Photochemical Cleavage Reactions of 8-Quinolinyl Sulfonates in Aqueous Solution

Yoshiyuki KAGEYAMA,[a] Ryosuke OHSHIMA,[a] Kazusa SAKURAMA,[b] Yoshihisa FUJIWARA,[c] Yoshifumi TANIMOTO,[c] Yasuyuki YAMADA,[a,d] and Shin AOKI*,[a,d]

[a] *Faculty of Pharmaceutical Sciences, Tokyo University of Science;* [d] *Center for Drug Delivery Research, Tokyo University of Science; 2641 Yamazaki, Noda 278–8510, Japan:* [b] *CMC Research Center, Mitsubishi Tanabe Pharma Corporation; 3–16–89 Kashima, Yodogawa-ku, Osaka 532–8505, Japan: and* [c] *Graduate School of Science, Hiroshima University; 1–1–1 Kagamiyama, Higashi-Hiroshima 739–8524, Japan.*

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Photochemical cleavage reactions of 8-quinolinyl benzenesulfonate derivatives and related sulfonates in aqueous solutions are reported. The 8-quinolinyl benzenesulfonates undergo photolysis upon photoirradiation at 300—330 nm to give the corresponding 8-quinolinols and benzenesulfonic acids with the production of only negligible amounts of byproducts. The effects of substituent groups of the 8-quinolinyl moiety and the benzene ring on the photolysis reactions were examined. Based on steady-state mechanistic studies using a triplet sensitizer, a triplet quencher, and electron donors, it was suggested that the photolysis proceeds mainly *via* the homolytic cleavage of S–O bonds in the excited triplet state.

Key words photolysis; sulfonate; 8-quinolinol; homolysis

Photochemical bond-cleavage reactions are potentially useful in organic chemistry, biological chemistry and chemical biology (*e.g.*; protection/deprotection in organic synthesis[1—4] and uncaging of chemically masked or caged molecules).[5—13] To date, the photolysis of sulfonic esters,[14—24] sulfonamides,[25—32] and sulfones[33,34] has been applied to photoresist materials,[15,26] protecting groups,[8,19,20,27—32] and other chemical reactions.[14,35—37] Based on the above findings, the development of new photocleavage reactions of sulfonic acid derivatives and related mechanistic studies would be useful in organic chemistry, bioorganic chemistry, analytical chemistry, and material sciences.

We recently reported on the use of 5-*N*,*N*-dimethylaminosulfonyl-8-hydroxyquinolinyl-pendant cyclen (cyclen=1,4,7,10-tetraazacyclododecane) **1** (H_2L^1) as a Zn^{2+} fluorophore. The compound forms a very stable Zn^{2+} complex **2** ($Zn(H_{-1}L^1)$) in aqueous solution (K_d=8 fM at pH 7.4), resulting in a 17-fold enhancement in the emission at 512 nm (excitation at 338 nm) (Chart 1).[38] The caged derivative **3** (H_2(BS-caged-L^1)), in which the 8-OH group of the quinolinol moiety is protected by a benzenesulfonyl (BS) group, was recently synthesized, in an attempt to improve the cell permeability and Zn^{2+}/Cd^{2+} selectivity of **1**. We were able to confirm that the benzenesulfonyl ester of **3** is removed by a nucleophilic attack of Zn^{2+}-bound HO^- (in **4b**) on sulfur atom in its Zn^{2+} complex **4** (Zn(BS-caged-L^1)) to give **2**.[39,40]

During a study of the hydrolytic uncaging reaction of **4**, we found that **3** undergoes photolysis to yield **1**, whose emission increased upon the addition of Zn^{2+}. In this study, we report on the photolysis of **3**, **4**, 8-quinolinyl sulfonate derivatives that contain no metal chelating group (**5**—**8**), and related compounds in aqueous solution (Chart 2). Some mechanistic aspects of this photolysis reaction are also discussed.

Results

Finding of Photolysis of 3 During the fluorescent titration of **3** (H_2(BS-caged-L^1)) with Zn^{2+}, an enhancement in emission was observed. Curve (a) in Fig. 1 shows the emission spectrum of **1** (5 μM) in the absence of Zn^{2+} in 10 mM *N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid (HEPES) (pH 7.4) with I=0.1 ($NaNO_3$) at 25 °C (excitation at 338 nm) (the emission spectra was obtained by rapid scanning (500—1000 nm/min)) and curve (b) shows a spectrum obtained after Zn^{2+}-promoted hydrolysis of **3** (*via* its Zn^{2+} complex **4**) for 3 h in the dark, as previously reported.[39] On the other hand, the photoirradiation of a mixture of **3** (5 μM) and Zn^{2+} (5 μM) at 328 nm, gave curve (c) having an emission maximum at 510 nm, which is in good agreement with curve (d) for **2** (5 μM) (emission maximum at 512 nm). Based on the observation in ^{1}H-NMR (Figs. 2, 3) and UV spectral changes (Fig. 4), it was suggested that **3** and its Zn^{2+} complex **4** were

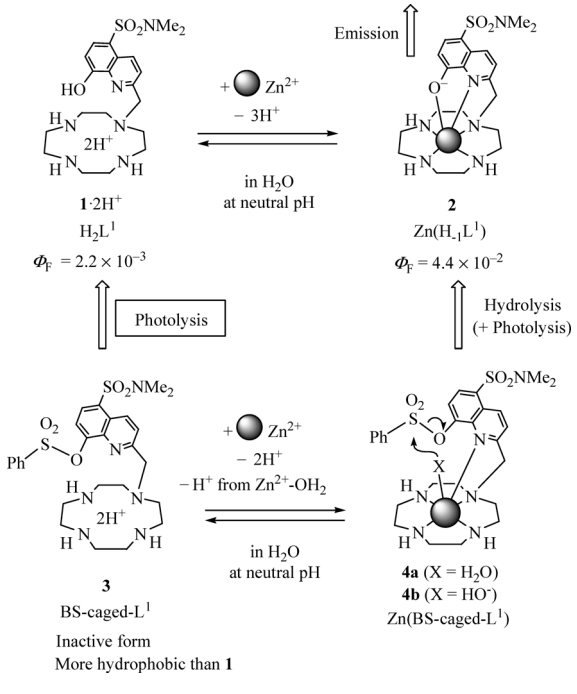
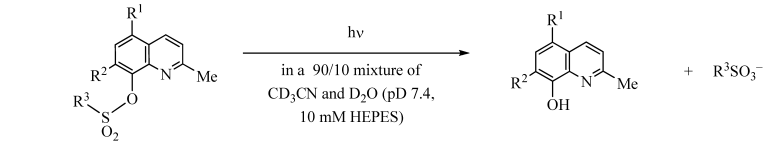
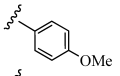


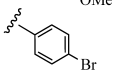
Chart 1

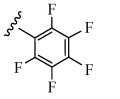
* To whom correspondence should be addressed. e-mail: shinaoki@rs.noda.tus.ac.jp



5a : R^1=SO_2NMe_2, R^2=H, R^3=Ph

5b : R^1=SO_2NMe_2, R^2=H, R^3= 

5c : R^1=SO_2NMe_2, R^2=H, R^3= 

5d : R^1=SO_2NMe_2, R^2=H, R^3= 

6 : R^1=R^2=H, R^3=Ph

7 : R^1=R^2=SO_2NMe_2, R^3=Ph

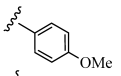
8 : R^1= SO_2NMe_2, R^2=H, R^3=Me

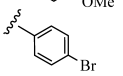
9 : R^1=SO_2NMe_2, R^2=H

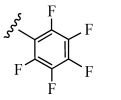
10 : R^1=R^2=H

11 : R^1=R^2=SO_2NMe_2

12a : R^3 = Ph

12b : R^3 = 

12c : R^3 = 

12d : R^3 = 

13 : R^3 = Me

Chart 2

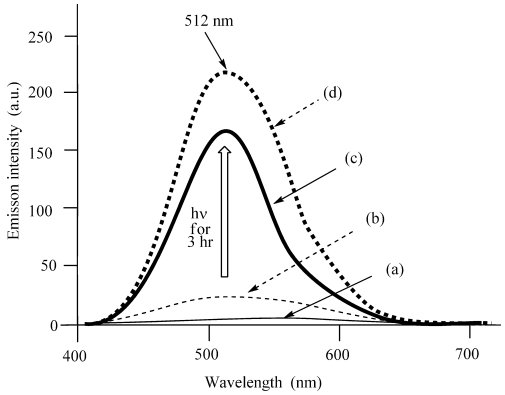


Fig. 1. Change in Emission Spectra of 5 μM **3** (BS-Caged-L^1) at pH 7.4 (10 mM HEPES with I=0.1 ($NaNO_3$)) and 25 °C upon Photoirradiation

(a) Emission spectra of 5 μM **3** obtained by a rapid scanning of the emission wavelength (excitation at 338 nm), (b) emission spectra of 5 μM **3** obtained 3 h after incubation in the presence of 5 μM Zn^{2+} at 25 °C in the dark, (c) emission spectra of 5 μM **3** after photoirradiation at 328 nm for 3 h in the presence of 5 μM Zn^{2+} (excitation wavelength for emission spectra measurement was 338 nm), and (d) emission spectra of 5 μM **2** ($Zn(H_{-1}L^1)$). Arbitrary unit is a.u.

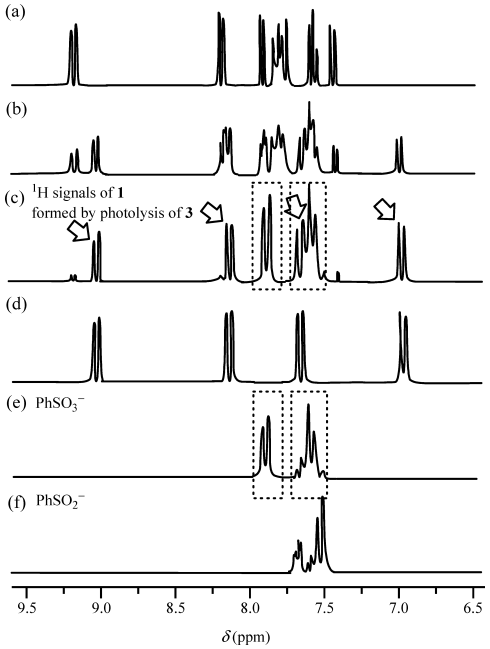


Fig. 2. Photolysis of **3** (1 mM) in D_2O at pD 7.4 (100 mM HEPES) and 25 °C Followed by ^{1}H-NMR (Aromatic Region)

(a) **3** before photoirradiation, (b) after photoirradiation of **3** at 328 nm for 1 h, (c) after photoirradiation of **3** at 328 nm for 3 h, (d)1 mM **1** (L^1), (e) 1 mM benzenesulfonate ($PhSO_3^-$), and (f) 1 mM benzenesulfinate ($PhSO_2^-$).

converted to **1** (H_2L^1) and **2** ($Zn(H_{-1}L^1)$), respectively, upon photoirradiation.

As shown in Fig. 5, **3** (50 μM) negligibly reacted in the absence of Zn^{2+} in the dark (dashed curve (a)). Upon the addition of 1 equivalent of Zn^{2+}, **4** was formed, which underwent slow hydrolysis in the dark to afford **2** ($Zn(H_{-1}L^1)$) (plain curve (b)). The photoirradiation of **4** at 328 nm then resulted in a considerable enhancement in fluorescent emission, indicating the formation of **2**.

Figure 6 shows the pH-rate profile for photoreactions of **3** (open circles) and **4** (closed circles), exhibiting negligible pH-dependency ([**3**]=[**4**]=10 μM). These results were in marked contrast to that for the pH-dependent hydrolysis of **4** (open squares in Fig. 6), implying that the presence of Zn^{2+}-bound H_2O (or HO^-) (shown in Chart 1) is not an important factor in the photoreaction of **4**. The quantum yields (Φ) for the photolysis of **3** and **4** at pH 7.4 were calculated to be 1.5×10^{-4} and 1.4×10^{-4}, respectively.

Photoreaction of Reference Compounds Having No Cyclen Unit In order to examine the mechanisms involved in the photohydrolysis of **3** and its Zn^{2+} complex **4**, some photoreactions of reference compounds that contain no cyclen unit, **5a**—**d** and **6**—**8**, were examined (Chart 2). As shown in spectra (a)—(c) in Fig. 7, **5a** (1 mM) underwent photolysis upon irradiation at 328 nm in a 90/10 mixture of CD_3CN and D_2O (10 mM HEPES at pD 7.4). Curves (d), (e), and (f) in Fig. 7 are ^{1}H-NMR spectra of **9**, benzenesulfonate ($PhSO_3^-$) **12a**, and benzenesulfinate ($PhSO_2^-$), respectively. A comparison of spectrum (c) in Fig. 7 with spectra (d), (e), and (f) strongly indicates that the photoproducts produced from **5a** are **9** and **12a**. The quantum yield for the photolysis of **5a** was estimated to be $(2.5\pm0.3)\times10^{-4}$ (photoirradiation at 328 nm) and the value was independent of the irradiation wavelength (data not shown).[41] An HPLC analysis of the

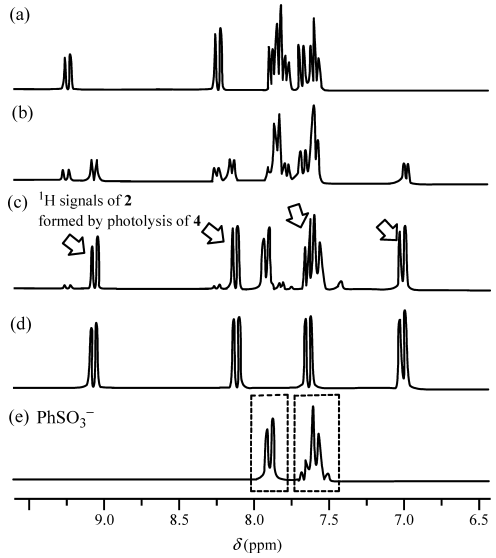


Fig. 3. Photolysis of **4** (1 mM) in D_2O at pD 7.4 (100 mM HEPES) and 25 °C Followed by ^{1}H-NMR (Aromatic Region)

(a) **4** before photoirradiation (15 min after mixing 1 mM **3** and 1 mM Zn^{2+}), (b) after photoirradiation of **4** at 328 nm for 1 h, (c) after photoirradiation of **4** at 328 nm for 3 h, (d) 1 mM **2** ($Zn(H_{-1}L^1)$), and (e) 1 mM benzenesulfonate ($PhSO_3^-$).

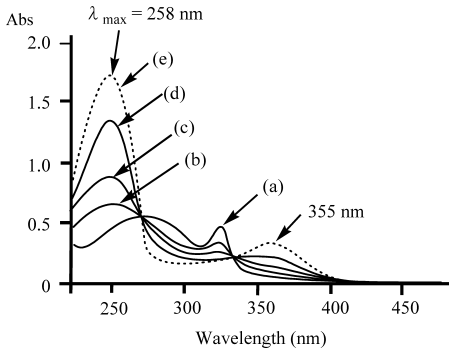


Fig. 4. Change in UV Absorption Spectra of 50 μM **4** (Formed *in Situ* by Mixing 50 μM **3** and 50 μM Zn^{2+}) upon Photoirradiation (at 328 nm) 10 mM HEPES (pH 7.4) with I=0.1 ($NaNO_3$) at 25 °C

(a) Before photoirradiation, (b) after photoirradiation for 20 min, (c) after photoirradiation for 40 min, (d) after photoirradiation after 1 h, and (e) UV spectra of 50 μM **2** ($Zn(H_{-1}L^4)$) in 10 mM HEPES (pH 7.4) with I=0.1 ($NaNO_3$) at 25 °C.

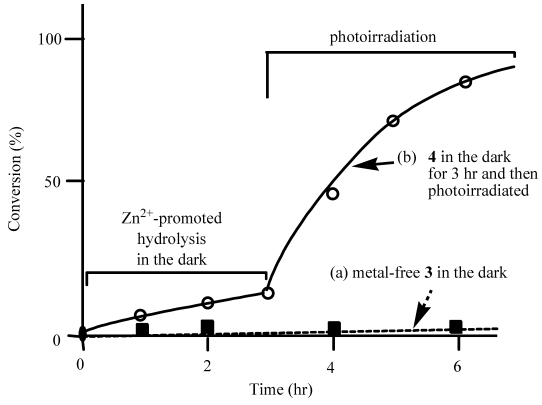


Fig. 5. Time Course for the Hydrolysis and Photolysis of 50 μM **4** at pH 7.4 (10 mM HEPES with I=0.1 ($NaNO_3$)) and 25 °C

Uncaging yields were determined by UV absorption spectra. (a) 50 μM metal-free **3** in the dark (closed squares), (b) 50 μM **4** in the dark for 3 h, followed by photoirradiation at 328 nm for 3 h (open circles).

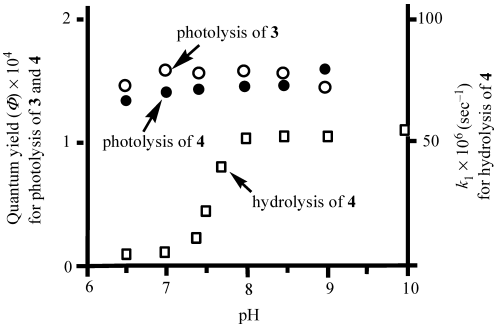


Fig. 6. pH–Quantum Yield Profile for the Photolysis of **3** (Open Circles) and **4** (Closed Circles) by Photoirradiation at 328 nm ([**3**]=[**4**]=10 μM in Good's Buffer with I=0.1 ($NaNO_3$) at 25 °C) in Comparison of pH–k_1 Profile Hydrolytic Uncaging of **4** (Open Squares) at [**4**]=50 μM

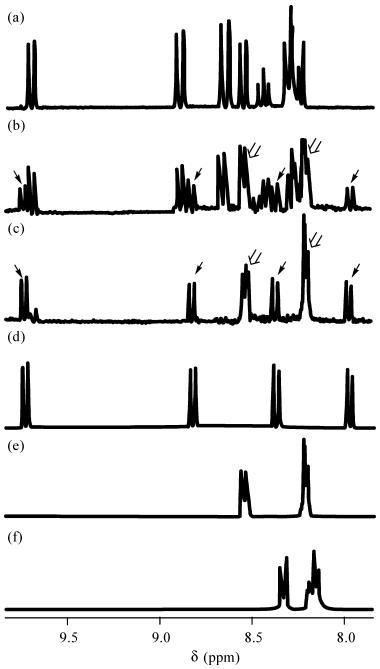


Fig. 7. Photolysis of **5a** (1 mM) in a Mixture of CD_3CN and D_2O (10 mM HEPES at pD 7.4) (90/10) at 25 °C Followed by ^{1}H-NMR (Aromatic Region)

(a) Before photoirradiation, (b) after photoirradiation at 328 nm for 0.5 h, (c) after photoirradiation at 328 nm for 3 h (d) **9** in a mixture of CD_3CN and D_2O (10 mM HEPES at pD 7.4) (90/10) at 25 °C, (e) benzenesulfonate ($PhSO_3^-$) **12a** and (f) benzenesulfinate ($PhSO_2^-$) under the same conditions. Plain arrows in (b) and (c) indicate ^{1}H signals of **9** and bold arrows indicate ^{1}H signals of **12a**.

photolysis products derived from **5a** also indicated that the photoirradiation of **5a** (50 μM) for 9 h (irradiated with weaker UV light at 328 nm than those for the NMR study mentioned above) gave **9** in 78(±3)% and unreacted **5a** in 21(±3)% with negligible byproduct formation (Fig. 8).

It was found that **5b**—**d** also undergo photolysis to afford **9** and the corresponding sulfonates **12b**—**d**, indicating that this photolysis is common to an 8-quinolynyl ester of aryl or alkylsulfonic acids. The quantum yields (Φs) for the photolysis of **5b**, **5c** and **5d** were found to be $2.4-2.5\times10^{-4}$, almost the same as that of **5a** (2.5×10^{-4}), implying that the substituent groups on the benzenesulfonyl moiety have negligible effect on this reaction (Table 1). It was also found that the photolysis of **6** and **7** gave the corresponding quinolinols (**10** or **11**) and **12a** with Φ values of 1.3×10^{-4} (photoirradiation

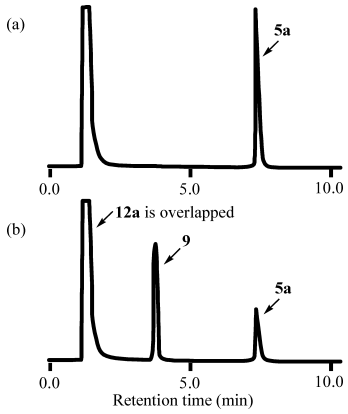


Fig. 8. HPLC Trace for the Photoreaction of **5a** (50 μM)

(a) Before irradiation and (b) after irradiation for 9 h at 328 nm in a mixture of CH_3CN and HEPES (10 mM, pH 7.4) (90/10). For HPLC analysis, ODS-column was used and the absorption at 220 nm was recorded (CH_3CN–phosphate buffer (pH 6.0) (1 : 1)).

Table 1. Quantum Yields for Photolysis of 8-Quinolinyl Sulfonates (**5**—**8**) (Include *ca.* 10% Experimental Errors)

Substrate	Irradiation wavelength (nm)	Quantum yield for photolysis (Φ)
5a	328	2.5×10^{-4}
5b	328	2.4×10^{-4}
5c	328	2.4×10^{-4}
5d	328	2.5×10^{-4}
6	320	1.3×10^{-4}
7	330	6.9×10^{-4}
8	328	1.6×10^{-4}

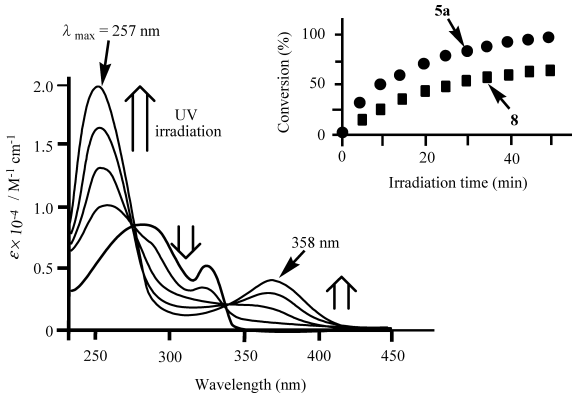


Fig. 9. Change in UV Absorption Spectra of 50 μM **5a** upon UV Irradiation at 328 nm in 10/90 CH_3CN/10 mM CHES (pH 9.0 with I=0.1 ($NaNO_3$)) at 25 °C

The inset shows the time course for the photolysis of **5a** (closed circles) and **8** (closed squares).

at 320 nm) and 6.9×10^{-4} (photoirradiation at 330 nm), respectively, suggesting that the substituents of the quinolinyl moiety somehow affect the photoreactivity of the sulfonate substrates (Table 1). The methylsulfonate analogue **8** also underwent photolysis (photoirradiation at 328 nm) to give **9** and methylsulfonate **13** in a somewhat smaller quantum yield than that of **5a** (Fig. 9 and Table 1).

For comparison, we also examined the photoreaction of other sulfonate derivatives **14**, **16**, and **18**—**21** (Chart 3). The photoirradiation of **14** gave 1-naphthol (**15**) and **12a** with

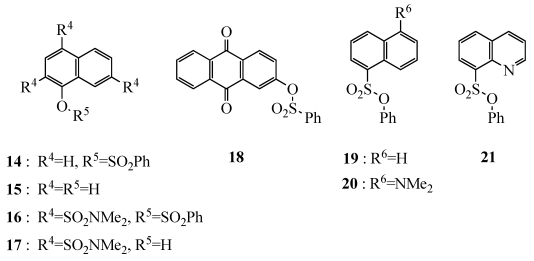


Chart 3

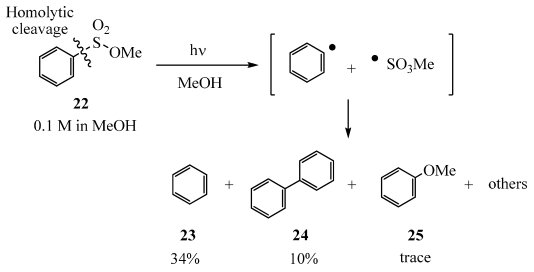


Chart 4

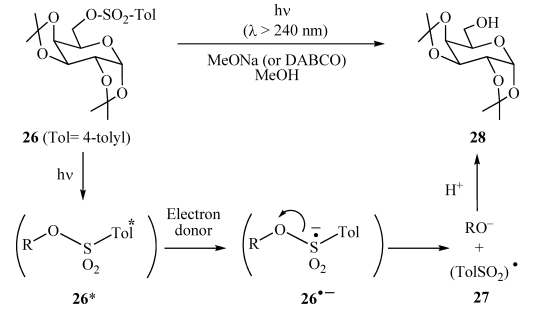


Chart 5

some unidentified byproducts.[42] The photolysis of **16** afforded the corresponding 1-naphthol **17** and **12a** with negligible side reaction.[42] The photocleavage of **18** was very slow in the absence and presence of benzophenone or Et_3N (see below), and the photocleavage of **19**, **20**, and **21** resulted in a formation of a complex mixture.[43]

Discussion

Several reaction pathways for the photolysis of sulfonate derivatives have been proposed to date. In 1975, Izawa and Kuromiya reported that the photolysis of methyl benzenesulfonate **22** in methanol led to the production of benzene **23**, biphenyl **24**, anisole **25**, and other products (Chart 4).[17] They postulated that the photolysis proceeds *via* homolytic cleavage of the C (benzene)–S bond in the excited singlet state, the lifetime of which was estimated to be in the order of nanoseconds.

Zen's group and Masanovi's group reported on the photolysis of tosylate derivatives (TsOR) such as the D-galactose derivative **26** under basic conditions. Masanovi *et al.* concluded that this photoreaction requires electron donors such as hydroxide or DABCO (1,4-diazabicyclo[2,2,2]octane), as shown in Chart 5.[18,19] It was generally assumed that the S–O bond of the radical anion **26**$^{\cdot-}$ ([Tol-SO_2-OR]$^{\cdot-}$), generated by electron transfer from electron donors, is cleaved to afford

the toluenesulfonyl radical **27** ([Tol-SO_2]$^{\cdot}$) and an alkoxide anion (RO^-), which is converted to alcohol **28**. Unfortunately, the photoproducts derived from **27** were not fully characterized.

In 1977, Ogata's group reported on the photo-Fries rearrangement of phenyl benzenesulfonate **29a** (Chart 6).[23] Based on the fact that the photoreaction of **29a** was unaffected by a triplet quencher and triplet sensitizers, they concluded that the reaction proceeds *via* the homolysis of the S–O bond in the lowest excited singlet state or in a triplet manifold, the rate of which is under the exceeding diffusion control. Barcley and Scaiano's group subsequently reported that photolysis of **29b** proceeds *via* a non-Fries type pathway to give phenol and *p*-toluenesulfonic acid as well as photo-Fries rearrangement products (Chart 6).[24] They observed transient spectra of a phenoxy radical by means of laser flash photolysis and concluded that the photodissociated products were formed as the result of the escape of a radical pair from the solvent cage.

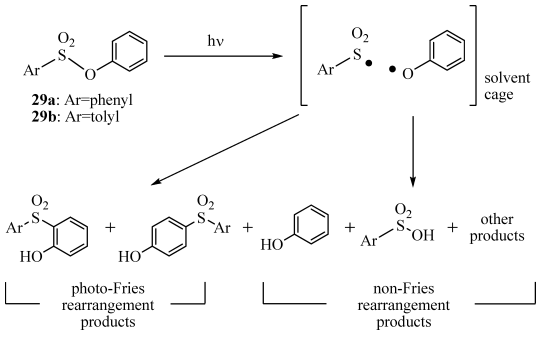


Chart 6

As described above, the photolysis of **3** (BS-caged-L^1), **4** (Zn(BS-caged-L^1)), and **5**—**8** proceeds even in the absence of a base such as methoxide and DABCO, to give the corresponding 8-quinolinols and sulfonates *via* S–O bond cleavage, and not *via* C–S bond fission. In addition, only negligible photo-Fries rearrangement products were detected. These data suggest that mechanism involved in the photolysis of 8-quinolinol sulfonates (**5**—**8**) in aqueous solution may be somewhat different from those for the photoreactions shown in Charts 4—6.

To investigate this further, we examined the mechanism for the photolysis of 8-quinolinyl sulfonates (**5**—**8**) using steady-state techniques. Our hypothesis for the mechanism of this photolysis is summarized in Chart 7, as evidenced by the following experimental data.

Triplet-Sensitizing Experiments for the Photolysis of 5a in the Presence of Benzophenone We carried out the photolysis of **5a** in the presence of benzophenone (BZ) (top part of Chart 7). BZ is a well-known sensitizer that has a triplet-state energy (E_T) value of 69 kcal mol^{-1} and brings about the triplet-state (T_1) of the substrates by energy transfer from the triplet state of BZ (BZ*(T_1)).[44—49] The E_T value of **5a** was estimated to be 61 kcal mol^{-1} from its phosphorescence spectra in a frozen MeCN/H_2O. Upon photoirradiation of a mixture of 1 mM of **5a** and 10 mM of BZ in CD_3CN/D_2O (10 mM HEPES at pD 7.4) (90/10) for 15 min at 355 nm, which is absorbed only by BZ, photolysis of **5a** proceeded in *ca.* 50%,

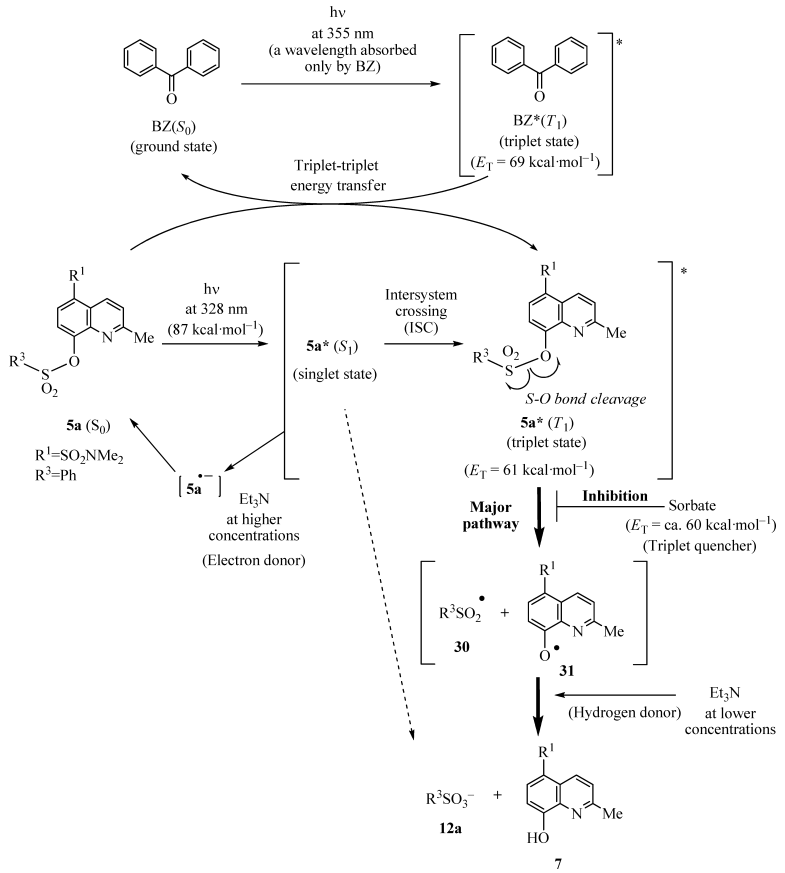


Chart 7

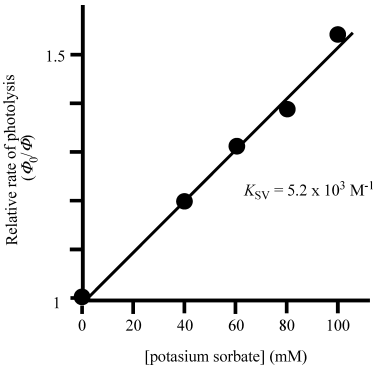


Fig. 10. Stern–Volmer Plot for the Photolysis of **5a** (50 μM) Irradiated at 328 nm with Potassium Sorbate (0—100 μM) in a Mixture of CH_3CN and 10 mM HEPES (pH 7.4) (90/10) at 25 °C

Φ_0 is the quantum yield in the condition without potassium sorbate.

as evidenced by ^{1}H-NMR experiments. In the absence of BZ, negligible amounts of photoproducts were produced under the same conditions.

The quantum yield for the BZ-sensitized photocleavage **5a** (1 mM) irradiated at 355 nm was estimated to be 7—8-fold larger than that for the direct irradiation of **5a** (328 nm excitation). Assuming that the triplet–triplet energy exchange is diffusion-controlled, the quantum yield of intersystem crossing (ϕ_{ISC}) from the excited singlet state to the excited triplet state and the kinetics of escape from the T_1 state (k_{esc}) were estimated to be 0.1 and $6-8\times10^3$ s^{-1}, respectively.[50]

Effect of Triplet-Quencher (Sorbate) It was observed that the photocleavage of **5a** was efficiently inhibited by the presence of potassium sorbate (*trans*,*trans*-2,4-hexadienoate), a triplet quencher, whose E_T is estimated to be about 60 kcal mol^{-1} based on the reported E_T value for methyl sorbate (62 kcal mol^{-1})[51] (right middle part in Chart 7). The Stern–Volmer plot showed a linear correlation between sorbate concentration and the relative kinetics with a slope (K_{SV}) of 5.2×10^3 M^{-1} (Fig. 10). According to the Eq. 1, in which K_{SV} is the Stern–Volmer constant (slope of Stern–Volmer plot), τ is the life time of an excited state, and k_q is the quenching kinetics constant, the life time of an excited state (τ) was estimated to be 0.3 μs, assuming a diffusion-controlled quench ($k_q=1.7\times10^{10}$ M^{-1} s^{-1}).[51] Consideration these results with the aforementioned BZ-sensitizing results led us to hypothesize that the photolysis of **5a** proceeds *via* the excited triplet state (**5a***(T_1)) rather than the singlet state (**5a***(S_1)).[52]

$$K_{SV}=\tau\times k_q \quad (1)$$

We also carried out the laser flash photolysis of **5a** (excitation using the 266 nm laser pulse). The transient absorption was observed with a λ_{max} of 410 nm with a lifetime (τ)<0.5 μs, which might be assigned to T_1 of **5a** (Fig. 11).[53]

Effect of Electron Donor (Et_3N) Masanovi's group and other groups reported that sulfonyl esters or sulfonamide derivatives undergo photolysis *via* intramolecular electron transfer[21,22,30] or intermolecular electron transfer.[18—20,31] As described above, the effect of substituent groups on the benzenesulfonyl moiety on the kinetics of the photolysis of **5a**—**d** was negligible (Table 1), indicating that intramolecular photoinduced electron transfer between two aromatic rings of **5a** is a minor pathway.

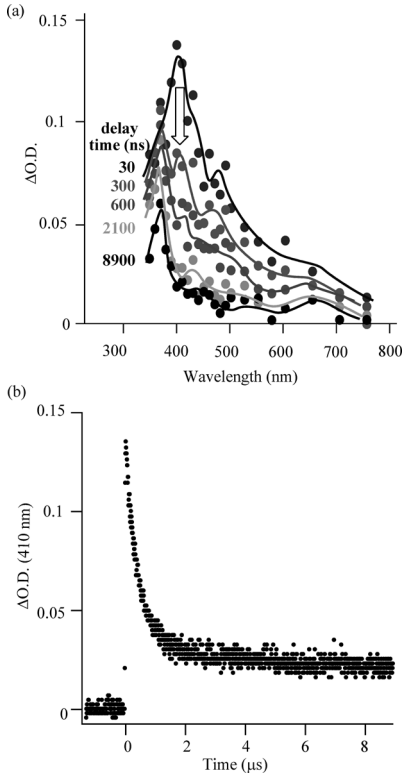


Fig. 11. (a) Transient Absorption Spectra Measured by the Photoexcitation of **5a** at 266 nm Laser Pulse in a 90/10 Mxture of CH_3CN and Water (10 mM HEPES at pH 7.4) and (b) Time Dependent Decrease in O.D. at 410 nm

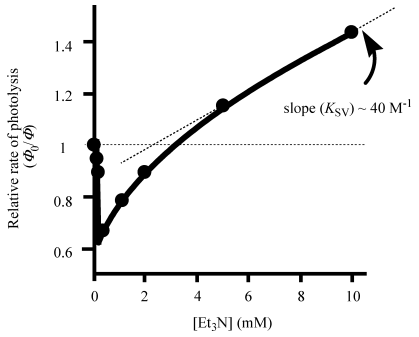


Fig. 12. Stern–Volmer Plot for the Photolysis of **5a** (50 μM) with Et_3N in a Mixture of CH_3CN and 10 mM HEPES (pH 7.4) (90/10) at 25 °C

We thus examined the kinetics of the photocleavage of **5a** (50 μM) in CH_3CN/10 mM HEPES (pH=7.4) (90/10) in the presence of Et_3N (0—10 mM), which serves as an external electron donor. Figure 12 shows the Stern–Volmer plot for the Φ_0/Φ values (Φ_0 is the quantum yield for the photoreaction in the absence of Et_3N) against the concentration of Et_3N. At [Et_3N]<0.02 mM, the Φ_0/Φ values decrease (the photoreaction is accelerated), indicating that Et_3N accelerates the photolysis *via* the longer-lifetime excited state (T_1) (bottom right part in Chart 7). In contrast, the Φ_0/Φ values increased (the photoreaction is decreased) at [Et_3N]>0.02 mM with a gradual slope ($K_{SV}\sim40$ M^{-1} at [Et_3N]=5—10 mM), indicating that Et_3N quenches the ns-lifetime excited state (S_1) (bottom left part in Chart 7).

It is generally assumed that hydrogen transfer from Et_3N to the radical intermediate **31** formed by the homolysis of

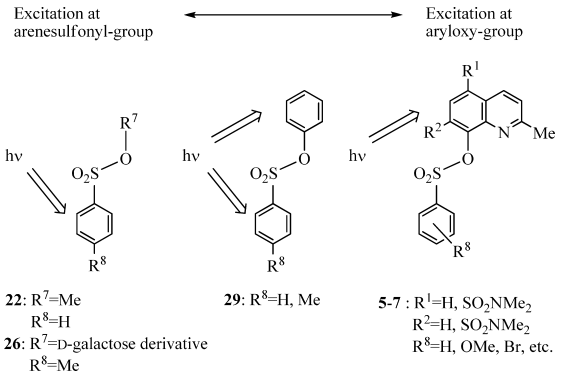


Chart 8

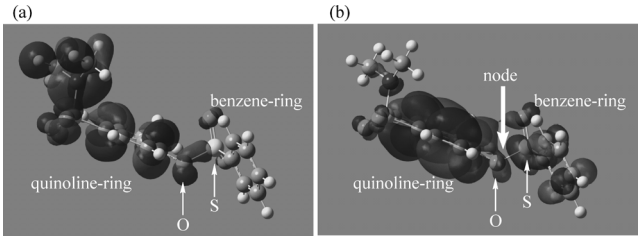


Fig. 13. DFT Calculation (B3LYP/6-31+G(d)) for (a) HOMO and (b) LUMO of **5a**

5a*(T_1) prevents the recombination of the **30** and **31** radical pair (Chart 7) resulting in an acceleration of the photolysis. We assume that Et_3N would donate its electron to **5a** in the excited states **5a*** at high concentrations of Et_3N to form $\mathbf{5a}^{\cdot-}$, which would be converted to the ground state (S_0), as a consequence, thus suppressing photolysis.[54,55]

The most plausible pathway for the photolysis of **5a** based on the aforementioned experimental results would be the homolysis of an S–O bond in the excited triplet state (T_1) to give the corresponding radicals **30** and **31**, which are then converted to **12** (*via* auto-oxidation or similar paths)[56] and **7**, respectively, as shown in Chart 7. The possibility that H_2O plays important roles (*e.g.* electron donor) cannot be completely excluded, because the photolysis of **5a** in anhydrous MeCN or in anhydrous 2-methyltetrahydrofuran affords, not only **7** and **12a** but also byproducts.

The difference in the reaction mechanism for the photolysis of **5** from those of **22** (Chart 4), **26** (Chart 5), and **29** (Chart 6) can be explained by Chart 8. In the photolysis of **22** and **26**, the arenesufonyl groups are excited.[17—20] In addition, in the photolysis of **29**, the arenesulfonyl and aryloxy groups are excited.[23,24] On the other hand, the photolysis of our substrate **5**—**8** is triggered by excitation of the 8-quinolinyl group, which may alter the reaction pathway.

Our hypothesis is consistent with a result of a density functional theory (DFT) calculation study of **5a**.[57] As shown in Fig. 13, the lowest unoccupied molecular orbital (LUMO) includes an anti-bonding sigma orbital (σ^*) between S and O (Fig. 13b), whereas the highest occupied molecular orbital (HOMO) contains a bonding sigma orbital (σ) (Fig. 13a). It is likely that the homolytic fission of the S–O sigma bond is triggered by the single electron excitation from HOMO to LUMO. In fact, attempt at structural optimization of **5a***(T_1) induced the S–O bond cleavage to give **30** and **31** (data not shown).

Conclusion

In this report, we described the photolysis of our caged Zn^{2+}-fluorophore **3** (H_2L^1), its Zn^{2+} complex **4** ($Zn(H_{-1}L^1)$), 8-quinolinyl sulfonates that have no Zn^{2+}-chelation unit and related compounds. It is noteworthy that the photolysis of **5**—**8** in aqueous solution is a very clean reaction, giving the corresponding sulfonates and 8-quinolinols with the production of only negligible amounts of byproducts, such as photo-Fries rearrangement products. Based on steady-state experiments and DFT calculations, we conclude that the photohydrolysis of **5a** (as well as **3** and **4**) proceeds *via* S–O bond homolysis in the excited triplet state (Chart 7).

Because photolabile protecting groups for caging biomolecules are limited,[58—69] these results may provide useful information concerning the design and synthesis of sulfonate-based photochemical protecting groups or reagents. Indeed, we have recently reported on the photocleavable biotin linker containing 8-quinolinyl sulfonate moiety for the isolation of dopamine-antibody complex[70] and photolabile liposome.[71] Moreover, 8-quinolinol derivatives have been reported as potential platforms for the inhibitiors of metal enzymes (*e.g.*; Zn^{2+} enzymes),[72] neuroprotective drugs,[73—75] regulators of gene expression,[76] and building blocks of supramolecular systems.[77] Therefore, photochemical characteristics of protected 8-quinoline derivatives and their derivatives would be useful in organic, bioorganic, and analytical chemistry and related areas.

Experimental

General Information All reagents and deuterated solvents were purchased at the highest commercial quality and were used without further purification. Solvents were purchased at the highest commercial quality and were used after distillation. All aqueous solutions were prepared using deionized and distilled water. Buffer solutions (CAPS, pH 10.0; CHES, pH 9.0; TAPS, pH 8.4 and 8.0; HEPES, pH 7.8, 7.6, 7.4, and 7.0; MES, pH 6.5) were used and the ionic strengths were adjusted with $NaNO_3$. The Good's buffer reagents (Dojindo) were commercially available: MES (2-morpholinoethanesulfonic acid, pK_a=6.2), HEPES (*N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid, pK_a=7.5), TAPS (*N*-(tris(hydroxymethyl)methylamino)-3-propanesulfonic acid, pK_a=8.4), CHES (2-(cyclohexylamino)-ethanesulfonic acid, pK_a=9.5), CAPS (3-(cyclohexylamino)propanesulfonic acid, pK_a=10.4). Melting points were measured on a Büchi 510 Melting Point Apparatus and are uncorrected. UV spectra were recorded on a Hitachi U-3500 spectrophotometer and JASCO UV/VIS spectrophotometer V-550, and fluorescence (excitation and emission) spectra were recorded on a JASCO FP-6500 spectrofluorometer at 25±0.1 °C. The quantum yield of fluorescence (Φ_F) was determined by comparison with the integrated corrected emission spectrum of a quinine sulfate standard, whose quantum yield in 0.1 M H_2SO_4 was assumed to be 0.55 (excitation at 366 nm). IR spectra were recorded on a JASCO FTIR-410 spectrophotometer at room temperature. ^{1}H- (300 MHz) and ^{13}C- (75 MHz) NMR spectra were recorded on a JEOL Always 300 spectrometer. Tetramethylsilane was used as an internal reference for ^{1}H- and ^{13}C-NMR measurements in $CDCl_3$ and CD_3CN. 3-(Trimethylsilyl)propionic-2,2,3,3-d_4 acid (TSP) sodium salt was used as an external reference for ^{1}H- and ^{13}C-NMR measurements in D_2O. The pD values in D_2O were corrected for deuterium isotope effects using pD=(pH-meter reading)+0.40. Elemental analyses were performed on a Perkin-Elmer CHN 2400 analyzer. Thin-layer (TLC) and silica gel column chromatographies were performed using a Merck 5554 (silica gel) TLC plate and Fuji Silysia Chemical FL-100D, respectively.

Material Preparation Quinolinol derivatives **9** and **11** were prepared according to the method reported by Imperiali *et al*.[78,79] The preparation of 8-quinolinol-pendant cyclen derivatives **1**, **2**, **3**, and **4** were reported previously.[38,40]

8-Benzenesulfonyloxy-5-*N*,*N*-dimethylaminosulfonylquinaldine (5a)[38] A solution of benzenesulfonyl chloride (164 μl, 1.28 mmol) in THF (10 ml) was added dropwise to a solution of 5-*N*,*N*-dimethylaminosulfonyl-8-hydroxy-quinaldine (**9**) (256 mg, 1.00 mmol) and Et_3N (210 μl, 1.5 mmol) in

THF (10 ml). After stirring for 5 h at room temperature, the reaction mixture was poured into water and the solution was extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq, 0.1 M aq. HCl, and brine. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting solid was recrystallized from CH_2Cl_2/EtOH to give **5a** (354 mg, 87% yield) as colorless crystals: mp 131.5—132.0 °C. IR (KBr) cm^{-1}: 3094, 2951, 1602, 1500, 1452, 1373, 1323, 1193, 1144, 1115, 1092, 1060, 957, 863, 834, 796, 756, 739, 726. ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s), 2.81 (6H, s), 7.36 (1H, d, J=9.0 Hz, ArH), 7.49 (2H, t, J=7.7 Hz, PhH), 7.62 (1H, t, J=7.5 Hz, PhH), 7.73 (1H, d, J=8.2 Hz, ArH), 8.01 (2H, d, J=7.1 Hz, PhH), 8.11 (1H, d, J=8.2 Hz, ArH), 8.92 (1H, d, J=9.0 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 25.1, 37.4, 121.3, 124.1, 124.7, 128.7, 128.8, 128.8, 131.8, 133.5, 134.1, 136.1, 141.3, 148.6, 160.5. *Anal.* Calcd for $C_{18}H_{18}N_2O_5S_2$: C, 53.19; H, 4.46; N, 6.89. Found: C, 52.73; H, 4.00; N, 6.76.

5-*N*,*N*-Dimethylaminosulfonyl-8-(4-methoxybenzenesulfonyloxy)quinaldine (5b) A solution of 4-methoxybenzenesulfonyl chloride (186 mg, 0.90 mmol) in CH_2Cl_2 (3 ml) was added to a solution of **9** (200 mg, 0.75 mmol) and Et_3N (99 mg, 0.98 mmol) in CH_2Cl_2 (5 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 1 h, to which H_2O (10 ml) was added and then the biphasic reaction mixture was vigorously stirred for 30 min. The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2. The combined organic layer was washed with saturated aq. K_2CO_3 and water, dried over K_2CO_3, filtrated, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1 : 3 hexanes/EtOAc) and recrystallization from AcOEt to afford **5b** (170 mg, 52% yield) as a colorless powder: mp 161.5—163.0 °C. IR (KBr) cm^{-1}: 3087, 2914, 2847, 1597, 1498, 1464, 1351, 1321, 1264, 1188, 1141, 1115, 1094, 1060, 1027, 957, 864, 829, 810, 782, 729, 585. ^{1}H-NMR ($CDCl_3$) δ: 2.61 (3H, s), 2.81 (6H, s), 3.86 (3H, s), 6.92 (2H, d, J=8.8 Hz), 7.37 (1H, d, J=9.0 Hz), 7.73 (1H, d, J=8.1 Hz), 7.92 (2H, d, J=8.8 Hz), 8.09 (1H, d, J=8.1 Hz), 8.92 (1H, d J=9.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.1, 37.4, 55.7, 113.9, 121.2, 124.0, 124.7, 127.3, 128.9, 131.2, 131.6, 133.5, 141.4, 148.8, 160.4, 163.6, 164.1. *Anal.* Calcd for $C_{19}H_{20}N_2O_6S_2$: C, 52.28; H, 4.62; N, 6.42. Found: C, 52.08; H, 4.32; N, 6.42.

8-(4-Bromobenzenesulfonyloxy)-5-*N*,*N*-dimethylaminosulfonylquinaldine (5c) This sulfonate was prepared as colorless needles (60% yield) from **9** and 4-bromobenzenesulfonyl chloride in a manner similar to that described for **5b**: mp 171.5—172.0 °C. IR (neat) cm^{-1}: 3097, 2912, 1599, 1575, 1496, 1377, 1343, 1189, 1150, 1092, 1059, 1011, 955, 796, 746, 720, 622, 437. ^{1}H-NMR ($CDCl_3$) δ: 2.55 (3H, s), 2.82 (6H, s), 7.38 (1H, d J=9.0 Hz, ArH), 7.63 (2H, d, J=8.7 Hz, BrArH), 7.75 (1H, d, J=8.1 Hz, ArH), 7.86 (2H, d, J=8.7 Hz, BrArH), 8.11 (1H, d, J=8.1 Hz, ArH), 8.93 (1H, d, J=9.0 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 25.1, 37.4, 121.6, 124.2, 124.7, 128.8, 129.5, 130.3, 132.1, 132.2, 133.4, 135.2, 141.2, 148.5, 160.6. *Anal.* Calcd for $C_{18}H_{17}BrN_2O_5S_2$: C, 44.54; H, 3.53; N, 5.77. Found: C, 44.46; H, 3.51; N, 5.81.

5-*N*,*N*-Dimethylaminosulfonyl-8-pentafluorobenzenesulfonyloxyquinaldine (5d) This sulfonate was prepared as a pale yellow powder (78% yield) from **9** and pentafluorobenzenesulfonyl chloride in a manner similar to that described for **5b**: mp 163—166 °C. IR (KBr) cm^{-1}: 3095, 2975, 1648, 1602, 1523, 1507, 1395, 1345, 1194, 1148, 1102, 1055, 994, 962, 866, 854, 832, 817, 722, 625. ^{1}H-NMR ($CDCl_3$) δ: 2.46 (3H, s), 2.83 (6H, s), 7.42 (1H, d, J=9.0 Hz, ArH), 7.80 (1H, d, J=8.1 Hz, ArH), 8.15 (1H, d, J=8.1 Hz, ArH), 8.99 (1H, d, J=9.0 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 24.8, 37.4, 122.1, 124.4, 124.4, 124.9, 128.8, 129.8, 133.0, 133.9, 134.0, 140.8, 147.2, 148.3, 160.7. HR-FAB-MS *m*/*z*: 497.0263 (Calcd for $C_{18}H_{14}F_5N_2O_5S_2$: 497.0264).

8-Benzenesulfonyloxyquinaldine (6)[78] This sulfonate was prepared as colorless needles (64% yield) from 8-hydroxyquinaldine (**10**) and benzenesulfonyl chloride in a manner similar to that for **5b**: mp 116.0—117.5 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.50 (3H, s), 7.19 (1H, d, J=8.4 Hz), 7.40—7.47 (3H, m), 7.57 (1H, tt, J=7.4, 1.3 Hz), 7.66 (2H, dt, J=8.8, 1.3 Hz), 7.95—8.00 (3H, m). ^{13}C-NMR ($CDCl_3$) δ: 25.2, 122.6, 123.1, 125.1, 126.8, 127.8, 128.5, 128.8, 133.7, 135.7, 136.5, 140.8, 144.9, 159.6.

8-Benzenesulfonyloxy-5,7-bis(*N*,*N*-dimethylaminosulfonyl)quinaldine (7) A solution of 5,7-bis(*N*,*N*-dimethylaminosulfonyl)-8-quinolinol (**11**)[78,79] (430 mg, 1.1 mmol) and benzenesulfonyl chloride (190 μl, 1.4 mmol) and 4-dimethylaminopyridine (28 mg, 0.24 mmol) in CH_2Cl_2 (5 ml) was stirred at the reflux temperature for 24 h. The separation and purification were carried out in a similar manner to that used for the preparation of **5b** to obtain **7** (475 mg, 74% yield) as a colorless powder: mp 151.0—152.5 °C. IR (neat) cm^{-1}: 3097, 3066, 2923, 1495, 1450, 1372, 1345, 1284, 1245, 1197, 1181, 1165, 1144, 1075, 968, 797, 764, 718, 607. ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s), 2.82 (6H, s), 2.91 (6H, s), 7.49 (1H, d, J=9.0 Hz, ArH), 7.62 (2H, t, J=8.4 Hz, PhH), 7.74 (1H, t, J=8.4 Hz, PhH), 8.06 (2H, d, J=8.4 Hz, PhH), 8.53 (1H, s, ArH), 9.00 (1H, d, J=9.0 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 24.8, 37.6, 37.6, 125.9 126.6, 128.1, 128.4, 128.8, 130.1, 132.2, 133.6, 133.8, 139.0, 142.2, 148.2, 161.5. *Anal.* Calcd for $C_{20}H_{23}N_3O_7S_3$: C, 46.77; H, 4.51; N, 8.18. Found: C, 46.77; H, 4.18; N, 8.16.

5-*N*,*N*-Dimethylaminosulfonyl-8-methylsulfonyloxyquinaldine (8) Methanesulfonyl chloride (28 μl, 0.36 mmol) was added to a solution of **9** (80 mg, 0.30 mmol) and Et_3N (28 μl, 0.39 mmol) in CH_2Cl_2 (2 ml) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, to which water (0.5 ml) was added. After the whole was vigorously stirred for 30 min, the reaction mixture was extracted with CH_2Cl_2. The combined organic layer was washed with sat. aq. K_2CO_3 and sat. aq. NaCl, dried over K_2CO_3, filtered, and concentrated under reduced pressure. The remaining residue was purified by silica gel column chromatography (hexanes/AcOEt) to afford **8** as a colorless powder. After recrystallization from hexane/AcOEt, **8** was obtained as colorless prisms (55 mg, 53% yield): mp 134—136 °C. IR (KBr) cm^{-1}: 3092, 2918, 1499, 1464, 1358, 1342, 1180, 1151. ^{1}H-NMR ($CDCl_3$) δ: 2.79 (3H, s), 2.84 (6H, s), 3.56 (3H, s), 7.50 (1H, d, J=9.0 Hz, ArH), 7.73 (1H, d, J=8.0 Hz, ArH), 8.13 (1H, d, J=8.2 Hz, ArH), 9.03 (1H, d, J=9.0 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 25.3, 37.5, 39.7, 122.0, 124.3, 124.9, 129.1, 132.1, 134.1, 141.4, 148.9, 168.8. *Anal.* Calcd for $C_{13}H_{16}N_2O_5S_2$: C, 45.34; H, 4.68; N, 8.13. Found: C, 45.41; H, 4.25; N: 8.00.

1-Benzenesulfonyloxynaphthalene (14)[80] This sulfonate was obtained as colorless fine cubic crystals (70% yield) from the reaction of 1-naphthol (**15**) and benzenesulfonyl chloride in a manner similar to that described for **5a**. ^{1}H-NMR ($CDCl_3$) δ: 7.20 (1H, d, J=7.3 Hz), 7.30—7.46 (5H, m), 7.57 (1H, t, J=7.5 Hz), 7.71 (1H, d, J=7.7 Hz), 7.77 (1H, d, J=8.0 Hz), 7.85—7.89 (3H, m). ^{13}C-NMR ($CDCl_3$) δ: 118.4, 121.5, 125.0, 126.6, 127.1, 127.1, 127.6, 128.3, 129.1, 134.2, 134.6, 135.4, 145.6.

2,4,7-Tris(*N*,*N*-dimethylaminosulfonyl)-1-naphthol (17) A mixture of 1-naphthol (1.0 g, 6.9 mmol) and chlorosulfonic acid (10 ml) was stirred at 130 °C for 2 h and poured into ice (50 g). The insoluble residue was isolated by filtration and dried under reduced pressure. The resulting solid was dissolved in CH_2Cl_2, to which a 2.0 M solution of Me_2NH (20 mmol) in THF (10 ml) was added, and the whole was stirred for 12 h at 25 °C. The solvent was removed under reduced pressure and the remaining residue was recrystallized from AcOEt to give **17** (1.2 g, 36% yield) as a colorless powder: mp 223—226 °C. IR (neat) cm^{-1}: 3244, 3021, 2970, 2893, 2815, 1616, 1563, 1500, 1459, 1342, 1262, 1189, 1163, 1073, 958, 763, 718, 604, 556, 425. ^{1}H-NMR ($CDCl_3$) δ: 2.81 (6H, s), 2.86 (6H, s), 2.89 (6H, s), 8.09 (1H, dd, J=9.0, 1.8 Hz), 8.37 (1H, s), 8.84 (1H, d, J=9.0 Hz), 8.94 (1H, d, J=1.8 Hz), 10.62 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 37.3, 37.7, 37.9, 112.5 125.1, 125.4, 125.5, 126.8, 128.4, 130.9, 133.7, 135.1, 158.2. HR-FAB-MS *m*/*z*: 466.0776 (Calcd for $C_{16}H_{24}N_3O_7S_3$: 466.0776).

1-Benzenesulfonyloxy-2,4,7-tris(*N*,*N*-dimethylaminosulfonyl)naphthalene (16) This sulfonate was isolated as a colorless powder (29% yield) from the reaction of **17** and benzenesulfonyl chloride in a manner similar to that described for **14**. IR (neat) cm^{-1}: 3097, 3019, 2961, 1555, 1451, 1344, 1163, 1054, 960, 746, 719, 450. ^{1}H-NMR ($CDCl_3$) δ: 2.63 (6H, s), 2.87 (6H, s), 2.97 (6H, s), 7.66 (2H, t, J=8.1 Hz, PhH), 7.80 (1H, t, J=8.1 Hz, PhH), 8.12—8.18 (3H, m), 8.61 (1H, s, ArH), 8.97 (1H, d, J=9.0 Hz, ArH), 9.18 (1H, d, J=1.5 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 37.5, 37.6, 38.0, 126.9, 126.9, 128.1, 128.3, 129.2, 129.3, 130.1, 130.8, 133.3, 133.8, 135.3, 136.4, 148.0. *Anal.* Calcd for $C_{22}H_{27}N_3O_9S_4$: C, 43.62; H, 4.49; N, 6.94. Found: C, 43.48; H, 4.16; N, 6.59.

2-Benzenesulfonyloxyanthraquinone (18) This sulfonate was obtained as a brown solid (70% yield) from 2-hydroxyanthraquinone and benzenesulfonyl chloride in a manner similar to that described for **5b**. IR (neat) cm^{-1}: 1677, 1591, 1480, 1449, 1381, 1325, 1291, 1203, 1183, 1132, 1091, 984, 931, 866, 790, 742, 712, 687, 443. ^{1}H-NMR ($CDCl_3$) δ: 7.50 (1H, dd, J=8.4, 2.4 Hz), 7.58 (2H, t, J=7.5 Hz), 7.72 (1H, t, J=7.5 Hz), 7.80—7.85 (3H, m), 7.90 (2H, d, J=8.1 Hz), 8.27—8.32 (3H, m). ^{13}C-NMR ($CDCl_3$) δ: 120.5, 127.4, 127.9, 128.5, 129.5, 129.7, 131.9, 133.2, 133.3, 134.3, 134.5, 134.8, 135.0, 135.3, 153.8, 181.8, 181.9. HR-FAB-MS *m*/*z*: 365.0484 (Calcd for $C_{20}H_{13}O_5S$: 365.0484).

1-Naphthalenesulfonic Acid Phenyl Ester (19)[81] A solution of 1-naphthalenesulfonyl chloride (226 mg, 2.0 mmol) in $CHCl_3$ (5 ml) was added to a solution of phenol (94 mg, 1.0 mmol) and Et_3N (0.28 ml, 2.0 mmol) in $CHCl_3$ (3 ml) at 0 °C. After stirring for 5 h at room temperature, the reaction mixture was washed with water, NH_4Cl aq., Na_2CO_3 aq., and brine. The organic layer was dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The remaining residue was purified by silica gel column chromatography (hexanes/CH_2Cl_2) to give **19** (248 mg, 87% yield) as a colorless

amorphous solid. IR (KBr) cm^{-1}: 1595, 1585, 1508, 1485, 1371, 1204, 1191, 1169, 1152, 1139, 855, 802, 786, 769, 729, 692, 587, 510. ^{1}H-NMR ($CDCl_3$) δ: 6.84—6.88 (2H, m), 7.14—7.26 (3H, m), 7.46 (1H, t, J=7.9 Hz), 7.68 (1H, t, J=7.4 Hz), 7.79 (1H, t, J=7.7 Hz), 8.08 (1H, d, J=7.4 Hz), 8.13 (1H, d, J=8.5 Hz), 8.83 (1H, d, J=8.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 121.9, 123.8, 124.9, 127.0, 127.2, 128.4, 128.8, 128.9, 129.5, 130.6, 131.1, 131.1, 133.9, 35.6, 149.5.

5-(*N*,*N*-Dimethylamino)naphthalenesulfonyloxybenzene (20)[82] A solution of dansyl chloride (135 mg, 0.50 mmol) in $CHCl_3$ (5 ml) was added to a mixture of phenol (47 mg, 0.50 mmol) and Et_3N (0.14 ml, 1.0 mmol) in $CHCl_3$ (1.5 ml) at 0 °C. After stirring for 5 h at room temperature, the reaction mixture was washed with water, NH_4Cl aq., Na_2CO_3 aq., and brine. The organic layer was dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The remaining residue was purified by silica gel column chromatography (hexanes/CH_2Cl_2) to give **20** (84 mg, 51% yield) as a pale yellow oil. IR (KBr) cm^{-1}: 1587, 1572, 1487, 1456, 1410, 1369, 1310, 1234, 1204, 1191, 1172, 1144, 861, 784, 724, 689, 629, 573. ^{1}H-NMR ($CDCl_3$) δ: 2.91 (6H, s), 6.87—6.91 (2H, m), 7.16—7.21 (3H, m), 7.25 (1H, d), 7.43 (1H, t, J=8.0 Hz), 7.68 (1H, t, J=8.2 Hz), 8.06 (1H, d, J=7.3 Hz), 8.48 (1H, d, J=8.6 Hz), 8.59 (1H, d, J=8.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 45.3, 115.5, 119.4, 122.0, 122.8, 126.9, 128.9, 129.5, 129.6, 130.0, 130.9, 131.1, 131.9, 149.6, 151.8.

8-Quinolinesulfonic Acid Phenyl Ester (21) 8-Quinolinesulfonyl chloride (250 mg, 1,1 mmol) was added to a solution of phenol (104 mg, 1.1 mmol) and Et_3N (220 mg, 2.2 mmol) in CH_2Cl_2 (6 ml) at 0 °C. The reaction mixture was stirred for 2 h and concentrated under reduced pressure. The resulting solid was recrystallized from AcOEt to give **21** (310 mg, 99% yield) as a colorless powder. IR (neat) cm^{-1}: 1596, 1561, 1487, 1372, 1216, 1192, 1144, 861, 836, 788, 737, 693, 589, 448. ^{1}H-NMR ($CDCl_3$) δ: 7.03 (2H, dd, J=7.7, 2.0 Hz), 7.14—7.24 (3H, m), 7.59—7.63 (2H, m), 8.14 (1H, dd, J=8.2, 1.3 Hz), 8.30 (1H, dd, J=8.2, 1.6 Hz), 8.38 (H, dd, J=7.4, 1.3 Hz), 9.27 (1H, dd, J=4.2, 1.6 Hz). ^{13}C-NMR ($CDCl_3$) δ: 122.1, 122.5, 125.2, 126.9, 128.9, 129.5, 132.6, 134.0, 135.3, 136.6, 144.0, 149.9, 152.3. HR-FAB-MS m/z: 286.0539 (Calcd for $C_{15}H_{12}NO_3S$: 286.0538).

Photoreactions Followed by NMR and HPLC In a typical experiment, a 1 mM solution of substrate in a 9 : 1 mixture of CD_3CN and D_2O (10 mM HEPES at pD 7.4) was irradiated with a 150 W Xe lamp equipped in a spectrofluorometer (JASCO FP-6500 with band-width 20 nm). The reaction mixtures were analyzed by ^{1}H-NMR and/or high performance liquid chromatography (HPLC) using an ODS column (Senshu Pegasil ODS S-100) or by gel permeation liquid chromatography (GPLC).

Determination of Quantum Yields of Photolysis Quantum yields for the photocleavage of **5** were determined as follows: Method A: A 5—50 μM solution of a given substrate in CH_3CN and HEPES buffered water (10 mM, pH 7.4) (9 : 1) was placed into 1×1 cm quartz cell, and irradiated with 150 W Xe lamp in a spectrofluorometer (JASCO FP-6500 with a band-width of 5 nm). The initial rate of the photolysis (v_i) was determined by a UV–Vis spectrometer and high performance liquid chromatography (HPLC, ODS-column with a CH_3CN–phosphate buffer (pH 6.0) (5 : 5) as the eluent). The quantum yield was calculated using the equation $\Phi = v_i \times V / \{I_0 \times (1 - 10^{-abs})\}$, where V is the volume of the reaction solution, I_0 is the number of photon per second at given wavelength, and *abs* is the initial absorbance (cell length=1 cm) of **5** (0.073 at 328 nm for **5a**). The I_0 value was determined by means of a ferroxalate actinometry.[46] Method B: A 2.0 ml of 2.0 mM solution of a given substrate in CH_3CN and HEPES buffered water (10 mM, pH 7.4) (9 : 1) was placed into 1×1 cm quartz cell, and irradiated with 150 W Xe lamp in a spectrofluorometer (JASCO FP-6200 with a band-width of 20 nm). The initial absorbance (cell length=1 cm) was >3. The numbers of reacted molecules after irradiation was determined by HPLC (ODS-column with a MeOH–phosphate buffer (pH 6.0) (6 : 4 or 7 : 3) as the eluent). The quantum yield was calculated using the equation Φ=(number of reacted molecules)/(I_0×irradiation time). Quantum yields of photolysis for other substrates were determined in a similar manner.

Quenching Examination The 50 μM solutions of substrates in CH_3CN and H_2O (10 mM HEPES at pH 7.4) with given concentrations of potassium sorbate or Et_3N were placed in a 1×1 cm quartz cell and irradiated with a 150 W Xe lamp. The relative rates of photocleavage were determined by UV–Vis spectrometry.

Benzophenone Sensitizing Examination A mixture of **5a** (1 mM) and benzophenone (10 mM) in a mixture of CD_3CN and D_2O (10 mM HEPES at pD 7.4) was irradiated using a 150 W Xe lamp (at 355 nm) for 15 min and the reaction mixture then analyzed by ^{1}H-NMR spectroscopy.

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43) The quantum yields for photodecomposition of **19**, **20**, and **21** were estimated to be 1.4×10^{-4} (irradiation at 322 nm), 0.3×10^{-4} (irradiation at 350 nm), 1.0×10^{-4} (irradiation at 313 nm), respectively.
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