodic peak potential = +1.51 V vs SCE in acetonitrile) to *o*-quinodimethane (**2**), triggered by photoinduced electron transfer (PET) using 9,10-dicyanoanthracene (DCA) or 1,4-dicyanonaphthalene (DCN) as a sensitizer.[1] Although the reaction is supposed to proceed via two radical cations, $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$, direct observation of them by laser flash photolysis (LFP) was not achieved. If **2** is stable under the LFP conditions used, it becomes easy to analyze kinetic data and allows us to study the kinetics for each process, especially the back electron-transfer (BET) process, converting $\mathbf{2}^{\cdot+}$ to **2**. Such a study will be of value, because the kinetics for the BET process involving reactive radical cation intermediates intervening in chemical reactions and the



Scheme 1. PET reactions of **1** under various conditions.

Keywords: Photochemistry; *o*-Quinodimethane; Radical cation; Back electron transfer; Kinetics.

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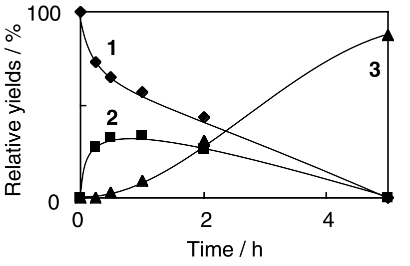


Figure 1. Time-dependent changes of the relative yields of products in the DCA-sensitized PET reaction of **1** in degassed dichloromethane-d_2. [**1**] = 50 mM.

corresponding neutral compounds is unprecedented in spite of its great importance.[2] For this purpose, we studied nanosecond time-resolved absorption spectroscopy on LFP and kinetics for the intermediates generated in the PET reactions of **1**. Herein, we report on a direct observation of $\mathbf{2}^{\cdot+}$ and the first agreement of the decay and rise rate constants of $\mathbf{2}^{\cdot+}$ and **2**, respectively.

Upon irradiating (80 W Rayonet lamp, 350 nm) DCA for 15 min in degassed dichloromethane-d_2 at 20 °C, **1** produced **2** as the sole product in 27% yield (Fig. 1). Similar irradiation for 2 h gave a dark-yellow mixture of **1**, **2**, and 1,2-dihydro-1,4-diphenylnaphthalene (**3**),[3] in 43%, 26%, and 31% yields, respectively. The reaction mixture containing **2** was stable in the dark for a full day, but readily converted to **3** in 87% yield after prolonged irradiation for 5 h. These findings indicate that **3** is formed secondarily and slowly by PET reaction of **2**. A similar reaction also proceeded in degassed benzene and acetonitrile. Interestingly, **2** was unstable in an aerated solution in the dark, resulting in decomposition to give a complex mixture.

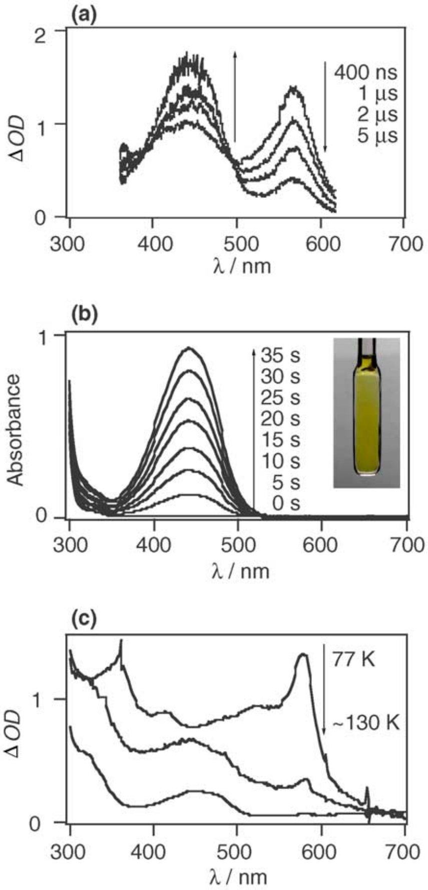


Figure 2. (a) Time-resolved absorption spectra observed in the LFP of **1** under $NMQ^+BF_4^-$–toluene-sensitized conditions in aerated acetonitrile. [**1**] = 10 mM, [$NMQ^+BF_4^-$] = 1 mM, [toluene] = 2 M. (b) UV–vis absorption spectra observed during a DCN-sensitized PET reaction of **1** in degassed acetonitrile. [**1**] = 10 mM, [DCN] = 0.02 mM. Inset: a photograph of the sample solution after irradiation for 30 s. (c) Absorption spectra observed during the annealing (77 to ~130 K) of an *n*-butyl chloride glassy matrix of **1** irradiated with γ-rays at 77 K. [**1**] = 5 mM.

Nanosecond time-resolved absorption spectroscopy upon LFP[4] was performed with *N*-methylquinolinium tetrafluoroborate ($NMQ^+BF_4^-$) and toluene as a sensitizer and a co-sensitizer, respectively.[5] As shown in Figure 2a, laser excitation (355 nm) of $NMQ^+BF_4^-$ with **1** in aerated acetonitrile gave two transient absorption bands with λ_{max} at 444 and 569 nm. The differential optical density (ΔOD) of the 444 nm band increased with decreasing ΔOD of the 569 nm band. Similar absorption spectra were observed under $NMQ^+BF_4^-$–toluene-sensitized conditions in degassed dichloromethane and acetonitrile, or under DCA–biphenyl (BP, co-sensitizer)-sensitized conditions in degassed acetonitrile. The 444 nm band is assigned to **2** because this band corresponds to the band with λ_{max} at 442 nm of **2** observed for a yellow solution (Fig. 2b and inset) of the DCN-sensitized PET reactions (80 W Rayonet lamp, 300 nm) of **1** in acetonitrile.[6] Conversely, the 569 nm band is attributed to $\mathbf{2}^{\cdot+}$, but not to $\mathbf{1}^{\cdot+}$, because the radical cation of 1,1-diphenylethylene, a subunit of **1**, did not have any intense absorption bands at this region in an *n*-butyl chloride glassy matrix irradiated with γ-rays at 77 K.[7] Interestingly, an absorption band with λ_{max} at 578 nm appeared in a similar matrix of **1** at 77 K, and disappeared with an appearance of **2** observed at ~440–450 nm upon annealing (77 to ~133 K) (Fig. 2c). No absorption band due to the precursor radical cation $\mathbf{1}^{\cdot+}$ was observed upon LFP or γ-ray irradiation. This may be due to the fixed *cisoid* form of two styrene units in **1**, which allows **1** to cyclize rapidly upon oxidation. The assignments are in accord with the decay and rise behaviors of the observed species (viz. $\mathbf{2}^{\cdot+}$ and **2**) with an isosbestic point at $\lambda = 494$ nm (Fig. 2a).

A kinetic analysis for $\mathbf{2}^{\cdot+}$ and **2** was achieved under $NMQ^+BF_4^-$ (2 mM) and toluene (0.4 M) conditions in degassed acetonitrile containing **1** (0.3 mM) at 25 °C (Fig. 3).[4] The decay rate constant for $\mathbf{2}^{\cdot+}$ observed at 570 nm, $k_{decay}(\mathbf{2}^{\cdot+}) = 5.6 \times 10^5\ s^{-1}$, agrees with the rise rate constant for **2** observed at 461 nm, $k_{rise}(\mathbf{2}) = 5.9 \times 10^5\ s^{-1}$, within the experimental error (~5%), confirming that $\mathbf{2}^{\cdot+}$ is quantitatively converted to **2** by single-electron reduction, probably BET from $NMQ^{\cdot}$. To the best of our knowledge, this is the first agreement of the decay and rise rate constants of a reactive radical cation intervening in chemical reaction and the corresponding species, respectively. Note that $k_{decay}(\mathbf{2}^{\cdot+})$ and $k_{rise}(\mathbf{2})$ are not the net values of the rate constant, k_{bet}, of BET from NMQ$^{\bullet}$ to $\mathbf{2}^{\bullet+}$ in a radical ion pair $[\mathbf{2}^{\bullet+}//\text{NMQ}^{\bullet}]_{\text{rip}}$, which was theoretically calculated to be $5.2 \times 10^{10}\ \text{s}^{-1}$,[8] by the latest electron-transfer theory.[9] Given the steady state approximation for $[\mathbf{2}^{\bullet+}//\text{NMQ}^{\bullet}]_{\text{rip}}$ generated in the BET sequence shown in Scheme 2, $k_{\text{decay}}(\mathbf{2}^{\bullet+})$ and $k_{\text{rise}}(\mathbf{2})$ are represented by Eq. 1, where k_{ass} and k_{dis} are the rate constants for the association and dissociation for $[\mathbf{2}^{\bullet+}//\text{NMQ}^{\bullet}]_{\text{rip}}$, and are estimated to be $1.9 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$,[12] and $2.4 \times 10^{9}\ \text{s}^{-1}$,[13] respectively. A numerical constant k_0 is $-1.6 \times 10^{5}\ \text{s}^{-1}$.[14] These assumptions conclude that the concentration of NMQ$^{\bullet}$, [NMQ$^{\bullet}$], is $\sim 4 \times 10^{-2}$ mM, which is reasonable, because the initial concentration of $\text{NMQ}^{+}\text{BF}_4^{-}$ is 2 mM. Consequently, the findings described here indicate that the kinetic analysis used in this work is quite appropriate in light of the latest electron-transfer theory.[9]

$$k_{\text{decay}}(\mathbf{2}^{+})\ \text{and}\ k_{\text{rise}}(\mathbf{2}) = \frac{k_{\text{ass}}k_{\text{bet}}}{k_{\text{dis}} + k_{\text{bet}}}[\text{NMQ}^{\bullet}] + k_0 \qquad (1)$$

We also investigated the reactivity of $\mathbf{2}^{\bullet+}$ and **2** toward molecular oxygen ($^3\text{O}_2$) and fumaronitrile (FN) by absorption spectroscopy in connection with the DCA-sensitized PET oxygenation of **1**, giving **5**,[1] and the PET cycloaddition reaction of **1** with FN (Scheme 1).[1] We found that under DCA–BP-sensitized conditions in acetonitrile, ΔOD of $\mathbf{2}^{\bullet+}$ was not changed very drastically, depending upon the concentration of $^3\text{O}_2$ on the timescale of LFP,[15] whereas the change in ΔOD of **2** was not examined because the absorption bands of $\text{BP}^{\bullet+}$ and **2** overlap each other. However, **5** was formed in 55% yield at 81% conversion in the tris(4-bromophenyl)aminium hexachloroantimonate $[(4\text{–BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^{-}]$ (0.4 mM)-catalyzed oxygenation of **1** (2 mM) under oxygen in dichloromethane (50 mL) in the dark, clearly indicating that $^3\text{O}_2$ added to radical cation,[16] $\mathbf{2}^{\bullet+}$. These findings suggest that not only the mechanism involving **2** and singlet oxygen ($^1\text{O}_2$)[1] but also the mechanism involving $\mathbf{2}^{\bullet+}$ and $^3\text{O}_2$ contributed to the DCA-sensitized PET oxygenation giving **5**. Probably, $\mathbf{2}^{\bullet+}$ reacts slowly with $^3\text{O}_2$ to give **5**. This may be due to the nondistonic nature of $\mathbf{2}^{\bullet+}$; the spin and charge are delocalized to the long π-conjugated system of $\mathbf{2}^{\bullet+}$. Needless to say, the spin densities at C-1 and C-4 are not very high compared with those of distonic radical cations that afford oxygenation products efficiently.[17]

$$\mathbf{2}^{\bullet+} + \text{NMQ}^{\bullet} \underset{k_{\text{dis}}}{\overset{k_{\text{ass}}}{\rightleftharpoons}} [\mathbf{2}^{\bullet+}//\text{NMQ}^{\bullet}]_{\text{rip}} \xrightarrow{k_{\text{bet}}} \mathbf{2} + \text{NMQ}^{+}$$

Scheme 2. A sequence of BET from NMQ$^{\bullet}$ to $\mathbf{2}^{\bullet+}$.

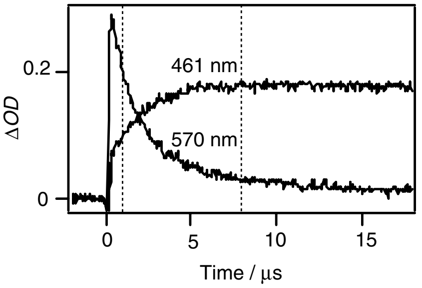
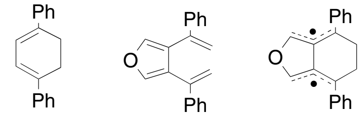


Figure 3. Time-profiles of ΔOD of $\mathbf{2}^{\bullet+}$ and **2** monitored at 570 and 461 nm, respectively, in the LFP of **1** under $\text{NMQ}^{+}\text{BF}_4^{-}$–toluene conditions in degassed acetonitrile. $[\mathbf{1}] = 0.3$ mM, $[\text{NMQ}^{+}\text{BF}_4^{-}] = 2$ mM, [toluene] = 0.4 M. Data from 0.76 to 7.8 µs were used for kinetic analyses. See notes 4 and 5.



6 **7** **8••**

Chart 1.

On the other hand, the cycloaddition reaction of **2** with FN, giving **4**, proceeded with the rate constant, $k_{\text{FN}} = 1.9 \times 10^{-2}\ \text{M}^{-1}\ \text{s}^{-1}$, at 25 °C in degassed benzene.[18,19] Interestingly, 1,4-diphenylcyclohexa-1,3-diene (**6**, Chart 1) did not react with FN in benzene at 80 °C. Moreover, the decay rate constant for $\mathbf{8}^{\bullet\bullet}$, which is formed from a structurally related furan derivative **7**, with FN, is $1.2 \times 10^{7}\ \text{M}^{-1}\ \text{s}^{-1}$ at 25 °C in dichloromethane under nitrogen.[20] The high reactivity of **2** compared with **6** is reasonably ascribed to the recovery of aromaticity in **4**. Conversely, the slow reactivity of **2** compared with $\mathbf{8}^{\bullet\bullet}$ is ascribed to the nonradical nature of **2**.

In conclusion, we directly observed an *o*-quinodimethane radical cation $\mathbf{2}^{\bullet+}$, which intervenes in the PET electrocyclization of **1** to **2**. Kinetic analyses for $\mathbf{2}^{\bullet+}$ and **2** confirmed for the first time that the decay rate constant of a reactive radical cation intervening in chemical reaction agrees with the rise rate constant of the corresponding reduced species formed by BET. A kinetic study of $\mathbf{2}^{\bullet+}$ toward $^3\text{O}_2$ and of **2** toward FN also revealed the kinetic characteristics of **2** and $\mathbf{2}^{\bullet+}$. Further studies are now in progress, and will be published elsewhere.

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Supplementary data

An energy diagram for $\text{NMQ}^{+}\text{BF}_4^{-}$-sensitized PET reaction of **1**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.01.124.

References and notes

1. Takahashi, Y.; Ohya, Y.; Ikeda, H.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1749–1750.
2. For the importance of BET in the PET reactions, see: (a) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101–2104; (b) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1107–1109; (c) Ikeda, H.; Minegishi, T.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1994**, 297–298; (d) Karki, S. B.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Zona, T. A. *J. Am. Chem. Soc.* **1997**, *119*, 431–432; (e) Ikeda, H.; Minegishi, T.; Abe, H.; Konno, A.; Goodman, J. L.; Miyashi, T. *J. Am. Chem. Soc.* **1998**, *120*, 87–95; (f) Ikeda, H.; Nakamura, T.; Miyashi, T.; Goodman, J. L.; Akiyama, K.; Tero-Kubota, S.; Houmam, A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1998**, *120*, 5832–5833; (g) Ikeda, H.; Takasaki, T.; Takahashi, Y.; Konno, A.; Matsumoto, M.; Hoshi, Y.; Aoki, T.; Suzuki, T.; Goodman, J. L.; Miyashi, T. *J. Org. Chem.* **1999**, *64*, 1640–1649; (h) Miyashi, T.; Ikeda, H.; Takahashi, Y. *Acc. Chem. Res.* **1999**, *32*, 815–824; (i) Roth, H. D. *J. Photochem. Photobiol. C* **2001**, *2*, 93–116; (j) Ikeda, H.; Akiyama, K.; Takahashi, Y.; Nakamura, T.; Ishizaki, S.; Shiratori, Y.; Ohaku, H.; Goodman, J. L.; Houmam, A.; Wayner, D. D. M.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9147–9157.
3. Abegg, V. P.; Hopkinson, A. C.; Lee-Ruff, E. *Can. J. Chem.* **1978**, *56*, 99–103.
4. Nanosecond time-resolved absorption spectroscopy upon LFP was carried out with a pulsed YAG laser (Continuum Surelite-10, Nd, THG, $\lambda_{ex} = 355$ nm, 55 mJ) and a Xe arc lamp (150 W) as the monitoring light. A cutoff filter (Y-46, $\lambda > 435$ nm) was used for the kinetic analysis of $\mathbf{2}^{\cdot+}$ and **2** so as to avoid possible side reactions of **1** and **2** initiated by absorption of the monitoring light. Reactions of **1** affording **2** were also observed under these co-sensitized PET conditions.
5. A use of cationic sensitizers and chemically unreactive aromatic hydrocarbons so-called co-sensitizers is effective to observe radical cations in the LFP experiments. Under these conditions, a substrate radical cation is formed via electron transfer from a co-sensitizer to a photoexcited sensitizer followed by hole transfer from a co-sensitizer radical cation to a substrate.
6. Because DCN is transparent in the vis region, DCN was used as a sensitizer instead of DCA in the monitoring experiment of the time-dependent changes of absorption spectra of the PET reaction of **1**.
7. A *n*-butyl chloride solution containing **1** (5 mM) was degassed by repeating five freeze (77 K)–pump (10^{-3} mmHg)–thaw (ambient temperature) cycles and sealed at 10^{-3} mmHg at 77 K. This matrix was irradiated at 77 K for 40 h with γ-rays from a 4.0 TBq ^{60}Co source at the Cobalt 60 γ Ray Irradiation Facility, Tohoku University.
8. The value of k_{bet} for the BET from NMQ$^{\cdot}$ to $\mathbf{2}^{\cdot+}$ at 25 °C in acetonitrile was calculated using the following Eqs.[9] 2 and 3 and parameters reported by Kikuchi and co-workers[10]

$$k_{\mathrm{bet}} = \left(\frac{4\pi^3}{h^2\lambda_s k_b T}\right)^{1/2} |V|^2 \sum_{w=0}^{\infty}\left(\frac{e^{-S}S^{w}}{w!}\right)\exp\left[-\frac{(\lambda_s+\Delta G_{\mathrm{bet}}+whv)^2}{4\lambda_s k_b T}\right] \qquad (2)$$

$$S = \lambda_v/hv \qquad (3)$$

where the parameters V, λ_s, λ_v, v, and ΔG_{bet} are, respectively, the electronic coupling matrix element (57 cm^{-1}), solvent reorganization energy (1.52 eV), vibration reorganization energy (0.25 eV), single average frequency (1500 cm^{-1}), and free energy change for BET process (−1.03 eV).[11] In addition, h, k_b, and T are Planck's constant, Boltzmann's constant, and the temperature (298 K), respectively.
9. (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057–5068; (b) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741–747; (c) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748–752; (d) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183–197; (e) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358–4368.
10. Inada, T. N.; Miyazawa, C. S.; Kikuchi, K.; Yamauchi, M.; Nagata, T.; Takahashi, Y.; Ikeda, H.; Miyashi, T. *J. Am. Chem. Soc.* **1999**, *121*, 7211–7219.
11. The value of $\Delta G_{bet} = -1.03$ eV was estimated by analyses for an energy diagram for the NMQ$^+$BF$_4^-$-sensitized PET reaction of **1**. See the Supplementary data.
12. The value of k_{ass} is supposed to correspond to the diffusion rate constant in acetonitrile at 25 °C, $k_{dif} = 1.9 \times 10^{10}$ M^{-1} s^{-1}.
13. The value of k_{dis} for [$\mathbf{2}^{\cdot+}$//NMQ$^{\cdot}$]$_{rip}$ with $\Delta G_{bet} = -1.03$ eV is supposed to correspond to that for [anisidine radical cation//*N*-methylacridinium radical] with $\Delta G_{bet} = -1.06$ eV and $k_{dis} = 2.4 \times 10^9$ s^{-1}.[10]
14. The value of k_0 was determined as the intercept of a linear relationship between $k_{decay}(\mathbf{2}^{\cdot+})$ or $k_{rise}(\mathbf{2})$ and the absorption efficiency of NMQ$^+$ (100-transmittance) on the assumption that [NMQ$^{\cdot}$] is proportional to the absorption efficiency of NMQ$^+$.
15. The values of half lifetime ($\tau_{1/2}$) of $\mathbf{2}^{\cdot+}$ under oxygen, air, and degassed conditions in acetonitrile were 1.7, 1.6, and 1.6 μs, respectively.
16. Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055–2065.
17. For recent examples of spectroscopic studies of chemical capturing distonic radical cation intermediates with ^{3}O$_2$, see Ref. 2e–g,j, and: Mizuno, K.; Tamai, T.; Hashida, I.; Otsuji, Y.; Kuriyama, Y.; Tokumaru, K. *J. Org. Chem.* **1994**, *59*, 7329–7334.
18. The ΔOD of $\mathbf{2}^{\cdot+}$ did not significantly change before or after adding FN (0.185 mM) in the LFP experiment of **1** (0.3 mM) under NMQ$^+$BF$_4^-$–toluene-sensitized conditions in dichloromethane.
19. A benzene solution containing **1** (1 mM), DCA (0.5 mM), and FN (0–100 mM) was degassed by repeating five freeze (77 K)–pump (10^{-3} mmHg)–thaw (ambient temperature) cycles and sealed at 10^{-3} mmHg at 77 K. After irradiation for 5 min with a Rayonet lamp (15 W, 350 nm) at 20 °C, the time-dependent change of the absorbance at 480 nm of the sample solution was monitored at constant temperature with a JASCO V-570 UV–vis/NIR

spectrophotometer equipped with ETC-505 Peltier-type thermostatic cell holder. The apparent rate constant, k_{ap}, was given as the slope of a linear relationship between absorbance and time. Plotting k_{ap} and [FN] gave k_{FN} at a temperature as the slope. Similar experiments were performed at 15.1, 20.0, 22.3, 24.7, 27.1, and 29.4 °C. Arrhenius plot analysis for k_{FN} and the theory of absolute reaction rate finally afforded the following kinetic parameters; $E_a = 9.3$ kcal mol^{-1}, $A = 1.3 \times 10^5$ M^{-1} s^{-1}, $\Delta G^{\ddagger}$(25 °C) = 19.8 kcal mol^{-1}, $\Delta H^{\ddagger}$(25 °C) = 8.7 kcal mol^{-1}, $\Delta S^{\ddagger}$(25 °C) = -37.1 cal mol^{-1} K^{-1}.

20. Yamada, M. Master Thesis, Tohoku University, 1995.