

Photochemistry of Squaraine Dyes. 1. Excited Singlet, Triplet, and Redox States of Bis[4-(dimethylamino)phenyl]squaraine and Bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine

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Singlet and triplet excited states and the reduced and oxidized forms of two squaraine dyes, bis[4-(dimethylamino)phenyl]squaraine (SQH) and bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine (SQOH), have been investigated by picosecond and nanosecond laser flash photolysis. Both singlet and triplet excited states of SQH and SQOH have distinct and intense absorption maxima in the visible region. The lifetime of $^1\text{SQOH}^*$ ($\tau_s = 3.0$ ns) is considerably higher than $^1\text{SQH}^*$ ($\tau_s = 1.5$ ns) as the substituent OH group restricts rotational relaxation of the excited state. Both squaraine dyes exhibit poor intersystem crossing efficiency ($\phi_{isc} < 0.001$). However, the excited triplets of SQH and SQOH can be generated by triplet-triplet sensitization. The oxidized forms of these dyes, which were generated by photolytic and pulse radiolytic methods, exhibit absorption maxima in the vicinity of the ground-state absorption. The cation radical of SQOH can also be generated by charge transfer between excited dye and TiO_2 semiconductor colloids.

Introduction

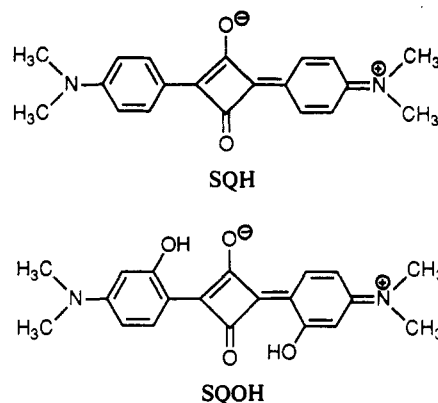
Photosensitizing dyes that absorb strongly in the visible region are important in various imaging applications and solar energy conversion processes.¹ In our earlier studies we employed various dyes to extend the photoresponse of large bandgap semiconductors.²⁻⁴ We have now undertaken a detailed photophysical and photochemical investigation of a series of squaraine dyes. Although technological applications of several squaraine dyes have been investigated extensively, the electronic spectral characterizations are limited to few absorption and emission studies.^{5,6}

Recently an effort has been made by Law to elucidate spectroscopic⁷⁻¹⁰ and electrochemical¹¹ properties of squaraine dyes. The symmetric D-A-D (donor-acceptor-donor) arrangement of squaraine dyes has an interesting effect on the formation of intramolecular charge-transfer states. With the aid of MNDO and CNDO calculations, it has been suggested that SQH is highly polarized, with the anilino moiety being an electron donor (D) and the central C_4O_2 unit being an electron acceptor (A).¹² The squaraines also form a solute-solvent complex in organic solvents, the equilibrium constant of which is dependent on D-A-D charge-transfer character of the squaraine. The coplanarity of the D-A-D structure of squaraine becomes increasingly distorted as the solute-solvent association increases.⁸ Emissions from the three different excited states, viz., free squaraine, solute-solvent complex, and a twisted excited state as a result of C-C bond rotation, have also been characterized in this study.

Substituent groups also vary the excited-state energetics and the electronic properties of squaraines.⁸ The influence of substituent groups on the excited-state processes can be important in determining the photosensitivity of squaraine dyes. We have now undertaken a detailed photophysical and photochemical investigation of a series of dyes. The behavior of excited singlet and triplet states as well as the reduced and oxidized forms of the two squaraine dyes bis[4-(dimethylamino)phenyl]squaraine (SQH) and bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine (SQOH) are presented here.

Experimental Section

Materials. SQH and SQOH were synthesized by reacting squaric acid with *N,N*-dimethylaniline and (dimethylamino)-phenol, respectively, by a reported procedure.¹³ 9,10-Dibromoanthracene (Aldrich) was used as supplied. All solvents were of spectrophotometric grade. Colloidal TiO_2 suspension in acetonitrile



was prepared by the method described earlier.²

Methods. All experiments were performed at room temperature (~ 296 K) unless otherwise stated, and solutions were deaerated by bubbling with nitrogen or argon. Absorption spectra were measured with a Perkin-Elmer 3840 diode array spectrophotometer. Corrected fluorescence emission spectra were recorded with a SLM photon-counting spectrofluorometer.

Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were performed with a Quanta-Ray DCR-1 Nd:YAG system to generate 532-nm (second-harmonic) laser pulses (~ 6 -ns pulse width).¹⁴ The experiments were performed in a rectangular

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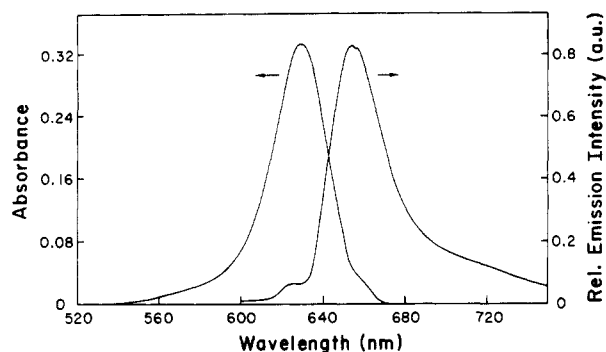


Figure 1. Absorption and emission spectra of 1.1 μM SQH in methylene chloride (excitation wavelength for corrected emission spectrum was 590 nm).

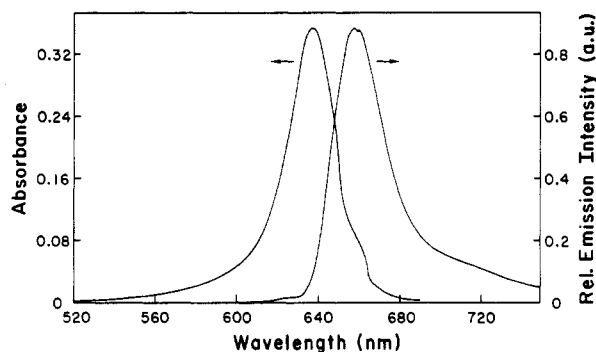


Figure 2. Absorption and emission spectra of 1 μM SQOH in methylene chloride (excitation wavelength for corrected emission spectrum was 590 nm).

quartz cell of 6-mm path length with a right-angle configuration between the directions of laser excitation and analyzing light. A typical experiment consisted of a series of 5–10 shots per single measurement, and the average signal was processed with an LSI-11 microprocessor interfaced to a VAX-370 computer.

Picosecond laser flash photolysis experiments were performed with a mode-locked 532-nm laser pulse from Quantel YG-501DP Nd:YAG (output, 4 mJ/pulse; pulse width, ~ 18 ps). The white continuum picosecond probe pulse was generated by passing the residual fundamental output through a $\text{D}_2\text{O}/\text{H}_2\text{O}$ solution. The excitation and the probe pulse were incident on the sample cell at right angles. The output was fed to a spectrograph (HR-320, ISDA Instruments, Inc.) with fiber optic cables and was analyzed with a dual diode array detector (Princeton Instruments, Inc.), interfaced with an IBM AT computer. The details of the experimental setup and its operation are described in detail elsewhere.^{15a,b} Time zero in these experiments corresponds to the end of the excitation pulse. All the lifetime and rate constants reported in this study are within the experimental error of $\pm 5\%$.

Pulse Radiolysis. For pulse radiolysis experiments, irradiation was performed with electron pulses (5 ns, $\sim 10^{17}$ eV g^{-1} pulse $^{-1}$) from the Notre Dame 7 MeV ARCO-LP-7 linear accelerator. A description of the computer-controlled kinetic spectrophotometer and data collection system is available elsewhere.¹⁶

Results and Discussion

Absorption and Emission Characteristics. The absorption and emission spectra of SQH and SQOH in methylene chloride are shown in Figures 1 and 2, and their spectral characteristics are summarized in Table I. Both SQH and SQOH have intense and sharp absorption bands in the visible region with absorption maximum at 628 and 636 nm, respectively. The reported extinction coefficients at the absorption maximum are 3.09×10^5

TABLE I: Excited-State Properties of Squaraine Dyes in Methylene Chloride

	SQH	SQOH
abs max ($S_0 - S_1$), nm	628 (627.6) ^a	636 (635.9) ^a
em max ($S_1 - S_0$), nm	654	658
excited singlet		
abs max ($S_1 - S_n$), nm	480	475
ϕ_f	0.45 (0.65) ^a	0.84 (0.86) ^a
τ_f , ns	1.5	3.0
excited triplet		
abs max ($T_1 - T_n$), nm	540	565
τ_T , μs	35.2	34.9
$\Delta\epsilon_T^{\text{max}}$, $10^4 \text{ M}^{-1} \text{ s}^{-1}$	3.05	1.30

^a From ref 8.

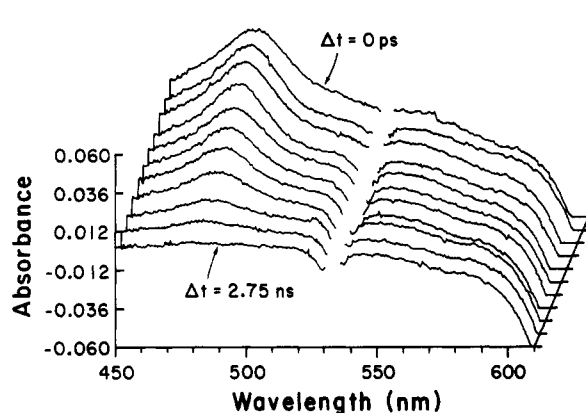


Figure 3. Transient absorption spectra of singlet excited SQH in methylene chloride. The spectra were recorded following the 532-nm laser pulse excitation of 10 μM SQH in methylene chloride at time intervals 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.35, 0.5, 0.75, 1.75, and 2.75 ns.

$\text{M}^{-1} \text{ cm}^{-1}$ for SQH and $3.31 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for SQOH.⁸

The singlet excited-state energies (E_s) of these squaraine dyes as determined from the crossover point between the normalized absorption and emission spectra were 186.3 kJ mol^{-1} for $^1\text{SQH}^*$ and 184.6 kJ mol^{-1} for $^1\text{SQOH}^*$. The emission maxima of SQH and SQOH were observed at 654 and 658 nm, respectively. In an earlier study⁸ it was reported that the emission spectrum consists of three emission bands, designated α , β , and γ in the order of decreasing intensity. By carefully studying the solvent and temperature effects, Law^{8,9} resolved these emission bands, which arise as a result of free dye (α), dye-solvent complex (β), and a twisted excited state resulting from C-C bond rotation (γ). In the present study the spectral resolution is rather limited to resolve the emission bands at room temperature. α and β bands are merged in the emission peak. A shoulder in the red region (~ 700 nm), which is mostly buried in the tail emission, is seen as a result of γ -emission.

The fluorescence quantum yield of SQH ($\phi_f = 0.45$) is slightly less than the reported value of 0.65.⁸ Measurements with dilute dye solutions were repeated several times to check this discrepancy in ϕ_f values. Such a discrepancy may arise from the dependence of ϕ_f values of squaraine dyes and geometry of apparatus as highlighted in a recent fluorescent study of squaraine dyes.¹⁰ The quantum yield of SQOH ($\phi_f = 0.84$) agreed well with the literature value. It has been reported⁸ that substituent OH groups and the increased dye-solvent interactions can enhance the fluorescence yields as they influence the excited-state relaxation processes.

Excited Singlet State. Earlier, we employed picosecond laser flash photolysis to characterize absorption characteristics of excited singlets of various dyes.^{17,18} The excited singlets of SQH and SQOH in methylene chloride were generated by direct excitation

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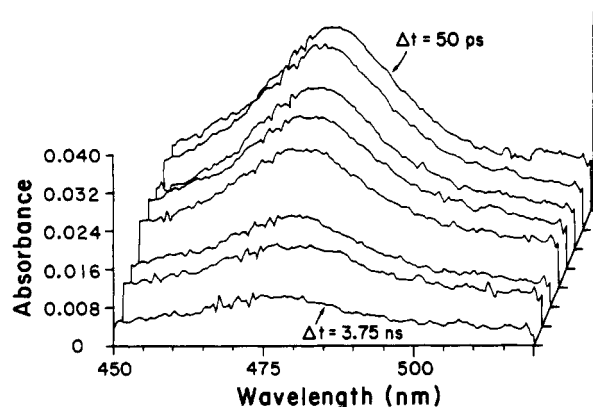


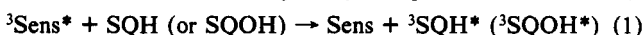
Figure 4. Transient absorption spectra of singlet excited SQOH in methylene chloride. The spectra were recorded following the 532-nm laser pulse excitation of 10 μ M SQOH in methylene chloride at time intervals 0.05, 0.15, 0.25, 0.5, 0.75, 1.75, 2.75, and 3.75 ns.

with 532-nm laser pulse. The transient absorption spectra recorded at different time intervals following the laser pulse (18-ps) excitation of SQH and SQOH are shown in Figures 3 and 4, respectively. The difference absorption spectra of 1 SQH* and 1 SQOH* exhibited absorption maxima at 480 and 475 nm, respectively. The decay of the transient was analyzed by fitting the absorption decay to the first-order kinetics. The lifetimes of 1 SQH* and 1 SQOH* were 1.5 and 3.0 ns, respectively. The lifetimes of these excited singlets were in good agreement with the fluorescence lifetimes measured by single photon counting technique. The emission decays of these dyes monitored at various wavelengths (in the region 630–700 nm) were single exponential, and the lifetime of the individual dye was independent of monitoring wavelength.

The fluorescence quantum yield and fluorescence lifetime of SQOH are about 2 times higher than for SQH. This suggests that the structural changes bring stability for the excited SQOH dye. The influence of structural changes on the electronic properties of squaraine dyes has been elegantly presented by Law.⁸ The substituent OH groups in SQOH facilitate H bonding between the C(2)OH group and the CO group in the four-membered ring, which in turn restricts the rotation relaxation process.

As discussed in an earlier section, the excited singlet of the squaraine dye can also exist in the solute-solvent complex form and a twisted excited state. An effort was made to probe these states in the transient absorption studies. Only a single absorption peak was observed in the wavelength region of 400–600 nm. Strong bleaching of the dye and the fluorescence emission limited the transient detection above 600 nm. It is possible that the previously proposed three forms of excited singlet states have absorption peaks in the region of 450–500 nm which collectively exhibit a broad absorption band. But so far our studies on excited singlet state, viz., emission lifetimes and transient absorption measurements, have failed to gather supportive evidence for the existence of multiple singlet excited states. It is necessary to carry out experiments that elucidate temperature and solvent effects on the transient absorption characteristics and time-resolved fluorescence measurements at different wavelengths for confirming the presence of multiple singlet excited states of squaraine dyes.

Excited Triplet State. The intersystem crossing efficiency for generation of triplet excited states of squaraine dyes was very small (<0.1%). Direct laser excitation of SQH and SQOH in CH_2Cl_2 produced negligibly small amounts of dye triplets. A triplet-triplet energy-transfer method¹⁹ was employed to generate 3 SQH* and 3 SQOH* in the laser flash photolysis experiments (reaction 1).



9,10-Dibromoanthracene ($E_T = 167.4 \text{ kJ mol}^{-1}$) was used as a sensitizer to generate the triplet excited state of the squaraine dye. Time-resolved transient absorption spectra recorded after

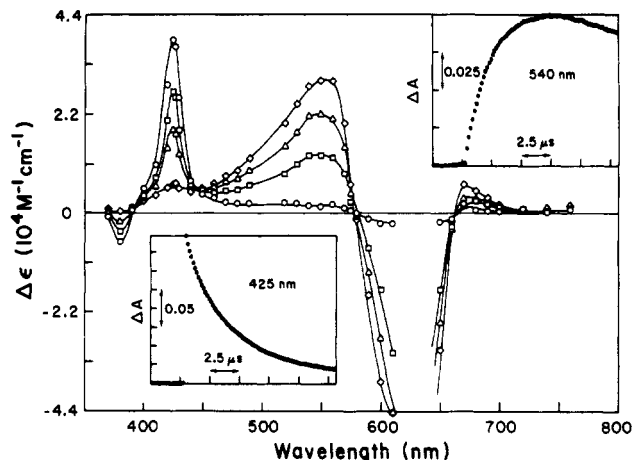


Figure 5. Energy transfer from triplet excited 9,10-dibromoanthracene to SQH in methylene chloride. Transient absorption spectra were recorded following 355-nm laser pulse excitation of a solution containing 0.1 mM 9,10-dibromoanthracene and 10 μ M SQH at time intervals (○) 0 μ s, (□) 1.3 μ s, (Δ) 3.0 μ s, and (◇) 8.0 μ s. The absorption-time profiles in the insets show the decay of 9,10-dibromoanthracene triplet at 425 nm and the formation of 3 SQH* at 540 nm.

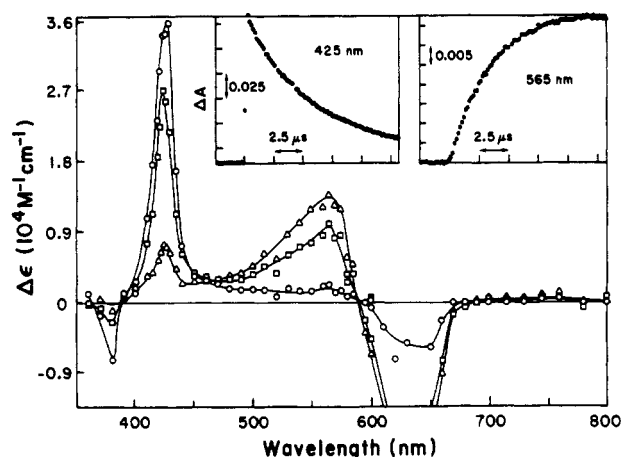


Figure 6. Energy transfer from triplet excited 9,10-dibromoanthracene to SQOH in methylene chloride. Transient absorption spectra were recorded following 355-nm laser pulse excitation of a solution containing 0.1 mM 9,10-dibromoanthracene and 10 μ M SQOH at time intervals (○) 0 μ s, (□) 1.3 μ s, and (Δ) 5.6 μ s. The absorption-time profiles in the insets show the decay of 9,10-dibromoanthracene at 425 nm and the formation of 3 SQOH* at 565 nm.

355-nm laser pulse excitation DBA in methylene chloride solution containing SQH and SQOH are shown in Figures 5 and 6, respectively. The transient absorption spectrum recorded immediately after the laser pulse excitation (λ_{max} 425 nm) corresponds to the sensitizer triplet. The difference absorption spectra recorded at time intervals greater than 10 μ s corresponded to the squaraine dye triplet. The absorption maxima of 3 SQH* and 3 SQOH* were at 540 and 565 nm, respectively. The growth at absorption peak matched well with the decay of the sensitizer triplet at 425 nm. The extinction coefficients were determined by recording the maximum absorbance values of 3 Sens* and 3 SQH* (or 3 SQOH*) and by the method described earlier.¹⁹ The maximum extinction coefficients of 3 SQH* and 3 SQOH* were 30 500 $\text{M}^{-1} \text{cm}^{-1}$ (540 nm) and 13 500 $\text{M}^{-1} \text{cm}^{-1}$ (565 nm), respectively.

The triplet lifetimes of both these dyes were $35 \pm 0.5 \mu\text{s}$. Although excited singlet lifetimes were different for these two dyes, the excited triplet lifetimes were similar. This shows that the decay of the triplet excited state is insensitive to the OH substituent group. The influence of other structural changes on the triplet excited state is currently being investigated.

One of the factors that influence triplet lifetimes in dyes is usually a self-quenching process. A diffusion-controlled self-quenching process has been observed for several dyes.^{12,20} Such

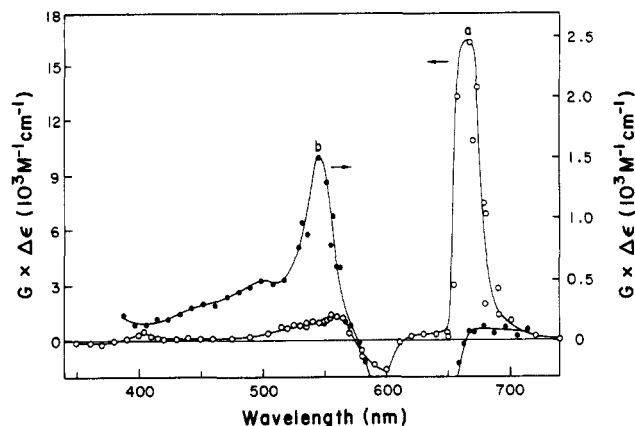


Figure 7. Transient absorption spectra of pulse radiolytically generated cation radical of (a) SQH and (b) SQOH in methylene chloride. The difference absorption spectra were recorded following the pulse radiolysis of O_2 -saturated CH_2Cl_2 solution containing 10–20 μM of (a) SQH ($\Delta t = 25 \mu s$) and (b) SQOH ($\Delta t = 60 \mu s$).

a quenching process was less significant ($k \lesssim 10^8 M^{-1} s^{-1}$) in the case of squaraine dyes. Because of low solubility of these dyes, it was not possible to study the triplet decay at high dye concentrations and determine the specific rate of self-quenching process precisely.

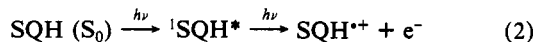
Pulse Radiolytic Oxidation of Squaraine Dyes. It has been shown recently that squaraine dyes exhibit two reversible oxidation peaks.¹¹ The oxidation potentials as determined by cyclic voltammetry were 0.35 and 0.41 V vs Ag/AgCl for SQH and SQOH, respectively. The low oxidation potentials facilitate oxidation of these dyes by oxidative radicals generated in pulse radiolysis. It has been shown earlier that radiolysis of chlorinated hydrocarbons such as methylene chloride produces highly oxidizing radical cations such as RCI^+ , which undergo diffusional charge transfer with an added substrate.²¹ The transient absorption spectrum of SQH^{++} recorded, following the pulse radiolysis of a solution of SQH in O_2 -saturated methylene chloride, is shown in Figure 7 (spectrum a). The transient difference absorption spectrum of SQH^{++} exhibits a sharp and intense band with a maximum at 670 nm. A strong overlap of SQH^{++} absorption with the SQH^{++} ground-state absorption was evident from the small bleaching observed in the S_0-S_1 absorption band of SQH.

The difference absorption spectrum of $SQOH^{++}$ (spectrum b in Figure 7) is distinctively different from that of SQH^{++} with a sharp maximum at 550 nm. An intense bleaching observed in the region of 585–675 nm corresponded to the depletion of the ground-state dye.

Photolytic Generation of Semioxidized Squaraine Dye. The cation radicals of squaraine dye can also be generated in laser flash photolysis experiments. We discuss here two separate methods that were employed to confirm the spectral features of SQH^{++} and $SQOH^{++}$, observed in pulse radiolysis experiments.

Photoionization of SQH. The dye SQH readily undergoes photoionization when subjected to high-intensity 532-nm laser excitation. The transient absorption spectra recorded following the laser flash excitation are shown in Figure 8. The sharp absorption band with a maximum at 670 nm closely matches the spectrum of SQH^{++} in Figure 7. The formation of SQH^{++} was prompt and decayed little during the time period of 50 μs .

Direct participation of the triplet excited state in the production of SQH^{++} can be ruled out since the intersystem crossing efficiency in this dye is rather poor. However, the singlet excited state, which has a tail absorption at 532 nm, is likely to undergo photoionization by absorbing the incident photons within the laser pulse duration (reaction 2). The evidence for this biphotonic process is gathered



from the dependence of SQH^{++} yield on the incident laser intensity.

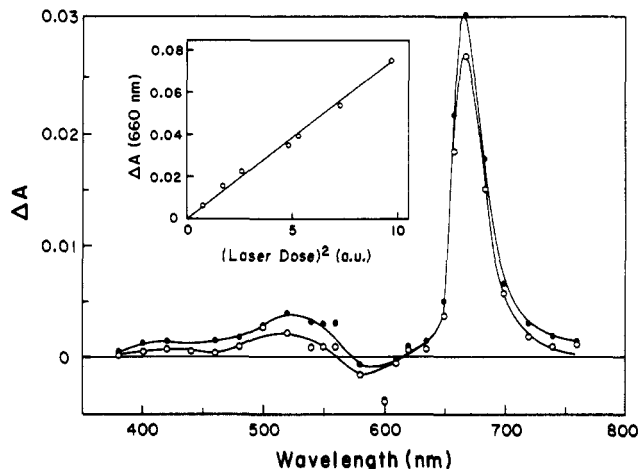


Figure 8. Photoionization of SQH in CH_2Cl_2 . The difference absorption spectra were recorded (●) 0 μs and (○) 50 μs after 532-nm excitation of 10 μM SQH in CH_2Cl_2 . The inset shows the dependence of SQH^{++} yield (ΔA at 660 nm) on the square of laser intensity.

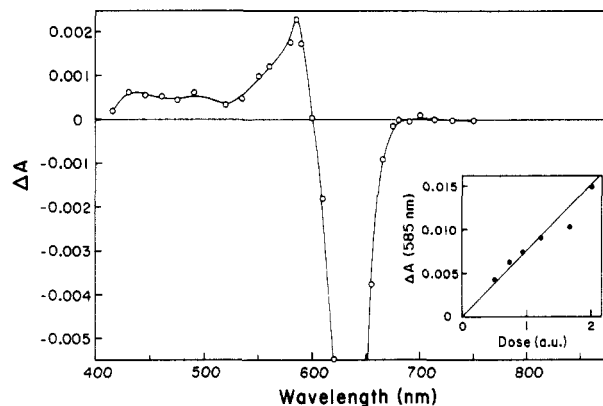


Figure 9. Generation of $SQOH^{++}$ in colloidal TiO_2 suspensions. Difference absorption spectra recorded following the 532-nm laser pulse excitation of 30 μM SQOH and 2 mM colloidal TiO_2 in 1:1 CH_2Cl_2/CH_3CN solution. Inset shows the linear dependence of $SQOH^{++}$ on the excitation laser intensity.

The linear dependence of SQH^{++} yield on square of the laser dose is shown in the inset of Figure 8.

Photoelectrochemical Generation of $SQOH^{++}$. We have recently investigated ultrafast photochemical processes which control the photosensitization properties of squaraine dyes.¹⁸ It was shown in this study that $SQOH$ is capable of injecting electrons into the conduction band of a large bandgap semiconductor such as colloidal TiO_2 (reaction 3). A majority of $SQOH^{++}$ generated in



this process recombined with injected electrons. Only a small fraction of $SQOH^{++}$ is able to survive such a recombination. The transient absorption spectra recorded following the 532-nm laser pulse excitation of $SQOH$ in colloidal TiO_2 suspension are shown in Figure 9. The transient absorption maximum at 580 nm closely matched the characteristics of $SQOH^{++}$ as observed in pulse radiolysis experiment (spectrum b in Figure 7). Surface adsorption and medium effect may be responsible for the red shift in the absorption maximum in colloidal TiO_2 suspension.

The laser intensity was kept low to avoid contributions from the photoionization process. The yield of $SQOH^{++}$ monitored from the absorbance at 585 nm exhibited a linear dependence on the laser dose. This intensity dependence clearly indicated that the production of $SQOH^{++}$ in colloidal TiO_2 suspension was monophotonic. The interfacial charge transfer between the semiconductor and the excited dye is important in controlling the photosensitization process.

Pulse Radiolytic Reduction of SQH. Pulse radiolysis of N_2 -saturated solutions of SQH in ethanol produced a transient with

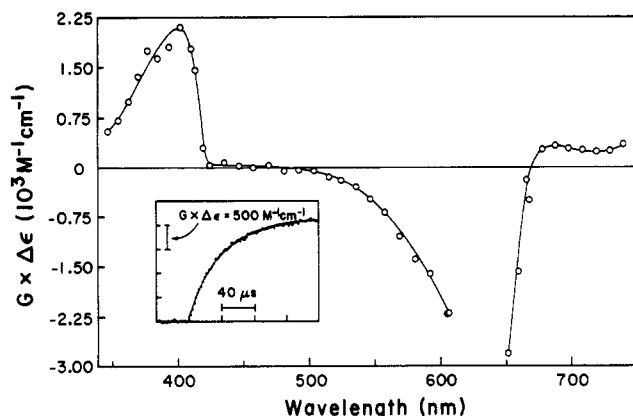


Figure 10. Transient absorption spectra of $\text{SQH}^{\bullet-}$ in methanol. The difference absorption spectrum was recorded following the pulse radiolysis of N_2 -saturated methanol solution containing $\sim 20 \mu\text{M}$ SQH. Inset shows the absorption time profile of $\text{SQH}^{\bullet-}$ at 405 nm.

an absorption maximum around 405 nm. The difference absorption spectrum of $\text{SQH}^{\bullet+}$ recorded 120 μs after pulse radiolysis of a solution of SQH is shown in Figure 10. The transient is assigned to the radical anion of SQH on the basis of the known reducing nature of irradiated ethanol.^{21,23} The formation of $\text{SQH}^{\bullet-}$, which is shown in the inset of Figure 10, exhibited pseudo-first-order growth with a half-life of 285 μs , and this is

attributed to the reaction between solvated electron and SQH. No decay of the radical anion was evident for up to 1 ms, following its formation. Because of the low solubility of SQOH in methanol, we were not able to characterize the radical anion of this dye. Photoelectrochemical reduction of SQOH in colloidal TiO_2 suspension indicates that the absorption maximum of $\text{SQOH}^{\bullet-}$ also lies in the region of 400 nm.²⁴

Conclusions

The two excited states (singlet and triplet) and oxidation and reduction states of SQH and SQOH studied in this work have distinct and intense absorption maxima in the visible or near-infrared region. The absorption maxima of cation radicals of these dyes lie in the vicinity of the ground-state absorption maxima. Direct optical excitation of these squaraine dyes leads to the production of only singlet excited state in large yields ($\phi = 0.45\text{--}0.84$). Hence, of the two excited states, the excited singlet state is expected to control the sensitization properties of squaraine dyes.

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Registry No. SQH, 43134-09-4; $\text{SQH}^{\bullet+}$, 136827-44-6; $\text{SQH}^{\bullet-}$, 136890-99-8; SQOH, 63842-83-1; $\text{SQOH}^{\bullet+}$, 136827-45-7; $\text{SQOH}^{\bullet-}$, 136891-00-4; TiO_2 , 13463-67-7; 9,10-dibromoanthracene, 523-27-3.

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Temperature Dependence of Solvated Electron Diffusion in H_2O and D_2O

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We present new measurements of hydrated electron mobility in both H_2O and D_2O for the full liquid temperature range at atmospheric pressure. Transient conductivity signals were measured following pulse radiolysis of aqueous alkaline solutions with 16-MeV electrons. The conductivity signal is proportional to the difference in specific conductance of the electron and the hydroxide (or deuteroxide) ion. To evaluate the signals in heavy water, ancillary measurements of the electron radiolysis yield vs temperature were made. The specific conductance of OD^- in heavy water is estimated using (light water) transfer numbers and tabulated here for the first time. In H_2O , the hydrated electron specific conductivity is found to be $184.0 \pm 0.7 \text{ S cm}^2$ at 298 K, giving a diffusion coefficient of $(4.90 \pm 0.02) \times 10^{-5} \text{ cm}^2/\text{s}$ with an average activation energy in the temperature range 15–90 °C of $4.81 \pm 0.03 \text{ kcal/mol}$, in good agreement with previous results. In D_2O the diffusion coefficient is $(3.88 \pm 0.03) \times 10^{-5} \text{ cm}^2/\text{s}$ at 298 K and has approximately the same activation energy ($4.69 \pm 0.04 \text{ kcal/mol}$). In comparison with classical ions, the electron diffusion has a higher activation energy, a more linear Arrhenius plot, and a slightly larger $\text{H}_2\text{O}/\text{D}_2\text{O}$ isotope effect. We suggest that these differences can be explained in terms of the essentially instantaneous adiabatic response of electrons to solvent librational motions coupled with the fast dielectric relaxation of water. The electron mobility in simple alcohols is apparently not enhanced because alcohol molecules cannot respond quickly enough to high-frequency distortions of the electron charge distribution.

I. Introduction

Apart from its broad and very intense absorption spectrum, one of the most distinctive properties of the hydrated electron is its very high rate of diffusion.¹ The fundamental physics behind the electron transport mechanism and its relationship to normal ion diffusion has been the object of theoretical speculation and modeling for many years.^{2–6} Coupled to the very high reduction

potential of hydrated electrons, this property ensures that many electron reactions are among the fastest "diffusion-controlled" processes in aqueous solution.⁷ Nevertheless, several hydrated electron reactions of key importance in the radiation environment

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