

Can H-Aggregates Serve as Light-Harvesting Antennae? Triplet–Triplet Energy Transfer between Excited Aggregates and Monomer Thionine in Aerosol-OT Solutions

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The cationic dye thionine undergoes slow dissolution in aerosol-OT (AOT) containing solutions of heptane and toluene. By controlling the ratio of [dye]/[AOT], it is possible to obtain varying amounts of monomer, dimer, and higher order aggregates (trimer) in dilute dye solutions. The thionine aggregates exhibit characteristic absorption maxima at 565 and 530 nm for the dimer and trimer forms, respectively. The singlet excited states of these dye aggregates are short-lived ($\tau = 40\text{--}63$ ps) as they undergo efficient intersystem crossing to generate the triplet excited states. Triplet energy transfer from the excited dye aggregates to monomeric thionine molecules was observed upon excitation with a 532 nm laser pulse. Pulse radiolysis experiments, in which the excited triplet states were generated indirectly, also confirm the finding that the triplet energy cascades down from excited trimer to dimer to monomeric dye. These studies demonstrate the possibility of using H-type dye aggregates as antenna molecules to harvest light energy whereby the aggregate molecules absorb light in different spectral regions and subsequently transfer energy to the monomeric dye.

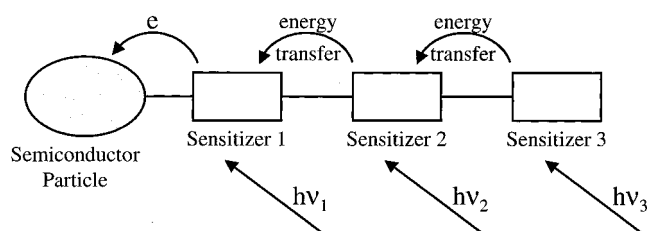
Introduction

A variety of photochemical approaches have been considered in recent years for mimicking natural photosynthesis. An important requirement for such systems is the ability to carry out directional energy and/or electron transport. In recent years, several chromophore-labeled polymers and supramolecular assemblies have been studied in order to achieve these goals.^{1–5}

Of particular interest are the uses of sensitizing dyes that absorb light in the visible region and initiate charge-transfer processes on semiconductor surfaces (Scheme 1). The ability of organic dyes to sensitize large band gap semiconductor materials has made them useful for the design of light-energy conversion devices.^{6–13} Often, the dye molecules aggregate on semiconductor surfaces, and these processes have been generally viewed as being detrimental to the performance of such devices. Since the dye aggregates have distinct absorption in the visible region (blue- or red-shifted absorption bands) compared to the monomers, design of systems wherein controlled energy transfer from the excited state of aggregates to monomers could be achieved would be highly desirable. Energy transfer from J-aggregates of different dye systems have been demonstrated in Langmuir–Blodgett films.^{14–18} Although the role of molecular aggregates as photosensitizers in color photography has been well recognized,^{19–22} spectroscopic studies on the role of the excited states of dye aggregates in these processes are rather limited.^{18,23–27}

In our previous studies,^{28–31} it has been shown that thiazine, oxazine, and rhodamine dyes readily form H-aggregates on negatively charged SnO₂ and SiO₂ nanocrystallites. As a result of the strong electrostatic interaction between cationic dye and negatively charged oxide surfaces, dye aggregation can be seen even at very low concentrations ($<10^{-5}$ M). These dye aggregates are electrochemically active and are capable of

SCHEME 1: Strategy for Harvesting Light Energy with Sensitizers that Absorb in the Different Parts of the Visible Spectrum^a



^a Directional energy transfer from sensitizer 3 to sensitizer 1 can ultimately be used to induce charge separation, for example, using a large band gap semiconductor nanoparticle.

extending the photoresponse of large band gap semiconductor materials.^{32–34} The participation of singlet and triplet excited states in the heterogeneous charge transfer at the semiconductor interface was demonstrated using femtosecond and picosecond transient absorption measurements.

In the past, the aggregation behavior of dye aggregates has been studied in heterogeneous media such as clays, micelles, vesicles, lipids, L-B films, polymers, and colloidal suspensions.^{35–41} Dye aggregation has also been observed in concentrated dye solutions or in mixed solvents.^{42–47} Self-aggregation of amphiphilic molecules can generate microdomains, which can systematically bind organic molecules by electrostatic or hydrophobic interactions providing an ordered assembly of molecules in liquid media. For example, J- and H-type aggregation of squaraine dyes has been achieved in poly(4-vinylpyridine) solutions.^{46,47} Such microdomains have also been used for the controlled synthesis of semiconductor and metallic nanoclusters.^{48–51} We have used the self-aggregation behavior of aerosol-OT in heptane and toluene for the controlled aggregation of a cationic dye such as thionine. By controlling the ratio of [dye]/[AOT], we can control the degree of aggregation. Using this procedure, dye aggregates can be formed at relatively low

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dye concentrations (10^{-5} – 10^{-4} M). This opens the possibility of employing transient absorption spectroscopic techniques such as laser flash photolysis or pulse radiolysis for investigating excited behavior of dye aggregates. Our preliminary studies that show the cascading of triplet energy from excited aggregate to monomer thionine are presented.

Experimental Section

Materials and Methods. Aerosol-OT and thionine were obtained from Aldrich Chemicals. All other chemicals and solvents were analytical reagents of the highest available purity. The surfactant solution was prepared by dissolving 12.8 g of AOT in 500 mL of heptane or toluene (5.8×10^{-2} M). A known amount of thionine (6–8 mg) was added to 100 mL of the AOT solution and stirred using a magnetic stirrer. With continued stirring, the color of the solution deepened, and the stirring was continued for 2 days to ensure complete dissolution of the dye. Please note that the dissolution was carried out in the absence of water. Absorption spectra were recorded using a Shimadzu 3101 spectrophotometer.

Laser Flash Photolysis Experiments. Nanosecond laser flash photolysis experiments were performed with a Quanta Ray model CDR-1 Nd:YAG system using 532 nm (third harmonic) laser pulses (~ 6 ns laser width) for excitation.⁵² The laser output was suitably attenuated to less than 10 mJ/pulse and defocused to minimize multiphotonic processes. The experiments were performed using a rectangular quartz cell of 6 mm path length with a right angle configuration between the direction of laser excitation and analyzing light. The photomultiplier output was digitized using a Tektronix 7912 AD programmable digitizer. A typical experiment consisted of a series of 5–10 replicate single shot measurements. The average signal was processed by a LSI-11 microprocessor interfaced to a VAX computer.

Picosecond laser flash photolysis experiments were performed using 532 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (output 2–3 mJ/pulse, pulse width ≈ 18 ps). The white continuum picosecond probe pulse was generated by passing the fundamental output through a D_2O/H_2O solution. 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 elsewhere.^{53,54} Time zero in these experiments corresponds to the end of the excitation pulse. The lifetimes and rate constants reported in this study have an experimental error of $\pm 5\%$.

Pulse radiolysis experiments were performed utilizing 2 ns pulses of 8 MeV electrons from a model Titan Beta-8/16-1S Electron Linear Accelerator.^{55,56} Dosimetry was based on the oxidation of SCN^- to $(SCN)_2^{\bullet-}$ ($G = 6$ in N_2O -saturated aqueous solutions). The solutions were saturated with nitrogen and flowed continuously through the sample cell during radiolysis.

Results

Aggregation of Thionine in AOT/Heptane Solutions. The cationic dye thionine (TH^+) undergoes slow dissolution in AOT-containing solutions of heptane or toluene. Figure 1A shows the absorption spectra of TH^+ in AOT-containing solutions of heptane. The concentrated TH^+ solution (spectrum e in Figure 1A) was diluted with an AOT/heptane solution, and spectra were recorded at different dye concentrations. The spectra are relatively similar in shape, with characteristic absorption bands

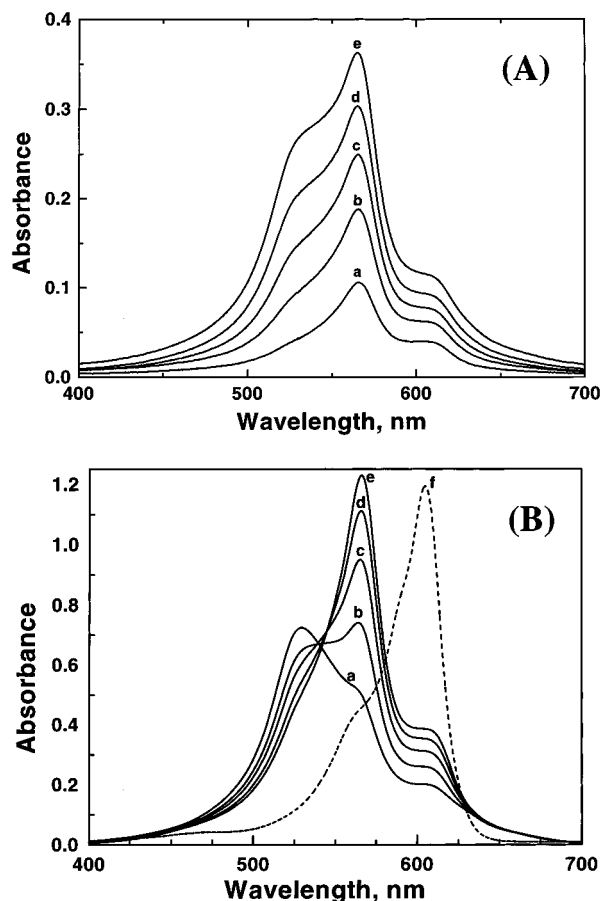
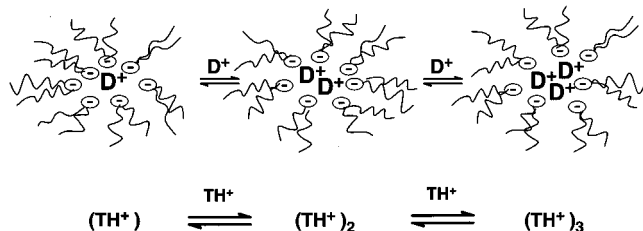


Figure 1. (A) Absorption spectra of thionine in toluene containing AOT: [AOT] = 5.8×10^{-2} ; [thionine] = (a) 0.64×10^{-4} , (b) 1.27×10^{-4} , (c) 1.91×10^{-4} , (d) 2.54×10^{-4} , and (e) 3.18×10^{-4} M. Spectra were recorded in a 1 mm path length cell. (B) Effect of varying AOT concentration on the absorption spectra of thionine in toluene: [thionine] = 6.4×10^{-5} M; [AOT] = (a) 1.0×10^{-2} , (b) 2.1×10^{-2} , (c) 3.1×10^{-2} , (d) 4.2×10^{-2} , and (e) 5.2×10^{-2} M; (f) Spectrum of thionine in ethanol, [thionine] = 1.3×10^{-5} . All spectra were recorded in a 1 cm path length cell.

at 610, 565, and 530 nm. A relative decrease in the intensity of the 530 nm shoulder compared to that of the 565 and 610 nm bands can be observed at lower thionine concentrations. The 610 nm band is a characteristic absorption feature of monomeric form (see spectrum f in Figure 1B). The absorption bands observed in the lower wavelength region can arise from two different aggregates. The band observed at 565 nm can be attributed to the H-type dimer aggregate similar to that observed in colloidal SiO_2 and SnO_2 solutions.^{28,29} We attribute the 530 nm band to a larger aggregate, possibly a trimer. Since the aggregate formation is dependent on the nature of the micelle core, one expects equilibrium between different forms of dye aggregates and the monomer. By changing the concentration of AOT or dye, one can shift the equilibrium to obtain desired ratios of monomer and aggregates. The equilibrium between the monomer and aggregate forms of the dye in the AOT core is illustrated in Scheme 2.

It is evident that the self-aggregation of AOT facilitates dissolution of the dye by providing a polar microenvironment in nonpolar solvents. The dye molecules would preferentially reside within the polar core provided by the self-assembled AOT molecules, thus enabling the interaction between two or more dye molecules. Strong electronic coupling between the molecules in dye aggregates causes either a blue shift (H-type) or red shift (J-type) in the absorption band. Theoretical studies have

SCHEME 2: Illustration of an Equilibrium between Trimer, Dimer and Monomer Forms of the Dye, D^+ (thionine, TH^+ in the Present Studies) in AOT Solutions



shown that the molecular orientation in aggregates determines the nature of spectral shift in the absorption band.^{57–60} Because the dye aggregation can be seen even at low dye concentrations ($\sim 10^{-5}$ M), it is evident that these dyes interact strongly with each other and exhibit spectral shifts arising from such interactions. Even at the lowest dye concentrations studied, the dye molecules prefer to be in the aggregated form.

To study the effect of AOT concentration on the dye aggregate formation, we probed the dye absorption spectrum by varying the AOT concentration and keeping the net thionine concentration constant in the solution. Stock solutions of thionine dissolved in AOT/heptane were diluted with heptane and AOT/heptane solutions to achieve the desired level of AOT concentration. The absorption spectra recorded at different AOT concentrations are shown in Figure 1B. The change in relative intensities of the 530 and 565 nm bands with changing AOT concentrations confirms the existence of two different types of aggregates. At very low AOT concentration, the higher aggregate form (trimer) with an absorption band at 530 nm dominates. The absorption bands corresponding to dimer and monomer forms of the dye only appear as shoulders at 565 and 600 nm. With increasing concentration of AOT, we see a decrease in the 530 nm band and a simultaneous increase in the 560 nm band. The presence of an isosbestic point at 545 nm at higher AOT concentrations confirms the equilibrium between trimer and dimer forms. A deviation from the isosbestic point seen at very low AOT concentrations (2×10^{-2} M) is indicative of the formation of higher order aggregates. The spectrum of the monomeric form of thionine in ethanol (spectrum f) is shown in Figure 1B for comparison.

Singlet Excited State. Time-resolved transient spectra were recorded following the excitation of dye solutions using a 532 nm laser pulse. The singlet excited thionine was generated in methanol solutions where the aggregation effects are minimal. Controlling the concentration of AOT optimized the concentration of dimer and higher aggregates. The transient absorption spectra that correspond to the singlet excited state of thionine monomer are shown in Figure 2. The singlet excited state of the monomer has a difference absorption maximum around 420 nm. The strong bleaching at 600 nm confirms the depletion of monomer thionine following the laser pulse excitation. With increasing time, the excited singlet state recovers via radiative and intersystem crossing processes. The spectra at longer times ($\Delta t = 4$ ns) essentially corresponds to the long-lived triplet excited state. From the transient absorption decay at 440 nm, we obtain a lifetime of 420 ps for the excited singlet state.

The singlet excited states of the dimer and trimer forms of the dye in AOT-containing solutions were similarly followed using 532 nm laser pulse excitation (Figures 3 and 4). Formation of the singlet excited states of $(TH^+)_2$ and $(TH^+)_3$ is marked by the depletion of corresponding ground-state absorption band at 565 and 530 nm, respectively. Both these excited states show

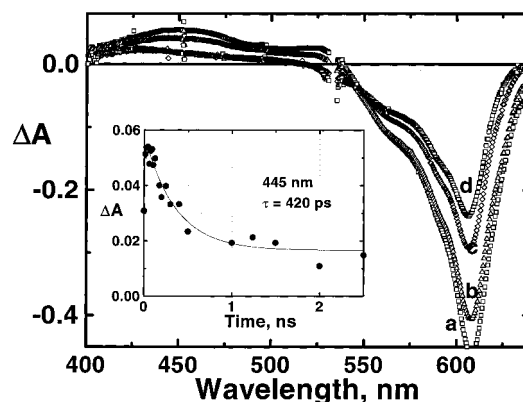


Figure 2. Transient absorption spectra recorded after 532 nm laser pulse excitation of 1.3×10^{-5} M thionine in ethanol at (a) 75, (b) 200, (c) 500, and (d) 1500 ps. The inset shows an absorption/time profile for the decay of $^1S^*$ of thionine monomer at 445 nm.

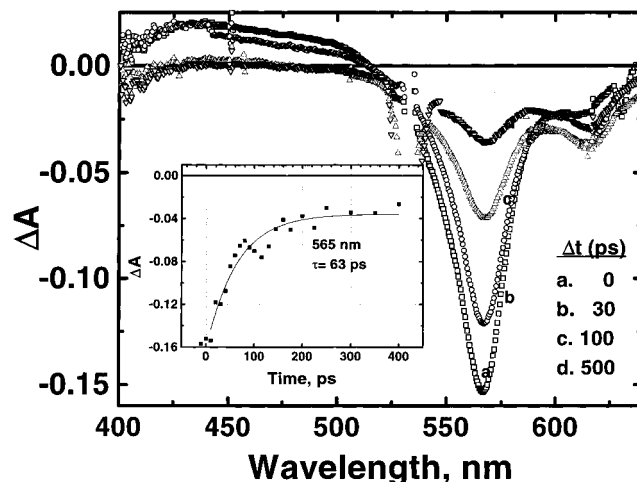


Figure 3. Transient absorption spectra recorded after 532 nm laser pulse excitation of N_2 -saturated solution of thionine (2.27×10^{-4} M) in heptane containing 5.75×10^{-2} M AOT at (a) 0, (b) 30, (c) 100, and (d) 500 ps. The inset shows an absorption/time profile for the recovery of the ground state of the thionine dimer at 565 nm.

weak and broad absorption in the 420–440 nm region. The excited singlet lifetimes measured from the recovery of the ground-state absorption of the aggregates were 60 ps for $(TH^+)_3^*$ and 40 ps for the $(TH^+)_2^*$, respectively. These lifetimes were significantly shorter than the excited singlet lifetime of monomer thionine. Although the bleaching of the 565 nm (Figure 3) and 520 nm (Figure 4) absorptions recover quickly, a residual depletion can be observed at longer times (100 ps). This is suggestive of a rapid intersystem crossing in these H-type aggregates to yield long-lived triplet excited states.

Scheme 3 shows the energy level diagram of the singlet and triplet excited states of the monomer and H-aggregate of an organic dye. For a weakly coupled composite system such as dye aggregates, the molecular exciton model proposed by McRae and Kasha^{58,59} provides a satisfactory treatment of excited states. According to this model, the excitonic singlet state of the dye aggregate splits into two levels (S_+ and S_-), one being lower and the other being higher in energy than the corresponding monomer singlet excited state. The transition to the upper state ($S_0 \rightarrow S_+$) is allowed for H-type aggregates. (This is evident from the blue-shifted absorption band in parts A and B of Figures 1.) The excitation of H-aggregates leads to the population of the S_+ state, which quickly relaxes to the S_- state by nonradiative internal conversion. This ultrafast internal

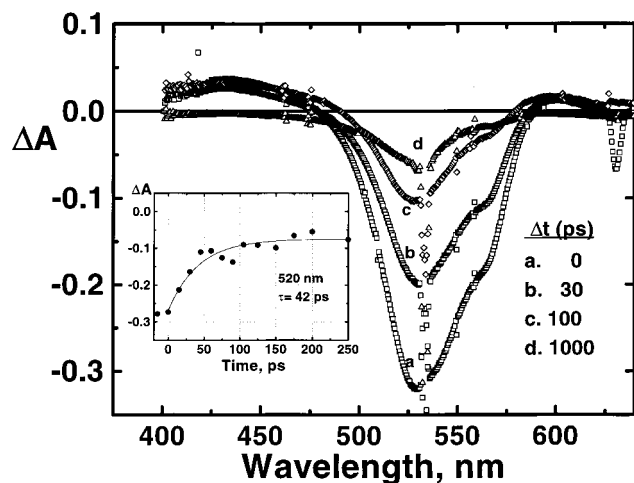
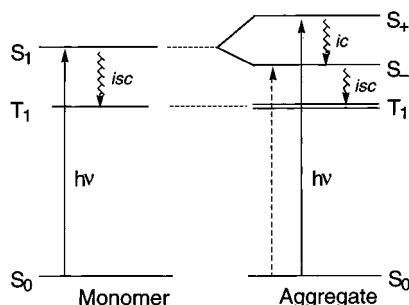


Figure 4. Transient absorption spectra recorded after 532 nm laser pulse excitation of an N_2 -saturated solution of thionine (2.27×10^{-4} M) in heptane containing 1.15×10^{-2} M AOT at (a) 0, (b) 30, (c) 100, and (d) 1000 picoseconds. The inset shows an absorption/time profile for the recovery of the ground state of the thionine trimer at 520 nm.

SCHEME 3: Illustration of the Energy Levels (S (Singlet) and T (Triplet)) of Monomer and Aggregate Forms, which Control the Excited State Dynamics⁵⁸



conversion process is expected to be complete within the laser pulse duration of 20 ps. The excited state observed in the transient spectra is essentially the S_- state of the dimer and trimers. Since the $S_- \rightarrow S_0$ transition is forbidden for H-aggregates, the deactivation of the S_- state primarily occurs via intersystem crossing to generate the triplet excited state of the aggregate. As shown earlier with cresyl violet H-aggregates, the conversion from singlet excited state to triplet excited state is a fast process (lifetime less than 100 ps). Accordingly, the spectrum recorded at longer times (spectra d in Figures 3 and 4) is attributed to the triplet excited state.

Triplet Excited States. Attempts were also made to characterize the triplet excited states of the dimer and trimer aggregates using nanosecond laser photolysis. Time-resolved transient absorption spectra recorded following 532-nm laser pulse excitation are shown in Figure 5, and the absorption-time profiles monitored at three different wavelengths (440, 570, and 590 nm) are compared in Figure 6.

The transient absorption spectrum recorded at short times ($\tau = 15 \mu s$) shows a broad bleach in the 530–568 nm region, suggesting simultaneous excitation of both dimer and trimer forms of thionine. The triplet excited states of these aggregated forms show a broad positive absorption in the 400–500 nm and 620–800 nm regions. The decay of the triplet absorption (trace a in Figure 6) is accompanied by a recovery of the absorption in the 500–580 nm region (trace b in Figure 6) and an increase in the bleaching of the monomer band in the 590–

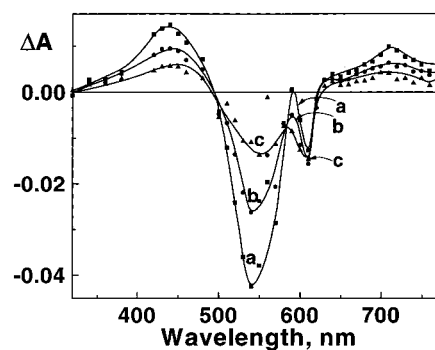


Figure 5. Transient absorption spectra recorded after 532 nm laser pulse (pulse width 6 ns) excitation of an N_2 -saturated solution of thionine (2.27×10^{-4} M) in heptane containing 5.75×10^{-2} M AOT at (a) 15, (b) 55, and (c) 125 μs .

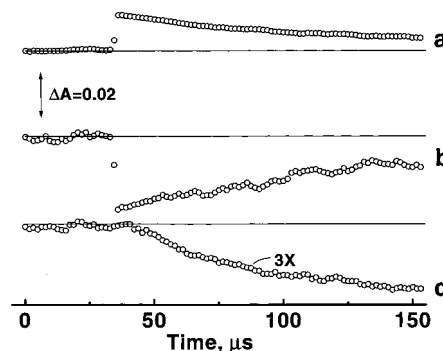


Figure 6. Absorption/time profile recorded following 532 nm laser pulse excitation of N_2 -saturated solutions thionine (2.27×10^{-4} M) in heptane containing 5.75×10^{-2} M AOT: (a) decay of the aggregate triplet monitored at 440 nm; (b) recovery of the ground-state aggregate monitored at 570 nm; (c) depletion of the monomer ground state monitored at 590 nm.

620 nm region (trace c in Figure 6). This process indicates possible formation of triplet excited state of thionine monomer via triplet–triplet energy transfer from excited state of the aggregates. As a result of a partial overlap in the ground-state absorption of the aggregated forms and the monomer at the excitation wavelength it was rather difficult to monitor the triplet states of these forms individually. The lack of selectivity in laser flash photolysis was overcome by employing the pulse radiolysis technique. (Pulse radiolysis enables us to monitor the individual energy transfer process by controlling the quencher concentration.)

Triplet–Triplet Energy Transfer Between the Aggregate Triplets and Monomer Forms of Thionine. Radiolysis of toluene solutions containing a high concentration of biphenyl is known to yield relatively long-lived excited biphenyl triplet with an absorption maximum at 360 nm. The resulting biphenyl triplet ($E_T = 64.8 \text{ kcal mol}^{-1}$) is capable of transferring energy to a molecule with lower triplet energy (e.g., thionine, $E_T = 38.8 \text{ kcal mol}^{-1}$). This method has been conveniently used for probing the triplet excited states of many organic molecules.^{61–63} In the present study, we have used $^3BP^*$ to initiate the primary triplet energy transfer to one of the dye aggregates present in solution. Since energy transfer is a diffusion controlled process, the selectivity of the T–T energy transfer can be achieved by controlling the concentration of one of the two aggregates. We have observed a bimolecular rate constant for the energy transfer between excited biphenyl and the dye aggregate of $\sim 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The slower bimolecular rate constant for the energy-transfer process is essentially due to the slower diffusion in the micellar medium.

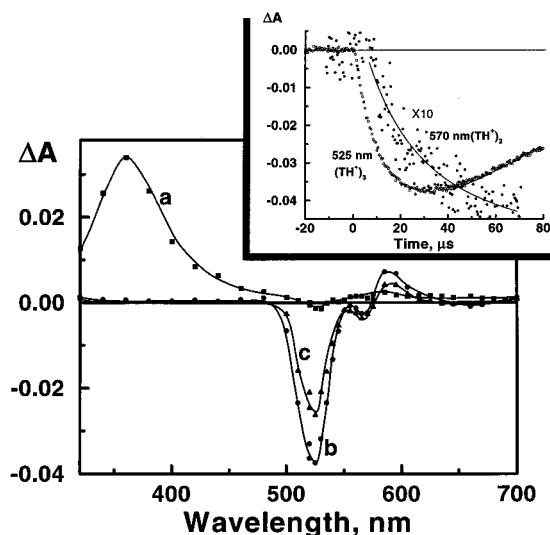
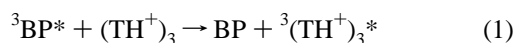


Figure 7. Transient absorption spectra recorded following pulse radiolysis of an N_2 -saturated solution of thionine (1.27×10^{-4} M) in toluene containing 2.3×10^{-2} M AOT and 2×10^{-2} M biphenyl at (a) 0.5, (b) 45, and (c) 100 μ s after the pulse. The inset shows an absorption/time profile for the (a) depletion and recovery of the ground-state trimer dye recorded at 525 nm (○) and (b) depletion of the ground-state dimer recorded at 570 nm (●) following pulse radiolysis of N_2 -saturated solution of thionine (1.27×10^{-4} M) in toluene containing 2.3×10^{-2} M AOT and 2×10^{-2} M biphenyl.

As indicated in the earlier section, by controlling the amount of AOT we can obtain relatively high concentrations of the trimeric form of thionine. Under these conditions, the decay of the biphenyl triplet absorption centered on 360 nm (spectrum a, Figure 7), is accompanied by a strong bleach at 530 nm and a growth in the 590 nm region (spectrum b, Figure 7). These results indicate that the triplet excited states of biphenyl decay mainly via triplet energy transfer to the aggregated trimeric form of thionine (reaction 1). Under these experimental conditions, the amount of energy transfer to the dimeric form was very small as seen from the bleaching at 565 nm. This T–T energy transfer to ground-state $(TH^+)_3$ process occurs within a time scale of 45 μ s.



The subsequent decay of the triplet excited state of the trimer is accompanied by bleaching in the 565 nm region. The insets in Figure 7 show the depletion and recovery of the bleaching at 525 nm (ground-state trimer) and the bleaching at 570 nm (ground-state dimer). As the bleaching due to excited trimer recovers, an increase in the dimer bleaching is seen. This is indicative of triplet energy transfer from the excited trimer to the thionine dimer. Since the concentration of the dimer under these experimental conditions was lower than that of the trimer, it was not a major participant in the initial energy transfer from triplet biphenyl. But, it was capable of interacting with the long-lived triplet excited state of the thionine trimer and participating in the secondary T–T energy transfer (reaction 2). This process occurred over a time period of 100 μ s.



The transient absorption spectrum recorded at 100 μ s shows an increased bleaching in the 565 nm region (spectrum c in Figure 7). The absorption profiles recorded at 535 and 570 nm (inset in Figure 7) clearly indicate the recovery of the excited trimer and the bleaching growth of thionine dimer.

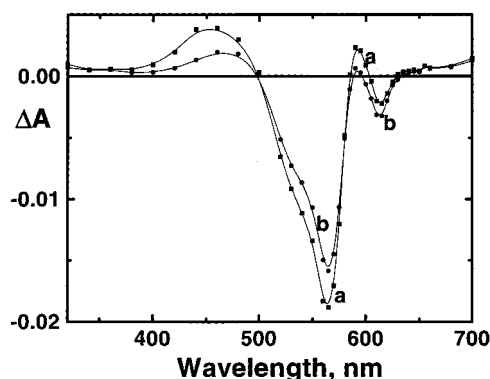


Figure 8. Transient spectra recorded following pulse-radiolysis of an N_2 -saturated solution of thionine (5.3×10^{-5} M) in toluene containing 5.8×10^{-2} M AOT and 2×10^{-2} M biphenyl at (a) 28 and (b) 103 μ s after the pulse.

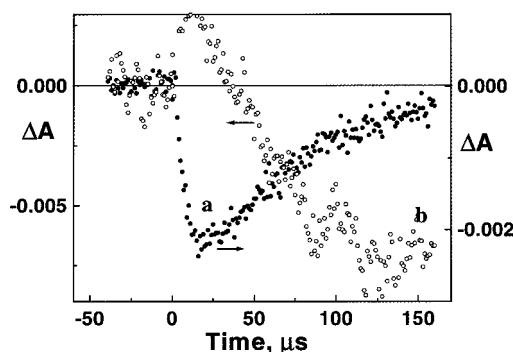


Figure 9. Absorption/time profiles recorded following pulse radiolysis of an N_2 -saturated solution of thionine (5.3×10^{-5} M) in toluene containing 5.8×10^{-2} M AOT and 2×10^{-2} M biphenyl: (a) recovery of the ground state of the dimer monitored at 565 nm and (b) depletion of the ground state of the monomer monitored at 610 nm.

The obvious question then would be whether it is possible for the excited-state energy to cascade down to the thionine monomer under appropriate conditions. To check this possibility, we prepared solutions containing high concentrations of AOT. Under these conditions, thionine exists predominantly in its dimeric form. The decay of the biphenyl triplet is accompanied by strong bleach centered on 565 nm, which is indicative of dimer depletion. A small amount of bleach is also observed, centered around 610 nm (Figure 8). This is indicative of energy transfer from the excited biphenyl triplet mainly to the thionine dimer and to a very limited extent to the monomer. At longer times, the excited triplet state of the thionine dimer decays and this process is accompanied by a bleaching growth in the 590–620 nm region, which corresponds to the thionine monomer depletion. Figure 9 shows the decay of $^3(TH^+)_2^*$ (curve a) and the corresponding bleaching of the ground state of thionine monomer (curve b).



Compared to the other two energy-transfer processes described above (reactions 1 and 2), reaction 3 is seen at a much slower time scale because of the lower monomer concentration in these experiments. Thus, by controlling the quenching dye concentration in a pulse radiolysis experiment, we were able to resolve the individual energy-transfer steps.

Discussion

The results presented in the previous section demonstrate the cascade of energy transfer between various forms of thionine.

One would expect the T–T energy transfer to proceed either via inter or intramolecular processes or both. Although the possibility exists for the T–T energy transfer between the pairs of dye molecules that exists within the same polar core of AOT, we consider the contribution of this process to be rather small. If this was the case, one would have seen a fast energy transfer between the two forms of dye molecules (i.e., within the laser pulse duration). The slower rate of energy transfer (which extends up to several microseconds) and the increasing rate of energy transfer with increasing concentration of monomer suggests that most of this energy transfer is due to an intermicellar energy-transfer process. As discussed in Scheme 2, the dye molecules upon solubilization in AOT solutions are constantly exchanged between different micellar cores. Such an intermicellar exchange is expected to facilitate diffusional interaction of the excited dye with the dye molecules from adjacent micellar cores.

While the excited singlet energy of the dye aggregate differs more significantly than that of the monomer (Scheme 3), we expect to see only small differences in the energy of dye triplets. This is mainly due to the fact that the splitting of the triplet energy in the excited dye aggregate is rather small. As discussed in the previous section, it is possible to achieve the energy-transfer processes corresponding to reactions 1–3. It may be noted that the difference in the energy-transfer rate mainly arises from the difference in the concentration of different species chosen in the present study. Thus, by controlling the concentration of different species, we were able to demonstrate an energy cascade from excited trimer to dimer to monomer dye.

Monomeric forms of organic dyes are desirable as photosensitizers since they have longer lifetime and higher singlet (S_1) energy than the S_n state of H-aggregates. However, the dye monomers exhibit sharp and narrow absorption bands in the visible, and this aspect often becomes a limiting factor for extending the photoresponse of organic-dye-based photochemical devices. Although H-aggregates of a sensitizing dye are considered to be less important in the direct conversion of light energy because of their short-lived singlet excited states and low-lying S_n state, they can be useful for harvesting a wider spectrum of visible light. Our present investigation demonstrates that such aggregates can transfer triplet energy to the monomeric form of the dye, which can serve as an active participant in the energy conversion process (e.g., dye sensitization of semiconductors). Thus, controlling the ratio of different aggregates and monomer forms of the dye on semiconductor surfaces by appropriate modification of the surfaces using surfactants could provide a convenient way for harvesting a wider band of the solar spectrum.

Conclusion

Spatially controlled intra- and intermolecular energy transfer between the two moieties is considered to be important in developing antenna systems for harvesting solar energy. Often, this is achieved by anchoring two or more functional groups to a polymer backbone² or to a solid support.^{29,64} In the present study, we have demonstrated the concept of directional energy transfer between different dye aggregates and the monomer by confining them in a reverse micellar environment. Since it is possible to control the extent and nature of aggregating species in the AOT solutions, it should be possible to tailor the property of light-absorbing antennas and harvest the desired fraction of visible light using a single dye molecule.

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