Spectroscopic Characterization of Phenazinium Dye Aggregates in Water and Acetonitrile Media: Effect of Methyl Substitution on the Aggregation Phenomenon

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Received: May 24, 2008

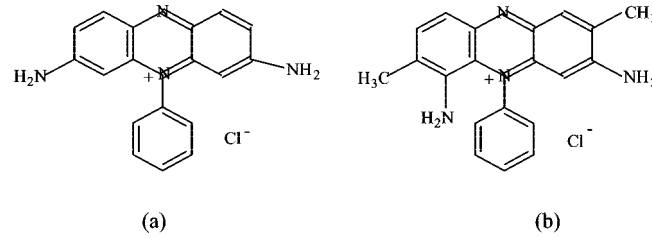
Absorption, fluorescence, and fluorescence excitation spectral studies of two planar, cationic phenazinium dyes, namely, phenosafranin (PSF) and safranin-T (ST), have been performed in protic and aprotic polar solvents. The studies reveal the formation of both J- and H-aggregates in concentrated solutions. The planarity of the phenazinium skeleton and the presence of a positive charge are attributed to be the driving force for this aggregation behavior. The aggregates are established to be dimers only. The positive inductive effect of the methyl substituents in safranin-T augments the aggregation process. The experiments reveal that for both dyes, the polar protic solvent favors the aggregation process more than the aprotic solvent.

1. Introduction

Spontaneous self-aggregation of molecules has been of prime importance in the fields of material science, colloid chemistry, analytical chemistry as well as in light-harvesting biological systems.[1] Dye aggregates have also been frequently used as mode-locking, Q-switching, and photographic sensitizing agents.[2] These aggregates exhibit strong nonlinear responses.[3] Most of the unique properties of the dye aggregates often arise from the fact that the constituent molecules are strongly electronically coupled so that the optical excitation of the chromophore produces a state that is delocalized over more than one monomer unit. Aggregation modifies the photophysical properties of the dyes in solutions, characterized by changes in band shape, large spectral shifts, and so forth relative to the monomeric forms of the same.[4,5]

The concept of aggregation of dyes in concentrated aqueous solutions was first invoked in order to explain the anomalous deviation of their absorption spectra from the Lambert−Beer's law.[6] Study of these aggregates thus has impact in terms of fundamental aspects. Self-association in solution or at the solid−liquid interface is a frequently encountered phenomenon in dyes and pigments due to strong intermolecular van der Waals attractive forces between the monomeric units. These aggregates can be best identified from the deformity in their absorption/excitation spectra and, often, a decrease in their emission yields.[7] The differences in the spectral behavior leads to various aggregation patterns of the dyes in different environments. The J-band has been coined by Jelly and co-workers for the bathochromically shifted band and the H-band for the one that is hypsochromically shifted in the absorption spectrum.[8,9] The bathochromic shift of the J-band and the hypsochromic shift of the H-band are explained by the molecular exciton coupling theory.[10] It is generally agreed that H-aggregates are composed of parallel dye molecules stacked plane-to-plane to form a two-dimensional lattice, and J-aggregates are formed by end-to-end stacking.[7] Thus, the dye molecule, according to the excitonic theory, is regarded as a dipole, and the excitonic state of the dye molecule splits into two levels through the interaction of the transition dipoles of the individual entities. In the H-dimer, there occurs a transition to the upper excited state (having parallel transition moments), while in the J-dimer, the transition occurs to the lower excited state (having perpendicular transition moments), leading to hypsochromic (or blue) and bathochromic (or red) shifts, respectively. Elaborate studies on such aggregation phenomena agreed with the suggestion that these aggregates probably exist as a one-dimensional assembly in solution in the form of a brickwork, a ladder, or a staircase type of skeleton.[7,11] Previous researchers have put forward many theories to explain the nature of the forces holding the dye molecules together in the solution.[9,12−15] The forces mostly considered are intermolecular hydrogen bonding, hydrogen bonding to solvent, the dispersion force, the electrostatic force, and so forth.

SCHEME 1: Structures of (a) Phenosafranin and (b) Safranin-T



The tendency of self-aggregation of a dye generally depends on several factors like the structure of the dye, the nature of the solvent, the temperature, the presence of electrolyte, and so forth. In this work, we have endeavored to address the first two aspects using two common dyes, phenosafranin (PSF, 3,7-diamino-5-phenyl phenazinium chloride) and safranin-T (ST, 3,6-diamino-2,7-dimethyl-5-phenyl phenazinium chloride) belonging to the phenazinium group. These phenazinium dyes have been extensively exploited in semiconductors, as energy sensitizers, and as probes for studying various microheterogeneous environments including micelles, reverse micelles, and polymeric matrixes.[12,16−19] They have also been looked into as intercalating dyes bound to DNA.[20] Both of the dyes studied here are red colored with a planar tricyclic phenazinium moiety, bearing a positive charge (Scheme 1).

In dilute aqueous solution, both dyes show broad absorption bands with maxima at around 520 nm. The overall absorption

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10.1021/jp804593v CCC: $40.75
Published on Web 09/11/2008

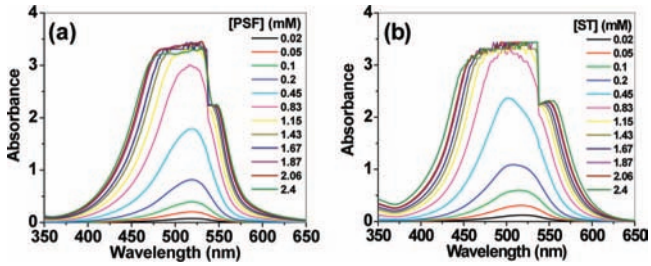


Figure 1. Absorption spectra of (a) PSF and (b) ST in water. The concentrations of PSF and ST are provided in the legends.

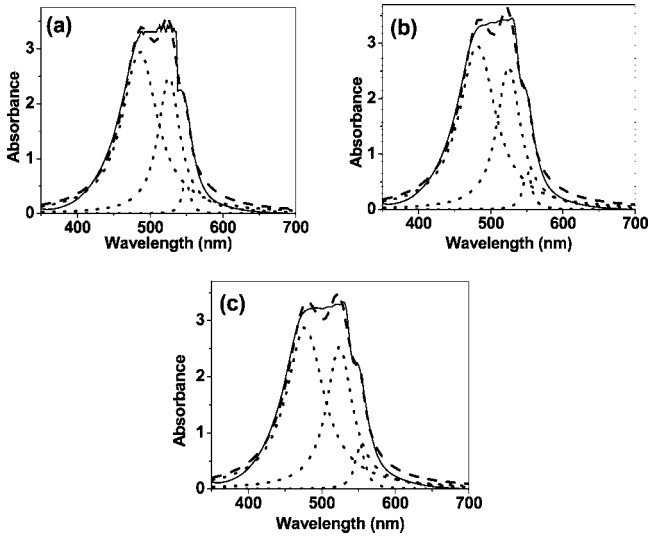


Figure 2. Resolved absorption spectra for PSF in water. Concentrations of PSF are (a) 1.67, (b) 1.87, and (c) 2.4 mM. Solid lines denote the experimental spectra, dotted lines denote the resolved spectra, and dashed lines denote the simulated spectra based on the resolved bands.

spectrum gets distorted as we move on to higher dye concentrations, reflecting the formation of the dye aggregates. Ample studies have been done on the aggregation behavior of different cyanine dyes,[7,21] azo dyes,[22] and porphyrin dyes.[23] To the best of our knowledge, there is no report on the identification and characterization of the aggregation behavior of the phenazinium dyes. To fill in this gap, we have investigated this program with two members of the phenazinium family. We are optimistic that these observations will open a new window into the arena of photosensitizers, laser dyes, and biological labeling.

2. Experimental Section

The dyes PSF and ST were purchased from Aldrich (U.S.A.) and used as received. Their purity was confirmed from absorption and emission spectra in standard solvents. Triply distilled water was used to make the experimental solutions. The acetonitrile used was of UV spectroscopic grade (Spectrochem, India). The concentrated stock solutions of the dyes were prepared by dissolving weighed amount of the dyes in the respective solvents.

Absorption and steady-state fluorescence measurements were performed using a Shimadzu UV-1700 spectrophotometer and a Spex fluorolog II spectrofluorimeter equipped with DM3000F software. Since for the concentrated solutions the absorbance goes out of range of the absorption spectrophotometer using the standard cell of 1 cm path length, the absorption measurements were made using a quartz cell of 1 mm path length. This enabled us to take the absorbance data up to a higher concentration level, although we could not go through the entire range of concentrations intended. For fluorescence studies, however, we could conveniently use the standard quartz cells. Quantum yields were determined using quinine sulfate in 0.1 N H_2SO_4 ($\varphi_f = 0.54$).[24] All of the experiments were performed at ambient temperature (27 °C) with air-equilibrated solutions.

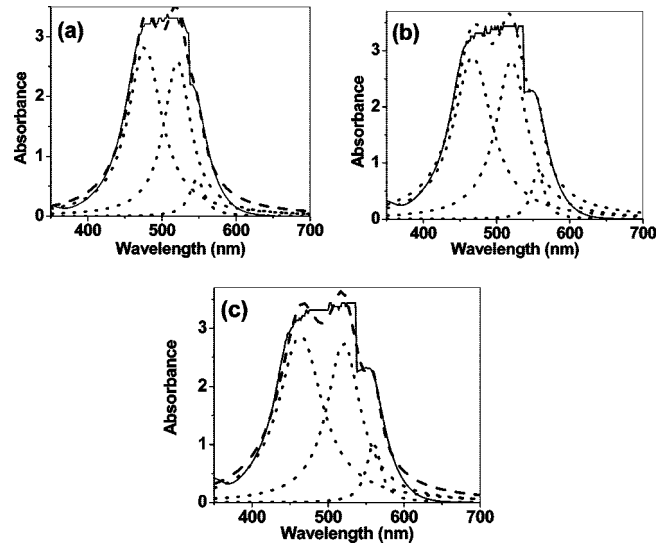


Figure 3. Resolved absorption spectra for ST in water. Concentrations of ST are (a) 1.15, (b) 1.87, and (c) 2.4 mM. Solid lines denote the experimental spectra, dotted lines denote the resolved spectra, and dashed lines denote the simulated spectra based on the resolved bands.

The absorption and excitation spectra were deconvoluted into overlapping Lorentzian curves using the MS Origin 6.1 fitting algorithm to obtain the minimum number of reproducible absorbing components using the adjustable parameters of the center, width, and amplitude for the resolved bands. Multiple attempts to fit the data with different initial parameters generally provided a survey of the extent of statistically equivalent parameter sets. Comparing several deconvolutions of an overall spectrum, a "good fit" was then judged by several criteria, including a minimum in the goodness fit parameter χ^2.[25] From these statistically acceptable fits, a good fit was further judged by the reproducibility in the values of the centers of the Lorentzian curves. A final, *albeit* subjective, criterion was to examine the fits for physically plausible results. Although people have mostly used Gaussian fittings,[25,26] we find that the absorption and the fluorescence excitation spectra are better fitted using Lorentzian components rather than Gaussian ones. Sharp band patterns, particularly for the J-aggregates, emphasize the significance of the Lorentzian function over Gaussian.

3. Results and Discussion

3.1. In Water. ***3.1.1. Absorption Study.*** Absorption spectra of aqueous solutions of PSF and ST show quite similar broad, unstructured lowest energy bands with maxima at around 520 nm in dilute solutions. The band is assigned to the monomeric species. The spectral feature remains unaltered (except, of course, with an increase in the absorbance) up to characteristic concentrations of PSF and ST. Above these concentrations, the absorption spectra start showing deformity, giving a sign of two new absorption bands (Figure 1), one moving to the blue (peak 1) and the other to the red (peak 3) relative to the monomer absorption band maximum (peak 2).

The absorption spectral deformity apparently originates from the self-association of the dyes in solution.[7,27−29] A

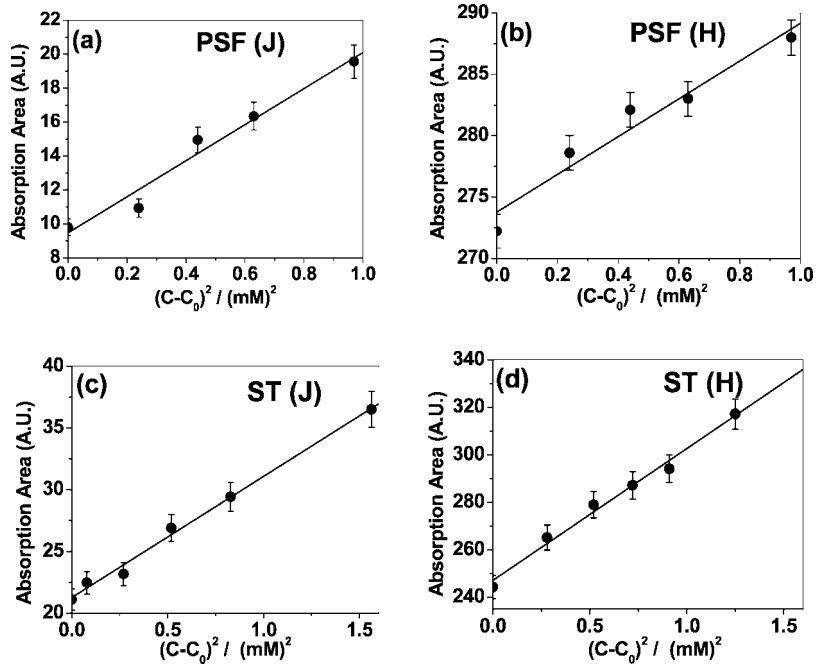
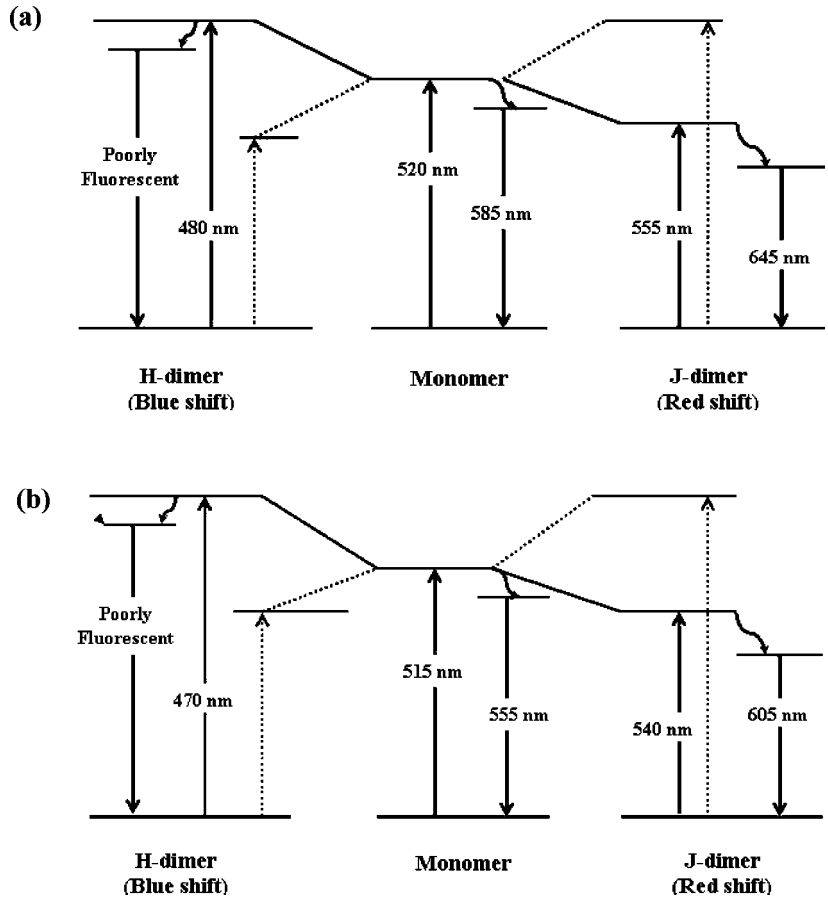


Figure 4. Plots of the area under the resolved absorption band for (a) the J-aggregate and (b) the H-aggregate of PSF against $(C - C_0)^2$; (c) and (d) are the corresponding plots for ST.

SCHEME 2: A schematic Energy Level Diagram for H- and J-Aggregates of PSF in (a) Water and (b) Acetonitrile[a]



[a] The primary splitting arises from the stacking interactions between the dimers.

closer scrutiny of the respective spectra reveals that the absorption spectrum of ST is not only broader but is also clearly more deformed than that of PSF at a preset concentration. The deformity in the absorption spectrum also starts at a lower dye concentration in the case of ST (0.2 mM in contrast to 0.4 mM for PSF). This leads us to propose that, compared to PSF, ST is more susceptible to aggregate. To comprehend the phenomenon occurring, we have resolved the absorption spectra using the method already described in the Experimental Section. At higher dye concentrations,

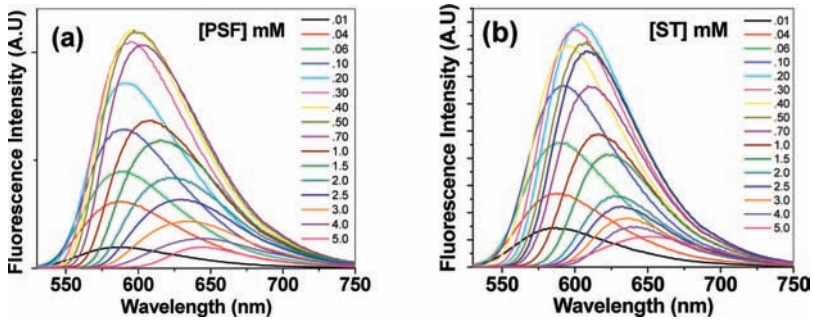


Figure 5. Emission spectra of (a) PSF and (b) ST in water as a function of concentration ($\lambda_{ex} = 520$ nm). The concentrations of PSF and ST vary from 0.01 to 5.0 mM.

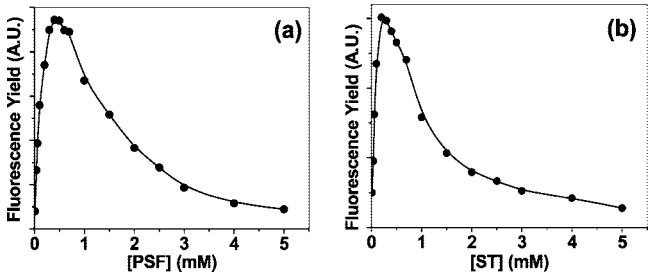


Figure 6. Variation of the fluorescence yield with concentration of (a) PSF and (b) ST in water.

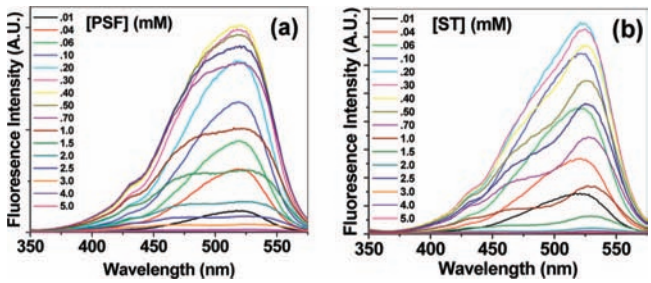


Figure 7. Excitation spectrum of (a) PSF and (b) ST in water as a function of concentration ($\lambda_{em} = 585$ nm). The concentrations of PSF and ST are provided in the legends.

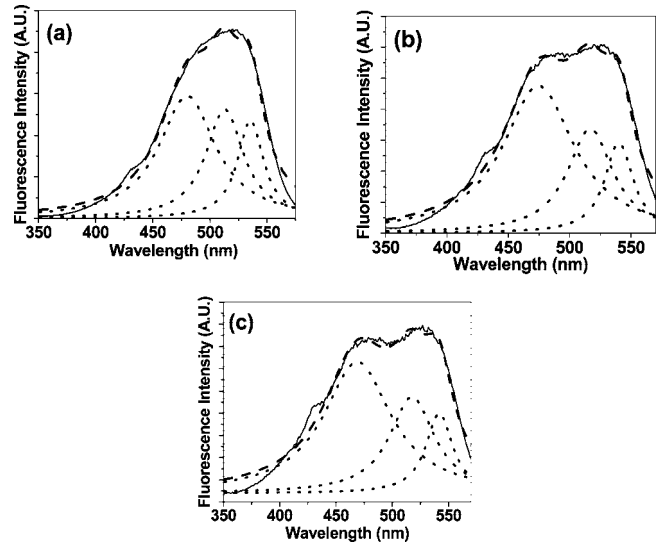


Figure 8. Resolved fluorescence excitation spectra for PSF in water. The concentrations of PSF are (a) 0.7, (b) 2.0, and (c) 4.0 mM. Solid lines denote the experimental spectra, dotted lines denote the resolved spectra, and dashed lines denote the simulated spectra based on the resolved bands.

each spectrum could be fitted well into a sum of three Lorentzian components. It was observed from the resolved absorption spectra for both dyes that the peak that developed at the lower wavelength considerably showed a blue shift with increasing dye concentration while that at the higher wavelength showed a gradual red shift (Figures 2 and 3). It is important to point out here that the disparity between the experimental and the simulated spectra in the region of the maximum is because of the limitation of the instrumental sensitivity.

Analysis of the resolved absorption spectra indicates that with an increase in concentration of PSF, the central peak (peak 2) remains almost invariant at 520 nm; peak 1 shows a continuous blue shift up to 480 nm, and peak 3 shows a monotonic red shift until 555 nm. For ST also, we observed similar shifts for peaks 1 and 3 relative to the unmoved peak 2. Consistent with the literature, peaks 1, 2, and 3 are assigned to the H-aggregate, the monomer, and the J-aggregate, respectively.

Since the dimer and also higher oligomers are often assigned to the aggregates, we took an endeavor to determine the stoichiometry of the aggregates for the two molecular systems studied here. This was achieved from a plot of the area of the resolved absorption bands corresponding to each of the identified aggregates against $(C - C_0)^n$, where C implies the total dye concentration, C_0 the threshold dye concentration above which the absorption spectrum starts showing deformity (concentration corresponding to the maximum yield in the fluorescence studies, vide discussion given in connection with the fluorescence studies), indicating a signature of aggregate formation, and n the number of monomer units that associate to form the aggregate (1, 2, or 3). It was found that for both dyes, the area under the resolved absorption bands corresponding to both J- and H-aggregates were linear for $n = 2$ (Figure 4) and nonlinear for $n = 1$ and 3. This confirms the dimeric nature of both aggregates, ruling out higher stoichiometries.

Literature suggests that when two molecules aggregate to form a dimer, the ground state remains unaffected but the excited state is split excitonically due to the dipole−dipole interactions between the interacting partners arranged in different orientations.[7,30] Because of the asymmetry of the charge distribution on the single molecules and the steric bulk introduced by the flanking phenyl group of the dyes studied here, the dimer moieties are unlikely to be exactly coplanar.[30] The twist angle (θ) between the individual chromophores in the aggregate is obtained as follows[26,30]

$$\theta = 2 \tan^{-1}(f_1/f_2)^{1/2} \quad (1)$$

where f_1 and f_2 are the oscillator strengths of the J- and the H-aggregates, respectively. Assuming the ratio of the areas under the resolved absorption bands of the two aggregates at a particular concentration corresponds to the ratio of their oscil-

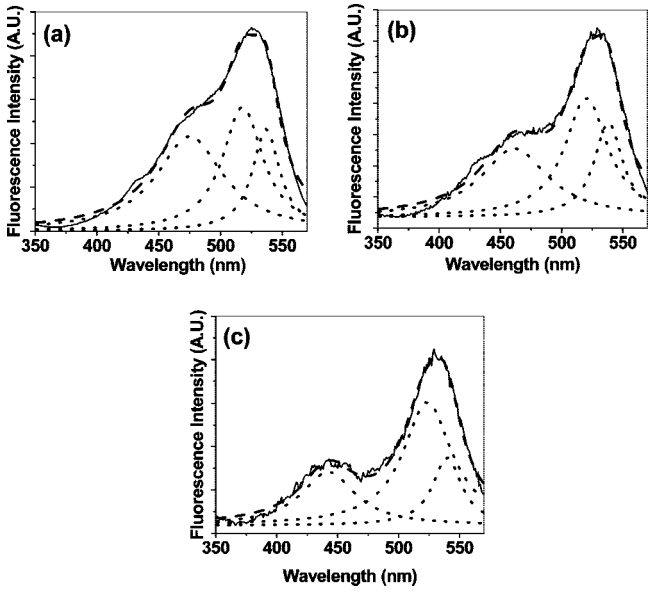


Figure 9. Resolved fluorescence excitation spectra for ST in water. The concentrations of ST are (a) 0.7, (b) 2.0, and (c) 4.0 mM. Solid lines denote the experimental spectra, dotted lines denote the resolved spectra, and dashed lines denote the simulated spectra based on the resolved bands.

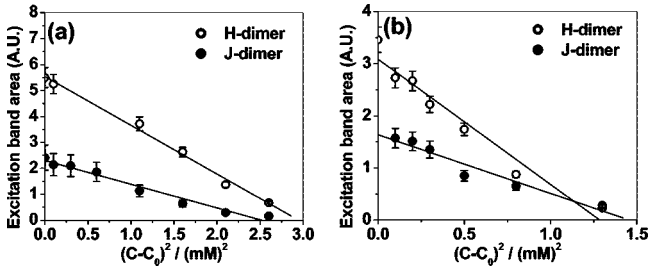


Figure 10. Plots of area under the resolved excitation bands for the J-aggregate and H-aggregate for (a) PSF and (b) ST in water against $(C - C_0)^2$.

lator strengths, we estimated the twist angle for the dye solutions above threshold concentrations. For both dyes, the values of θ did not vary appreciably with a variation in concentration. It is, however, interesting to note that the mean value of θ was much greater for PSF (θ for PSF $= 74.5 \pm 2°$, and θ for ST $=34.0 \pm 2°$). It is known that for a perfect aggregate, the monomer units are parallel ($\theta = 0°$). Deviation from this ideal value reflects formation of imperfect (or weak!) aggregations. A lower value of θ implies a better stacking in ST compared to that in PSF.

All the above observations suggest that at higher concentrations, the monomeric moieties of the two dyes coexist with the corresponding J- and H-dimers. Thus, the changes produced in the absorption spectrum can be attributed to the dimer formation by the equilibrium reaction M + M $\rightleftharpoons$ D.[21] Determination of the dimerization constant looses its significance due to the coexistence of two types of aggregates, namely, J and H, in the present case.

3.1.2. Fluorescence and Fluorescence Excitation Study. Dilute aqueous solutions of PSF and ST show broad emission spectra with maxima in both cases at around 585 nm when excited at 520 nm. The mirror image relationship between the emission and the absorption/excitation spectra holds well for both molecular systems.

As the concentration increases, there is a remarkable modification in the fluorescence spectra of the dyes. There is an initial enhancement in the fluorescence yield up to a threshold concentration (0.4 mM for PSF and 0.2 mM for ST) associated with a small red shift. After this optimum concentration, there is a sharp decrease in the fluorescence intensity with large red shifts (Figure 5). The first part is ascribed principally to the enhancement in the number of monomeric dye molecules in the solution. The sharp decrease is, however, not explainable until and unless we invoke the formation of the aggregates. The optimum concentration is considered to be the threshold for the aggregates to start showing signature.[26] It is interesting to notice that for both dyes, the emission spectra shifts continually to red (~60 nm for PSF and ~70 nm for ST) despite the fact that the absorption spectra reveal formation of both H- and J-aggregates with blue and red shifts, respectively. A drastic decrease in the fluorescence yield after the threshold dye concentration suggests that the aggregates are remarkably less fluorescing in nature. The monotonic red shift of the emission band further indicates that either the H-aggregate is nonfluorescent or its fluorescence yield is much less compared to that of the J-aggregate that emits at a longer wavelength. Existing literature proposes both nonfluorescent[30−33] and feebly fluorescent[34] H-aggregates for various cyanine dyes. Observation of the blue-shifted fluorescence excitation band, characteristic of the H-aggregate (vide supra), reveals that the H-aggregates of the studied phenazinium dyes have feeble fluorescence. In concentrated solutions, the mirror relationship between the overall emission and absorption/excitation spectra is lost, indicating the formation of the aggregates. A closer scrutiny, however, reflects that there is a mirror relationship for the emission and absorption/excitation spectra of the species emitting in the red end and confirms the formation of the J-aggregate. A similar confirmation for the H-aggregate was not possible due to its feeble emissive character.

A plot of emission yields against the concentration of the dyes pictorially gives an estimate of the threshold aggregation concentrations (Figure 6). The figure reflects that ST forms aggregates at a lower concentration than PSF. The result infers that ST is more prone to aggregation than PSF in aqueous medium. This is rationalized in the light of the positive inductive effect of the methyl groups present in ST. During aggregation, the positive charge on the nitrogen atom in the phenazinium moiety probably interacts with the electron cloud of the phenyl group. In ST, the presence of two additional methyl groups develops a higher electron density around the phenyl groups, resulting in, perhaps, a favorable situation for a better aggregation.

The excitation spectra monitored at 585 nm appeared as a broad single band at 520 nm at lower concentrations of both dyes. However, at higher dye concentrations, the excitation spectra are visibly deformed, as in the case of absorption spectra. Excitation spectra in concentrated solutions show distinctly two humps, one at a higher wavelength and the other at a lower wavelength (Figure 7). As already mentioned, in dilute solutions, there remains a mirror relationship between the emission and the excitation spectra which is lost at higher concentrations. It is interesting to note that the excitation spectra corroborate with the corresponding absorption spectra, confirming that the existing species are geometrically stable even in the photoexcited state.

To sense the relative affinity for self-aggregation of PSF and ST, we have resolved the fluorescence excitation spectra. This could overcome the limitation of the absorption spectrophotometer in recording the absorption spectra in concentrated solutions. At higher concentrations, Lorentzian fits of the excitation spectra yield three resolved bands for both dyes.

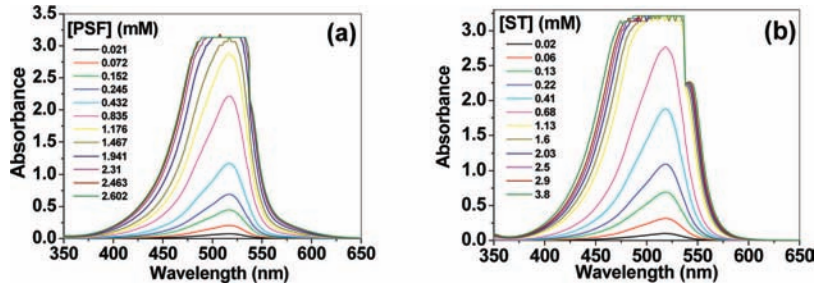


Figure 11. Absorption spectra of (a) PSF and (b) ST in acetonitrile. The concentrations of PSF and ST are provided in the legends.

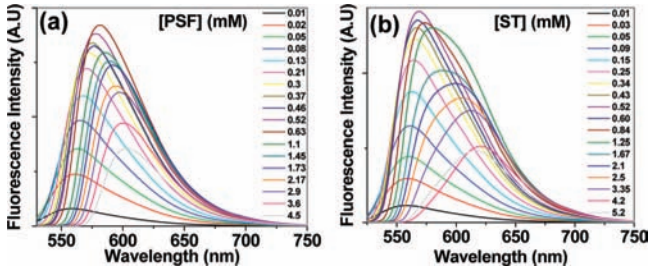


Figure 12. Emission spectra of (a) PSF and (b) ST in acetonitrile as a function of concentration ($\lambda_{ex} = 515$ nm). The concentrations of PSF and ST are provided in the legends.

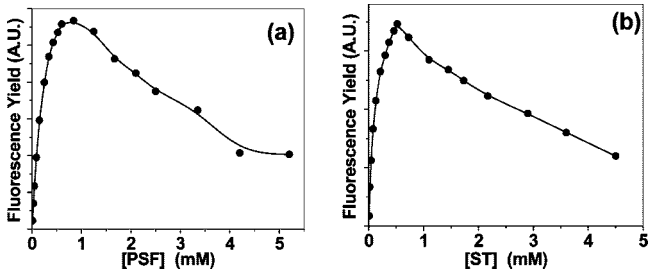


Figure 13. Variation of the emission yield with concentration of (a) PSF and (b) ST in acetonitrile.

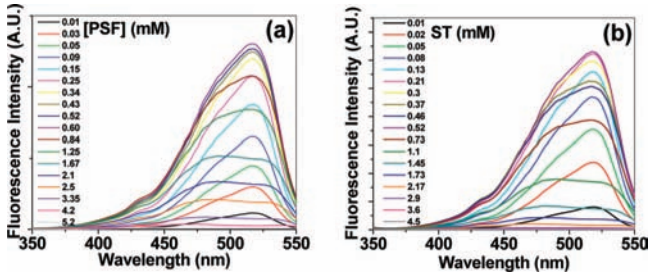


Figure 14. Excitation spectra of (a) PSF and (b) ST in acetonitrile as a function of concentration ($\lambda_{em} = 560$ nm). The concentrations of PSF and ST are provided in the legends.

Consistent with the absorption data, for both dyes, peak 1 shows a gradual blue shift, peak 2 remains undisturbed, and peak 3 shows a gradual red shift (Figures 8 and 9), the extent of shifts differing slightly for the two dyes. For both dyes, peaks 1, 2, and 3 correspond to the H-dimer, the monomer, and the J-dimer, respectively. Since the intensity of a fluorescence excitation band depends on both the absorbance and fluorescence quantum yield of the species involved, observation of the excitation bands corresponding to both J- and H-aggregates in the present case suggests that both aggregates are emissive in nature. A gradual red shift in the emission maximum with an increase in the dye concentration, however, proposes that the H-aggregate is remarkably less fluorescent than the J-aggregate. The figures emphatically show that at the same concentration, ST gives a very deformed excitation spectrum relative to that of PSF.

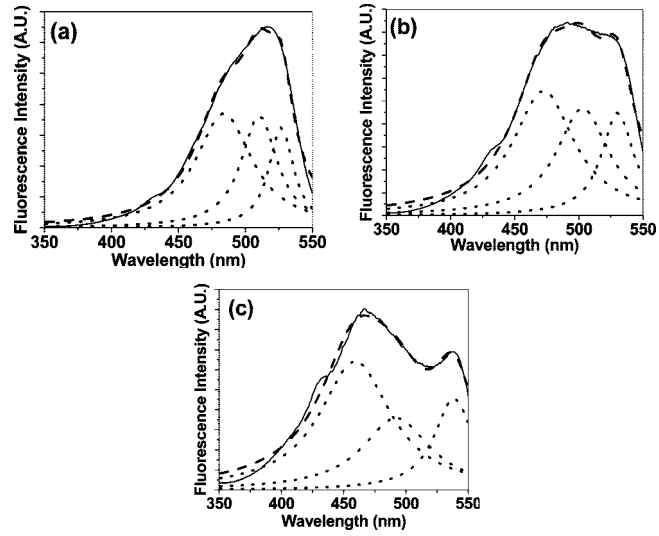


Figure 15. Resolved excitation spectra for PSF in ACN. Concentrations of PSF are (a) 0.60, (b) 2.1, and (c) 4.2 mM, respectively. Solid lines denote the experimental spectra, dotted lines denote the resolved spectra, and dashed lines denote the simulated spectra based on the resolved bands.

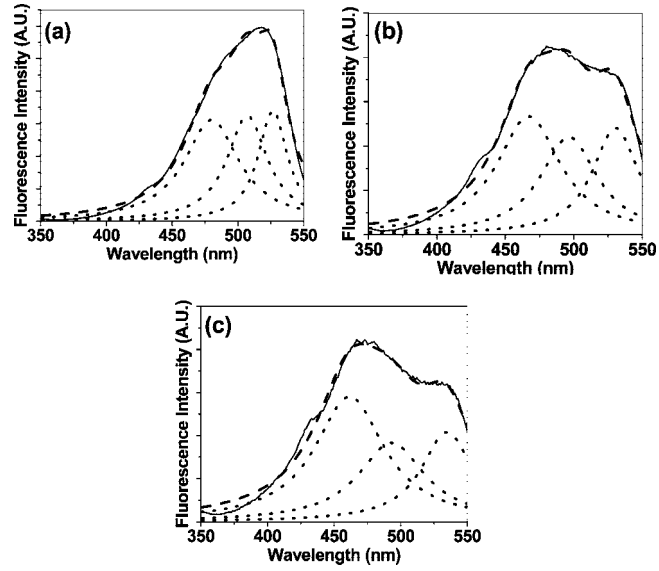


Figure 16. Resolved excitation spectra for ST in ACN. Concentrations of ST are (a) 0.52, (b) 1.73, and (c) 3.6 mM, respectively. Solid lines denote the experimental spectra, dotted lines denote the resolved spectra, and dashed lines denote the simulated spectra based on the resolved bands.

Considering the deformity of the absorption/excitation spectra to be the fingerprint of the extent of aggregation, the results suggest that ST is more apt to aggregate than PSF in aqueous media.

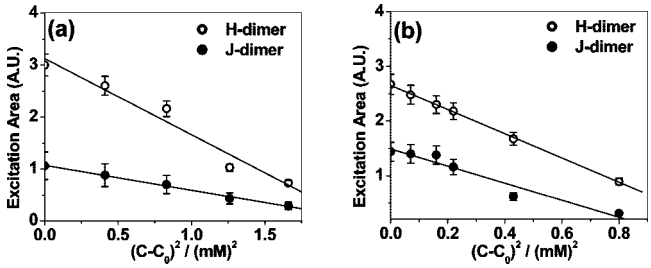


Figure 17. Plots of the area under the resolved excitation bands for the J-aggregate and the H-aggregate of (a) PSF and (b) ST in ACN against $(C - C_0)^2$.

The fluorescent nature of the aggregates, although poor, allowed us to establish the stoichiometry of the aggregates through resolution of the fluorescence excitation spectra following a similar procedure as that adopted in the absorption studies. Plots of the area of the resolved excitation bands corresponding to each of the identified aggregates against $(C - C_0)^n$ revealed that the aggregates are dimers and not oligomers (Figure 10). The negative slopes are expected from the decrease in the fluorescence yield, implying that the dimers are less fluorescent than the monomeric species. A greater slope corresponding to the H-aggregate indicates that this aggregate is much less fluorescent than the other, namely, J-aggregate.

The whole set of experimental results given above proposes that in concentrated solutions, both PSF and ST form dimeric J- and H-aggregates in water. The affinity for aggregation is, however, found to be more in the case of ST compared to that in PSF, which is ascribed to the presence of additional methyl groups in the former compound. Since PSF and ST are both ionic compounds, they are insoluble in nonpolar solvents (high dye concentration is obviously not achievable in nonpolar solvents). Therefore, to see the effect of the polarity and the protic factor of the solvent on the aggregation phenomenon, we have chosen acetonitrile to investigate the aggregation process further.

3.2. In Acetonitrile. ***3.2.1. Absorption Study.*** Absorption spectra of PSF and ST in dilute acetonitrile solutions show broad unstructured bands like those in water, the bands being slightly blue-shifted with maxima at ~515 nm ascribed to the monomeric species. At higher concentrations, the spectra are deformed, showing two new shoulders, one moving toward blue while the other moves toward red with respect to the monomer absorption maximum. Consistent with similar studies in water, this spectral change is assigned to the self-aggregation process, and the new bands correspond to the H- and J-aggregates, respectively. The concentration at which the absorption spectrum starts deforming is different for PSF and ST (Figure 11). The observation reveals that aggregation takes place in acetonitrile solvent as well, although the extent of deformation of the absorption spectra implies that aggregation is less favorable in ACN as compared to that in water. A lower threshold concentration of ST for aggregation compared to that for PSF leads to the proposition that in acetonitrile medium also, aggregation is more favorable for ST. Since in ACN the absorption spectra are not well resolvable, the dimeric nature of the aggregates could not be established as was done in water medium (vide Figure 4). The same limitation barred us from estimating the twist angles in the J-aggregates in ACN solution (vide infra).

3.2.2. Fluorescence and Fluorescence Excitation Study. Emission spectra of PSF and ST in acetonitrile resemble broadly their counterparts in water medium. At lower concentrations, both dyes show broad unstructured emission bands at 555 nm (contrary to 585 nm in water) having a mirror image relationship to their corresponding absorption/excitation spectra. An appreciable blue shift of the emission band maximum indicates that the charge-transfer state in the photoexcited state (S_1) is reasonably less stabilized in less polar ACN than that in water. Upon increasing the dye concentration, the emission band gets red-shifted similar to that observed in the case of aqueous solutions of both dyes. The shift in acetonitrile was found to be ~50 nm for PSF and ~60 nm for ST (Figure 12).

Since the fluorometric observations are parallel to those observed in aqueous medium, we can straightaway propose that in ACN also, the aggregates have lower fluorescence quantum yields, the H one being remarkably less fluorescent than the J-aggregate. The fluorescence studies determine the threshold concentrations of the dyes from the variation of the fluorescence yield against dye concentration. These come out to be 0.6 and 0.5 mM for PSF and ST, respectively (Figure 13). A comparison of the threshold values suggests that both PSF and ST show better aggregation affinity in water than in acetonitrile. A lesser stabilization of the aggregated forms (through solvation and hydrogen bonding) in less polar and aprotic solvent might be the plausible reason behind it.

In dilute solutions, the excitation spectra of both dyes monitored at 560 nm show broad single bands peaking at 515 nm, resembling the absorption spectra under similar situations. With an increase in the dye concentration, the spectra are visibly deformed, showing two humps, one at ~485 nm and the other at ~530 nm (Figure 14). The mirror relationship between the emission and excitation spectra is destroyed, establishing the formation of the aggregated moieties in both cases.

In order to obtain clearer spectral characteristics of the aggregates, the excitation spectra were resolved as before. With an increase in concentration of PSF, peak 1 is blue-shifted to 470 nm, peak 2 remains invariant at about 515 nm, and peak 3 is red-shifted to 540 nm (Figure 15). For ST also, we observed nearly similar shifts for peaks 1 and 3, while peak 2 remained, as before, unmoved (Figure 16). The three bands (1, 2, and 3) correspond to the H-aggregate, the monomer, and the J-aggregate, respectively.

The stoichiometries of the aggregates were determined in ACN from the fluorescence excitation studies following the same technique as that adopted for an aqueous environment, and the aggregates were confirmed to be dimers (Figure 17). The negative slopes and a greater slope for the H-aggregate were looked into with the same perspective as before.

With all of the absorption, fluorescence, and fluorescence excitation spectral data in tune with the literature,[7,33] we have constructed a schematic Jablonskii diagram for PSF as a model in water and acetonitrile solvents (Scheme 2). Although simple, it is instructive to assess the structural patterns of the dimer. It is known that a transition to the upper state having parallel transition moments and a transition to a lower state with a perpendicular transition moment lead to hypsochromic (blue, H-type) and bathochromic (red, J-type) shifts, respectively.[7,33] Excitonic splitting of the S_1 state of the dimers and transition from the ground state (S_0) to the upper one in the case of the H-aggregate and to the lower one in case of the J-aggregate due to parallel and perpendicular transition moments of the participating monomers leads to the hypsochromic and bathochromic shifts for the H- and J-aggregates, respectively, as reflected in the scheme.

4. Conclusion

PSF and ST undergo self-aggregation in polar protic and aprotic solvents to form H- and J-aggregates, which are

established to be dimeric in nature. The planarity of the molecular skeleton, electrostatic interactions, hydrogen bonding, and so forth are ascribed to be responsible for the aggregation phenomenon. Spectroscopic studies involving absorption, fluorescence, and fluorescence excitation of both the dyes in water and acetonitrile reveal that ST is more vulnerable toward aggregation compared to PSF in both solvents. Further, it has been observed that the aggregation is more favored in water than that in acetonitrile. This being the first report on the identification and characterization of the aggregation property of the dyes of the phenazinium group, it invites more experimental as well as theoretical works relating to such molecular systems in the arena of photosensitizers and biological labeling.

Acknowledgment. Financial support from DST and CSIR, Government of India, is gratefully acknowledged. D.S. and P.D. thank CSIR for the research fellowships.

References and Notes

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JP804593V