Triplet Excited-State Properties of the Monomer and Aggregate of Bis(2,4,6-trihydroxyphenyl)squaraine

U. Santhosh and Suresh Das*

Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum, 695 019, India

Received: September 14, 1999; In Final Form: November 17, 1999

The monomer and aggregate of the squaraine dye bis(2,4,6,-trihydroxyphenyl)squaraine (SQ) form weak complexes with triplet sensitizers such as benzophenone and 1-pyrenecarboxaldehyde. Excitation of the complex results in static triplet energy transfer from the sensitizer to the monomer and aggregate of SQ. The aggregate triplet undergoes unimolecular decay to its ground state ($\tau = 6.7\ \mu$s), whereas self-quenching of the monomer triplet state results in the formation of the aggregate ground state. The aggregate formed in this process undergoes a slow decay ($\tau = 0.69$ ms) to establish the ground-state monomer−aggregate equilibrium.

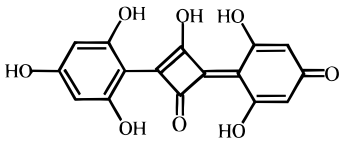
Introduction

The sharp and intense absorption of squaraine dyes in the visible and near-infrared region makes them attractive candidates for applications in optical recording,[1−3] photovoltaic,[4−7] and electrophotographic devices.[1,8] More recently, the nonlinear optical properties of these dyes have attracted a lot of attention.[9−13] Aggregation of the dyes within the heterogeneous environment present in most of the above applications tends to bring about drastic changes in their absorption and photophysical properties. For example, aggregation can have detrimental effects in the performance of photovoltaic devices,[14] whereas formation of noncentrosymmetric aggregates in Langmuir−Blodgett films has been shown to favor the second harmonic generating properties in squaraine dyes.[9,13] In view of this, there have been several efforts to study the nature of squaraine aggregates as well as the driving forces involved in the aggregation process.[13,15−22] Recent studies have shown that squaraine dye aggregates can exist as head-to-tail (J-type),[15] head-to-head (H-type),[16,22,23] and cyclic chiral[19] structures. Most spectroscopic studies of the excited states of dye aggregates have mainly dealt with their singlet excited states. Studies of Langmuir−Blodgett films, for example, have shown that cyanine J-aggregates behave as large arrays of coupled oscillators in which the singlet excitation energy can migrate efficiently.[24] Singlet energy transfer from and to dye aggregates from various molecules has been extensively studied. In contrast, the triplet excited-state properties of dye aggregates have not been well explored.[25−27] A triplet energy cascade from H-type aggregates of thionine to its monomer form has been reported recently.[26]

Singlet excited-state properties of J- and H-aggregates of squaraine dyes have been studied by time-resolved spectroscopy.[15,16] The aggregates were observed to undergo photodissociation in the excited state followed by “in cage” recombination, which led to the recovery of the ground state of the aggregate. Since the intersystem crossing efficiency of squaraine dyes is very low, their triplet-state properties could not be studied by direct excitation. We have recently observed that the monomer and aggregate of the squaraine dye bis(2,4,6-trihydroxyphenyl)squaraine (SQ) form ground-state complexes with triplet sensitizers such as benzophenone and 1-pyrenecarboxaldehyde. Excitation of the complex led to static energy transfer from sensitizer to SQ, resulting in the formation of the triplet excited state of the monomer and aggregate.

Experimental Section

Materials and Methods. Bis(2,4,6-trihydroxyphenyl)squaraine (SQ), synthesized from squaric acid and 1,3,5-trihydroxybenzene by a reported procedure,[28] was recrystallized twice from glacial acetic acid and dried in a vacuum at 368 K for 4 h to remove any acetic acid. All other chemicals and solvents were analytical reagents of the highest available purity.



SQ

Solutions were prepared in dry spectroscopic grade methanol or acetonitrile. Absorption spectra were recorded on a Shimadzu UV-3101 PC UV−vis−NIR scanning spectrophotometer.

Nanosecond laser flash photolysis experiments were carried out in an Applied Photophysics model LKS-20 laser kinetic spectrometer using the third harmonic (355 nm) of a Quanta Ray GCR-12 series pulsed Nd:YAG laser with a pulse duration of 10 ns and energy of 70 mJ/pulse. All solutions were deaerated by bubbling argon for a minimum of 15 min.

Results and Discussion

The squaraine dye bis(2,4,6-trihydroxyphenyl)squaraine (SQ) has been shown to form J-type aggregates in acetonitrile solution.[15] The monomer and aggregate have distinct absorption bands with maxima centered at 470 and 565 nm, respectively. A plot of log(OD$_{\text{dimer}}$) versus log(OD$_{\text{monomer}}$) gives a slope of 2 at dye concentrations of $<11\ \mu$M, indicating that under these conditions the aggregate exists predominantly as a dimer. At higher concentrations the slope deviates from linearity, indicating the formation of higher order aggregates. In the present study aggregates refer mainly to the dimer of SQ.

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* To whom correspondence should be addressed. E-mail: das@csrrltrd.ren.nic.in.

10.1021/jp993255b CCC: $19.00

The intersystem crossing efficiencies of squaraine dyes are generally very poor. To generate the triplet states of the monomer and aggregate forms of SQ, well-known triplet sensitizers such as benzophenone and 1-pyrenecarboxaldehyde were used. Absorption and nanosecond laser flash photolysis studies indicated that these sensitizers form complexes with the monomer and dimer of SQ in acetonitrile.

Complex Formation of Benzophenone with the Monomer and Dimer of SQ. Addition of benzophenone (BP) to acetonitrile solutions of SQ brought about interesting changes in the absorption spectrum of the dye (Figure 1). With increasing concentration of benzophenone a gradual decrease in intensity of the 475 nm band and an increase in intensity of the 565 nm were observed, indicating a shift in equilibrium in favor of the dimer. Since these changes are observable even at millimolar concentrations of benzophenone, they cannot be attributed to any solvent effect. The changes in the absorption spectra brought about by addition of benzophenone suggest direct interaction of benzophenone with the dye, possibly via the formation of a weak complex. The enhancement in aggregation of rose-bengal-(2′ethyl ester) on addition of potassium nitrate[29] and in SQ on addition of iodine[15] has been attributed to the formation of a complex of the dyes with the additives. By analogy, the following mechanism can be proposed for the observed effects of benzophenone addition to the absorption spectrum of SQ in acetonitrile.

SCHEME 1

$$\mathrm{SQ} + \mathrm{BP} \overset{K'}{\rightleftharpoons} \mathrm{SQ{\cdots}BP} \qquad (1)$$

$$2(\mathrm{SQ{\cdots}BP}) \overset{K''}{\rightleftharpoons} (\mathrm{SQ{\cdots}BP})_2 \qquad (2)$$

Considering this reaction scheme, the equilibrium constants, K' and K'' may be expressed as

$$K' = \frac{[\mathrm{SQ{\cdots}BP}]}{[\mathrm{SQ}][\mathrm{BP}]} \quad \text{or} \quad [\mathrm{SQ{\cdots}BP}] = K'[\mathrm{SQ}][\mathrm{BP}] \qquad (3)$$

$$K'' = \frac{[\mathrm{SQ{\cdots}BP}]_2}{[\mathrm{SQBP}]^2} \quad \text{or} \quad K'' = \frac{[\mathrm{SQ{\cdots}BP}]_2}{K'^{\,2}[\mathrm{SQ}]^2[\mathrm{BP}]^2} \qquad (4)$$

$$\frac{[\mathrm{SQ}]^2}{[\mathrm{SQ{\cdots}BP}]_2} = \frac{1}{K'^{\,2}K''[\mathrm{BP}]^2} \qquad (5)$$

A plot of $[\mathrm{SQ}]^2/[\mathrm{SQ{\cdots}BP}]_2$ versus $1/[\mathrm{BP}]^2$ is shown in Figure 2. The linearity of this plot supports the mechanism proposed in eqs 1 and 2. From the slope, a value of 9.5×10^6 M^{-3} was obtained for the product of the two equilibrium constants, $K'^{\,2}K''$.

Further evidence for the formation of complexes of benzophenone with the monomer was obtained through nanosecond laser flash photolysis studies.

Triplet Excited State of the SQ Aggregate. Excitation (355 nm) of acetonitrile solutions of benzophenone (0.01 M) reveals transient spectral features with a maximum centered around 520 nm (Figure 3a). On the basis of earlier studies, this absorption can be attributed to the triplet excited state of benzophenone.[30] Figure 3b shows the transient absorption spectrum, obtained immediately after the laser pulse excitation of a acetonitrile solution containing benzophenone (0.01 M) and SQ (16 μM). At these concentrations, SQ exists mainly in its aggregated form. The transient spectrum has been normalized at 520 nm to that obtained for benzophenone alone. Comparison of the spectra indicates a dip in the absorption in the 565 nm region, which corresponds to the ground-state absorption of the SQ dimer. It may be mentioned that no transient absorption was observed on excitation of a solution containing only SQ.

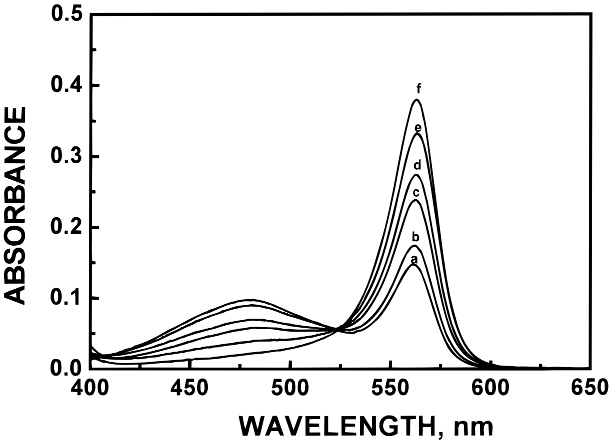

Figure 1. Effect of benzophenone on the absorption spectra of SQ in acetonitrile at 300 K for [SQ] = 2.5 μM and benzophenone concentrations of (a) 0 M, (b) 0.08 M, (c) 0.17 M, (d) 0.19 M, (e) 0.22 M, and (f) 0.25 M.

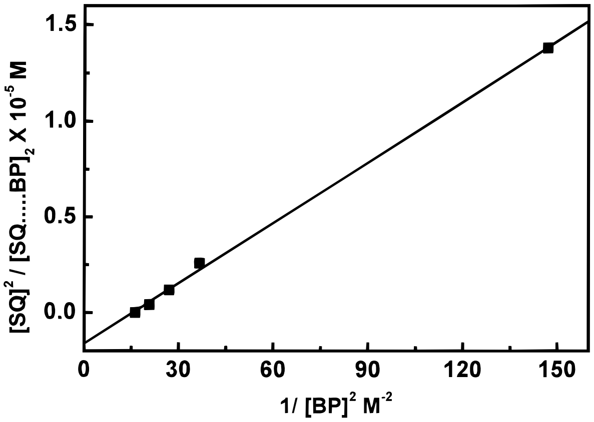

Figure 2. Plot of $[\mathrm{SQ}]^2/[(\mathrm{SQ{\cdots}BP})_2]$ versus $1/[\mathrm{BP}]^2$ for SQ in dry acetonitrile at 300 K.

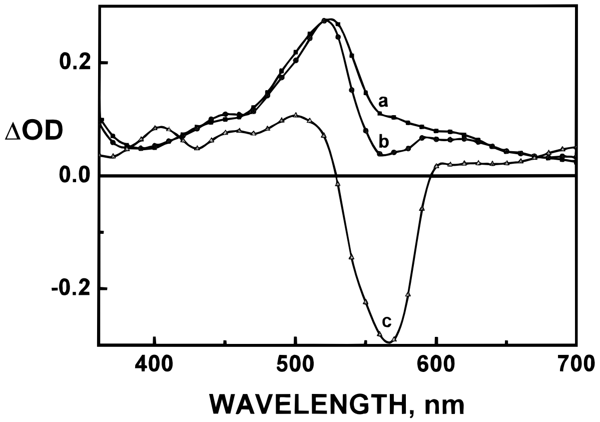

Figure 3. Transient absorption spectra measured immediately (Δt = 0.1 μs) after 355 nm laser pulse excitation of acetonitrile solutions of (a) benzophenone (0.01 M) and (b) benzophenone (0.01 M) and SQ (16 μM). Curve c shows the spectrum obtained for the latter solution measured 4 μs after the laser pulse.

These results indicate that along with the benzophenone triplet, a transient species arising from the SQ dimer is also formed within the laser pulse. Since the concentration of the dye aggregate used in this study is very low (~8 μM), the formation of the transient species could not be attributed to a diffusion-controlled energy transfer from benzophenone to the

SQ dimer. Moreover, the strong absorption at 520 nm indicates that most of the benzophenone triplet has not decayed within this time scale. On the basis of this, it can be concluded that the formation of the transient squaraine species could be due to excitation of the benzophenone−squaraine dimer complex, which leads to an intracomplex energy transfer from benzophenone to the SQ dimer. Since the ground state of benzophenone does not have any absorption at 565 nm and assuming minimal absorption for the triplet state of SQ in this region, the change in absorption at this wavelength following the laser pulse can be described by

$$\Delta\mathrm{OD} = \epsilon_1 c_1 - \epsilon_2 c_2 \qquad (6)$$

where ϵ_1 and c_1 represent the extinction coefficient and concentration of the triplet excited state of benzophenone and ϵ_2 and c_2 represent the ground-state extinction coefficient of the SQ dimer that has been depleted. At shorter time scales the benzophenone triplet undergoes a unimolecular decay to its ground state. Since the concentration of the SQ dimer is very low, diffusion-controlled energy transfer is not observed. This is confirmed by the observation that the rate constant for decay of the benzophenone triplet analyzed at 520 nm ($k = 8 \times 10^5$ s^{-1}) is the same as that of the benzophenone triplet in the absence of SQ. Analysis of the kinetics of the bleach at 560 nm reveals a biexponential process: a fast process with a rate constant of $2 \times 10^6\ \mathrm{s}^{-1}$ and a slower process with a rate constant of $8 \times 10^5\ \mathrm{s}^{-1}$. The slow process can be attributed to the decay of the benzophenone triplet. The faster component corresponds to the static energy transfer within the bezophenone−squaraine dimer complex. The difference absorption spectrum observed at 4 μs, following completion of the decay of the benzophenone triplet (Figure 3c), can be attributed to the triplet state of the SQ aggregate. The recovery of the ground-state absorption of the SQ aggregate, corresponding to the decay of its triplet state, occurs at much longer times with a rate constant of 1.6×10^5 s^{-1}. The observed results can be explained on the basis of the mechanism shown in Scheme 2.

SCHEME 2

$$\mathrm{BP} \xrightarrow{h\nu} {}^3\mathrm{BP}^* \qquad (7)$$

$$(\mathrm{SQ}\cdots\mathrm{BP})^2 \xrightarrow{h\nu} (\mathrm{SQ}\cdots{}^3\mathrm{BP}^*)_2 \qquad (8)$$

$${}^3\mathrm{BP}^* \rightarrow \mathrm{BP} \qquad (9)$$

$$(\mathrm{SQ}\cdots{}^3\mathrm{BP}^*)_2 \rightarrow 2\mathrm{BP} + {}^3(\mathrm{SQ})^*{}_2 \qquad (10)$$

$${}^3(\mathrm{SQ})^*{}_2 \rightarrow (\mathrm{SQ})_2 \qquad (11)$$

Benzophenone is a well-known triplet sensitizer, and triplet energy transfer from benzophenone to various phenols has been reported earlier.[31,32] It has been reported that in polar solvents triplet energy transfer predominates for benzophenone, whereas in nonpolar solvents such as benzene hydrogen atom abstraction by benzophenone prevails.[33] In the present study, where acetonitrile was used as solvent, the energy transfer from the excited state of benzophenone to SQ is expected to be the major mode of energy dissipation.

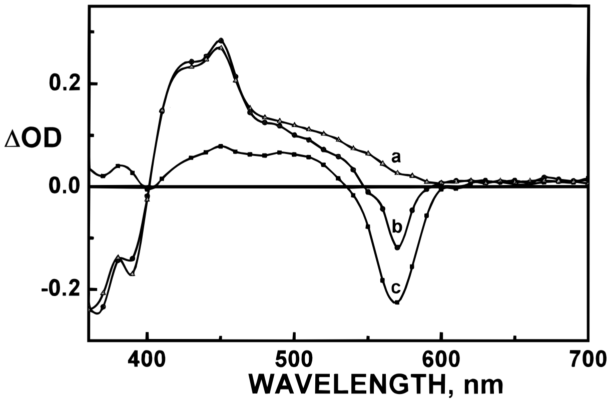

Figure 4. Transient absorption spectra measured immediately ($\Delta t = 0.1\ \mu$s) after 355 nm laser pulse excitation of acetonitrile solutions of (a) 1-pyrenecarboxaldehyde (0.1 mM) and (b) 1-pyrenecarboxaldehyde (0.1 mM) and SQ (16 μM). Curve c shows the spectrum obtained for the latter solution measured 8 μs after the laser pulse.

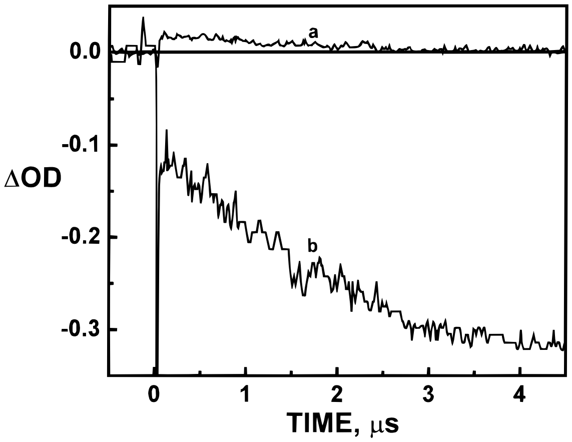

Figure 5. Transient decay profile recorded at 560 nm for the acetonitrile solution containing (a) 1-pyrenecarboxaldehyde (0.1 mM) and (b) 1- pyrenecarboxaldehyde (0.1 mM) and SQ (16 μM).

To confirm that triplet energy transfer was indeed involved, the experiments were repeated using an alternative triplet sensitizer, namely, 1-pyrenecarboxaldehyde. Figure 4 shows the transient absorption spectra obtained immediately after the laser pulse in (a) acetonitrile solution containing 1-pyrenecarboxaldehyde and (b) acetonitrile solution containing 1-pyrenecarboxaldehyde and SQ (16 μM), where SQ exists predominantly in its aggregate form. As was observed in the studies using benzophenone, the transient spectrum obtained immediately after the laser pulse shows a large dip in the 565 nm region corresponding to the ground-state absorption maximum of the aggregate, indicating that the energy transfer to the SQ from 1-pyrenecarboxaldehyde must occur via a static process and not via diffusion-controlled quenching of the triplet state of 1-pyrenecarboxaldehyde. The involvement of static energy transfer becomes clearly evident on comparing the transient absorption profile at 560 nm corresponding to the ground-state absorption maximum of the SQ aggregate (Figure 5). In the absence of SQ a weak transient absorption of the 1-pyrenecarboxaldehyde triplet is observed (Figure 5a). In the presence of SQ, however, a depletion in absorption is observed within the laser pulse (Figure 5b), which is followed by a slower depletion corresponding to the decay of the 1-pyrenecarboxaldehyde triplet. Because of the longer lifetime of the 1-pyrenecarboxaldehyde triplet, some amount of diffusion-controlled energy transfer is observed even at these low concentrations of SQ used. The transient absorption spectrum measured at longer times (8 μs) following the decay of 1-pyrenecarboxaldehyde triplet state (Figure 4c) is identical to the transient spectrum obtained at longer times in the benzophenone-containing solution (Figure 3c) and can be attributed to the triplet state of the SQ aggregate.

Triplet Excited State of the SQ Monomer. The triplet excited-state spectrum of SQ in methanol has been reported.[34]

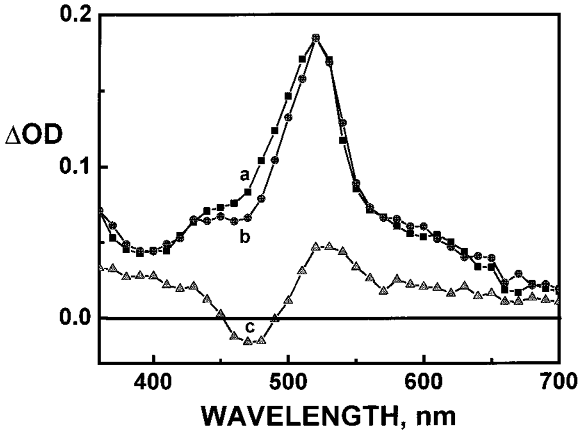

Figure 6. Transient absorption spectra measured immediately ($\Delta t = 0.15$ μs) after 355 nm laser pulse excitation of acetonitrile solutions of (a) benzophenone (0.01 M) and (b) benzophenone (0.01 M) and SQ (2.8 μM). Curve c shows the spectrum obtained for the latter solution measured 30 μs after the laser pulse.

Excitation of 1-pyrenecarboxaldehyde in the presence of SQ in methanol leads to diffusion-controlled energy transfer from the triplet excited state of 1-pyrenecarboxaldehyde to SQ. Formation of the triplet state of SQ within the laser pulse was not observed in these solutions, indicating that the monomer of SQ does not form a complex with 1-pyrenecarboxaldehyde in methanol. As mentioned earlier, SQ also does not have the propensity to form dimers or aggregates in methanol.

In acetonitrile-containing solutions, however, there was evidence for the formation of such a complex. Figure 6 shows the transient absorption spectrum obtained immediately after laser pulse excitation for solution containing (a) benzophenone (0.01 M) and (b) benzophenone (0.01 M) and SQ (2.8 μM). At this concentration SQ exists predominantly in its monomer form. The spectra show a maximum at 520 nm, indicating the formation of the benzophenone triplet. For solutions containing benzophenone and SQ, a dip in absorption around 470 nm, corresponding to the ground-state maximum of the monomer, is also seen. This is indicative of the monomer form undergoing transformation within the laser pulse. Since direct excitation at 355 nm does not result in any transient formation of the monomer, the depletion has to arise from energy transfer from benzophenone to the monomer within the complex. This is similar to that observed in the benzophenone-sensitized generation of the aggregate triplet in acetonitrile solutions. The rate constant for decay of the benzophenone triplet is 8×10^5 s^{-1}, which is the same as that of the benzophenone triplet in the absence of SQ, indicating that the diffusion energy transfer is negligible. The spectrum obtained on completion of the decay of the benzophenone triplet (Figure 6c) can be attributed to the triplet excited state of the squaraine monomer.

Figure 7 shows the transient decay profile at 470 nm for acetonitrile solutions containing benzophenone and varying concentrations of the SQ monomer. The traces show a fast decay of the transient absorption leading to depletion in absorption. A slower process leading to further depletion in absorption follows this. The extent as well as rate of the slower depletion was observed to increase with an increase in concentration of SQ. While the fast process can be attributed to the decay of the triplet state of benzophenone to its ground state, the slow process appears to arise via the self-quenching of the monomer.

The transient absorption profiles at 560 nm for acetonitrile solutions containing varying amounts of the SQ monomer are shown in Figure 8. The traces show a fast decay of transient absorption, attributable to the decay of the benzophenone triplet. This is followed by a slower growth in transient absorption. As observed in the slow depletion at 470 nm, the rate and extent of growth at 560 nm, which corresponds to the ground-state absorption maximum of the SQ aggregate, increase with increasing concentration of the SQ monomer. Figure 9b shows the transient absorption spectra measured following completion of this process. The spectrum measured at shorter times (Figure 9a) can be attributed to the triplet state of the SQ monomer. The spectra measured at longer times indicate that the self-quenching of the monomer triplet leads to the formation of the ground state of the SQ aggregate. The rate constant for the self-quenching process was estimated as 8.6×10^9 M^{-1} s^{-1} from the plot of the observed rate constant for growth of the transient at 560 nm versus monomer concentration (Figure 10). On the basis of these results, the mechanism shown in Scheme 3 can be proposed for the decay of the triplet excited state of the monomer.

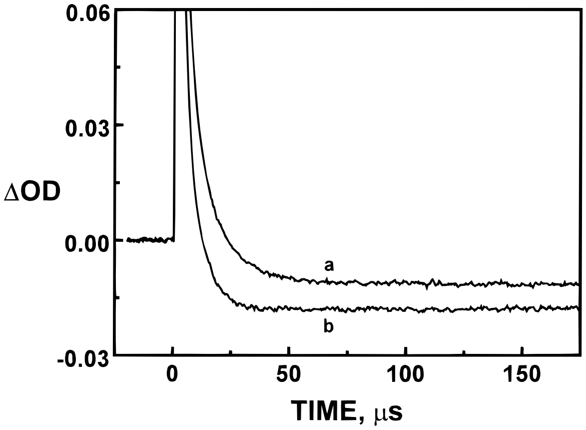

Figure 7. Absorption−time profiles recorded following 355 nm pulse excitation of argon-saturated acetonitrile solutions of SQ and 1-pyrenecarboxaldehyde (0.1 mM) at 470 nm. SQ concentrations were (a) 1.8 and (b) 2.8 μM.

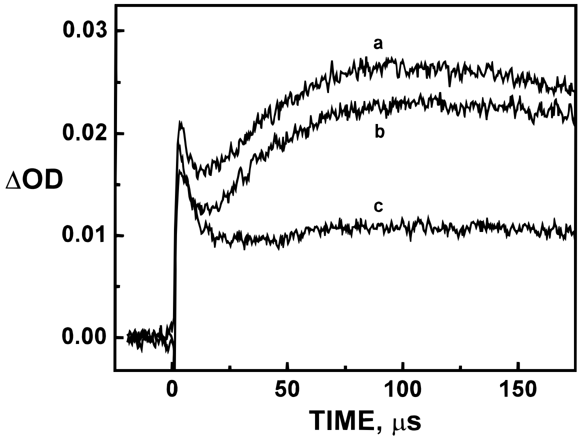

Figure 8. Absorption−time profiles recorded following 355 nm pulse excitation of argon-saturated acetonitrile solutions of SQ and 1-pyrenecarboxaldehyde (0.1 mM) at 560 nm. SQ concentrations were (a) 2.8, (b) 2.4, and (c) 1.8 μM.

SCHEME 3

$$^3SQ^* + SQ \rightarrow {}^3(SQ\cdots SQ)^* \tag{12}$$

$$^3(SQ\cdots SQ)^* \rightarrow (SQ)_2 \tag{13}$$

$$(SQ)_2 \rightarrow 2SQ \tag{14}$$

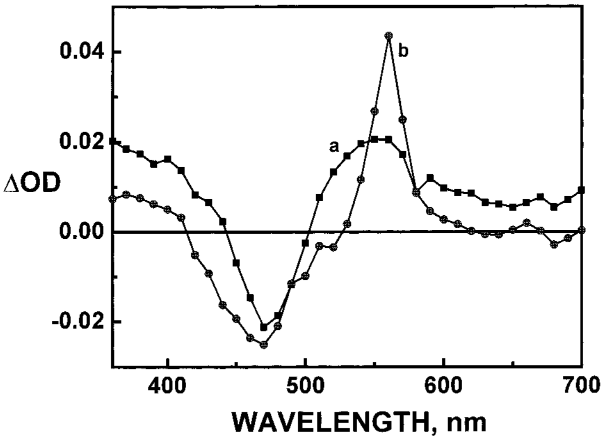

Figure 9. Transient absorption spectra measured for acetonitrile solutions containing benzophenone (0.01 M) and SQ (2.8 μM): (a) 6 μs after the 355 nm laser pulse excitation; (b) 30 μs after the 355 nm laser pulse excitation.

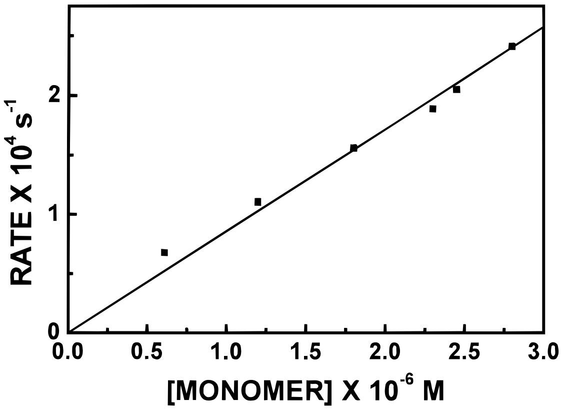

Figure 10. Plot of the observed rate constant for the growth at 560 nm versus concentration of SQ.

The formation of the ground-state dimer can occur via a short-lived triplet excimer species as shown in eq 11. Formation of triplet excimers via self-quenching of the triplet excited state has been reported before.[35] Triplet excimers in general are less stable because of the smaller magnitude of exciton resonance and also because of a smaller charge-transfer contribution. Because of the short lifetime of the triplet excimer, eq 12, involving self-quenching of the monomer triplet, would be the rate-determining step for the formation of the ground state of the aggregate in the self-quenching of the monomer triplet.

Self-quenching of the triplet excited states leading to the formation of photodimers has been reported earlier for a few molecules such as anthracene[35−37] and thymine.[38,39] However, to the best of our knowledge, there are no reports on the formation of an aggregate via self-quenching of the triplet.

Figure 11 shows the transient absorption profile at 470 and 560 nm at longer times. The decay of the transient absorbing around 565 nm is accompanied by the recovery of the monomer absorption centered on 470 nm (with a lifetime of 0.69 ms). This is indicative of the slow dissociation of the aggregate leading to the formation of the monomer, which occurs in order to establish the ground-state equilibrium between the monomer and the aggregate.

Conclusion

The monomer and aggregate forms of SQ form weakly bonded complexes with triplet sensitizers such as benzophenone and 1-pyrenecarboxaldehyde. Excitation of the complex results in static triplet energy transfer from the sensitizer to the monomer and aggregate of SQ. Static triplet−triplet energy transfer has been earlier observed in molecules adsorbed on solid surfaces as well as in covalently linked systems.[27,40,41] Although such processes can play an important role in organized assemblies and naturally occurring systems such as photosynthesis, reports on static triplet−triplet energy transfer within weakly bound entities in homogeneous and in the heterogeneous media are rare.[42]

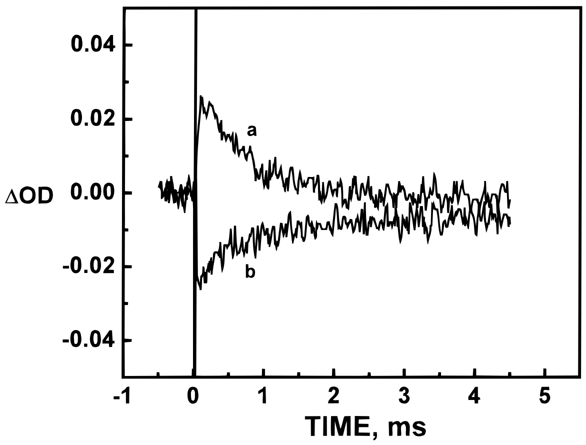

Figure 11. Absorption−time profiles recorded following 355 nm pulse excitation of acetonitrile solutions of 2.5 μM of SQ containing 1-pyrenecarboxaldehyde (0.1 mM): (a) 560 nm; (b) 470 nm.

The triplet state of the SQ aggregate is relatively long-lived and decays back to the ground state by a unimolecular process ($\tau = 6.7\ \mu$s). The triplet excited state of the monomer, however, undergoes self-quenching, leading to the formation of the squaraine aggregate. Formation of the aggregate occurs by self-quenching of the monomer excited triplet state probably via the intermediacy of a short-lived excimer.

Acknowledgment. This work was supported by the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India. This is Contribution No. RRLT-PRU-114 from RRL, Trivandrum.

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