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# Characterization of an Aggregate-Sensitive Single-Component Energy-Transfer System

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**Abstract:** Energy transfer is studied in a system consisting of Langmuir–Blodgett monolayers of the hemicyanine dye, *N*-(3-sulfopropyl)-4-(*p*-dioctylaminostyryl)pyridinium. Deposition from $CHCl_3$ solution onto the air-water interface results in self-assembly into two-dimensional aggregates with an absorption band significantly blue-shifted (9000 $cm^{-1}$) from that of the monomer in solution. Calculation of structural parameters consistent with this extremely large blue-shift, in the extended dipole approximation, indicates the structure of the aggregate is considerably more compact than the average structure observed in the Π-A isotherm. However, the residual monomer, which is <0.5% of the total population from absorption measurements, dominates the fluorescence spectrum, typically yielding excitation bands of comparable intensity to the aggregate. This observation along with the identical nature of the fluorescence emission excited in either the aggregate or monomer absorption bands leads us to propose that energy migration in this system occurs primarily from the aggregate to the monomer. Thus, the donor (aggregate) and acceptor (monomer) species differ solely in aggregation state, not in chemical structure, as in more traditional energy-transfer experiments. This study has direct implications for the possible migration pathways in a variety of systems where energy transfer is of importance.

## Introduction

The formation and structure of organic monolayer and multilayer systems is of considerable interest in purely fundamental studies, in direct analogy to biological systems, and in the possible fabrication of chemical sensors and switches.[1,2] While not as well defined as crystalline systems, these molecular assemblies possess considerable order in the alignment, orientation, and spatial arrangement of molecules. The structured geometry of these systems has been used to advantage in the study of energy-transfer processes,[3-8] where understanding the molecular-level spatial alignment and distance are essential. Kuhn and co-workers[3] pioneered these studies in the 1960s by fabricating structures containing donor and acceptor species in different layers, often separated by a layer of aliphatic surfactant. These multilayer systems allow the independent control of both donor and acceptor concentrations as well as the distance between these species. More recent studies have incorporated the donor and acceptor molecules within a single layer.[5,8] As expected, energy transfer in these monolayer systems is more efficient than the comparable interlayer energy migration[5] and is dependent on the average aggregate coherence length.[8]

Previous studies of energy transfer have utilized donor and acceptor species of differing chemical structure, chosen to exhibit varying degrees of energy overlap. These studies are commonly accomplished utilizing multiple layers of dyes at low concentration in an inert fatty acid matrix or a single layer of acceptor dye containing a low concentration of donor species. However, such systems do not represent reasonable models for the ultimate collection and transport of photon energy as occurs in biological systems or is desired in the microfabrication of energy-harvesting devices. In such systems, high concentrations of dye are required, and aggregate formation is probable. For this reason, a small number of studies have begun to focus on energy transfer to or from aggregated states,[9,10] but none to our knowledge has examined energy transfer between aggregated and monomeric states of the same molecule. In this study, the possibility of this aggregate-sensitive energy transfer is examined within a monolayer of pure hemicyanine dye. In constrast to typical energy-transfer studies, this approach has the added advantage of a significantly decreased spatial distribution between donor and acceptor species, increasing the efficiency of energy transfer. Thus, proximity and orientation both favor facile energy transfer in this interesting system, where the aggregation state, and not the chemical structure, is central to the energy-transfer process.

## Experimental Methods

The molecule utilized in this study is the hemicyanine dye, *N*-(3-sulfopropyl-4-(*p*-dioctylaminostyryl)pyridinium (**I**), fabricated in a monolayer assembly using the Langmuir–Blodgett technique.[1,2] Initial characterization is accomplished by systematically investigating the aggregation process in forming the monolayer at the air–water interface and the subsequent transfer to a solid substrate.

*Monolayer Formation.* The hemicyanine dye, **I**, is obtained from Molecular Probes and is used without further purification. Pure dye monolayers are prepared using a KSV Instruments (Model 5000) Langmuir–Blodgett trough. A 1 mM solution of dye **I** in chloroform (Baxter Health Care) is spread onto a pure water subphase (Millipore Corporation, Model Milli-Q UV plus) maintained at 25 °C. Sixty minutes are allowed for the chloroform to evaporate and for the film to equilibrate at the air–water interface. The film is subsequently compressed at 500 $mm^2/min$ to a surface pressure of 30 mN/m, a process requiring approximately 60 min.

The resulting monolayer is then transferred onto a 25 × 25 × 0.15 mm fused-silica substrate (Heraeus-Amersil), which was immersed in the

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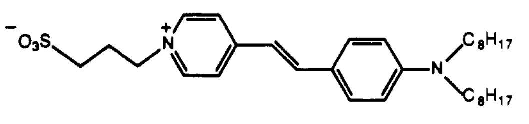

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water subphase prior to the spreading of the dye solution. A deposition rate of 15 mm/min results in a reproducible transfer ratio of 1.1 ± 0.05. Prior to deposition, substrates are cleaned in hot sulfuric acid and a 4:1 mixture of ammonium hydroxide/hydrogen peroxide and rinsed with copious amounts of water (>18 MΩ-cm).

*Monolayer Characterization.* Measurements of absorbance spectra during monolayer formation are accomplished by reflecting light from a xenon arc lamp between mirrors placed above and below the water surface. In this manner, four passes through the air–water interface are achieved before light is collected with a fused-silica fiber optic bundle (Fiberguide Industries) and transmitted through a spectrograph (Instruments SA, Model CP200) onto a photodiode array (Tracor-Northern, Model 6500). Noise caused by vibration and air circulation is minimized by supporting the entire system on a vibration-isolated optical table (Newport) and surrounding the trough within a plexiglas enclosure.

Fluorescence measurements of the transferred monolayer are accomplished using a dual-monochromator system with a thermoelectrically cooled photomultiplier tube (Spex, Model DM1B). The substrate is placed at 45° relative to the excitation beam, and collection is performed in a front-face geometry, 30° relative to the excitation beam.

## Results and Discussion

*Air–Water Interface.* Initial characterization of aggregate formation is accomplished by monitoring the absorption spectra of the dye molecules at the air–water interface. As illustrated in Figure 1, the spectrum immediately following the deposition of the dye on the water surface (90 Å$^2$/molecule) is similar to the solution spectrum in methanol. The low-energy band (490 nm) corresponds to the $\pi \rightarrow \pi^*$ transition over the entire chromophore in the trans configuration. In contrast, the high-energy transition (280 nm) primarily arises from the isolated transition on the pyridinium and benzene moieties and, therefore, contains contributions from both the trans and cis configurations. For simplicity, these low-energy and high-energy bands will be referred to as $S_1$ and $S_2$, respectively. As the molecules are allowed to equilibrate on the water surface, both the $S_1$ and $S_2$ bands decrease considerably. Approximately 45 min after the initial deposition, a new band appears at 340 nm, which reaches steady-state by 60 min. This transition is conjectured to arise from aggregation of the monomer species at the air–water interface (vide infra). It is interesting to note that the time required to achieve a steady-state condition is much longer than the 10 min commonly allowed for evaporation of the chloroform carrier solvent,[1] leading to speculation that this type of self-aggregation may be more common than is now appreciated. Finally, all spectra have been acquired with minimal exposure time (<15 s/spectrum), and the possibility of photoinduced processes have been considered and rigorously eliminated.[11]

After this initial equilibration period, the surface is slowly compressed, and the surface pressure/molecular area isotherm is measured (Figure 2). Upon compression, the $S_1$ band is no longer detectable, and the 340-nm band continues to increase, until it is the sole feature in the absorption spectrum. The absorbance of the aggregate species at 340 nm as a function of surface concentration yields a linear relationship at surface concentrations greater than 1.8 molecules/nm$^2$. Based on the measured absorbance cross sections of the monomer ($1.1 \times 10^{-16}$ cm$^2$) and aggregate ($0.39 \times 10^{-16}$ cm$^2$) at the air–water interface, an upper limit of 0.5% is established for the fraction of monomer in the final (i.e., 25 mN/m) monolayer structure. Thus, aggregate structures most likely form at low surface concentrations, and, thereafter, only the number of aggregates in the viewed area is increased. The lack of a further wavelength shift in the aggregate band upon compression is also consistent with this hypothesis.

*Fused-Silica Substrate.* Transfer of the monolayer to a fused-silica substrate is accomplished in the Z configuration, in which the hydrophilic moiety interacts with the silica surface. The absorption spectrum of the transferred monolayer is identical to the final spectrum at the air–water interface. Thus, based on the electronic spectra, the aggregate structure formed at the air–water interface is successfully transferred onto the substrate. As in studies of other hemicyanine dyes,[12,13] the absorption spectra indicate the presence of only aggregate species, and no monomeric species are observed above a detection limit of 0.01 molecules/nm$^2$. However, the fluorescence excitation spectrum of the transferred monolayer (Figure 3) indicates the presence of both aggregate ($\lambda_{ex}$ = 344 nm) and monomer ($\lambda_{ex}$ = 468 nm) species, with the monomer excitation maximum identical to that in methanol solution. Since the population of aggregate species is much greater, the apparent fluorescence quantum efficiency of the monomer must be considerably enhanced over that of the aggregate. A lower limit for the ratio of emission efficiencies resulting from monomer and aggregate ($\eta_{mono}/\eta_{aggr}$) may be estimated using eq 1,

$$\frac{\eta_{mono}}{\eta_{aggr}} = \frac{I_{mono}\sigma_{aggr}N_{aggr}}{I_{aggr}\sigma_{mono}N_{mono}} \tag{1}$$

where $I_{mono,aggr}$ is the intensity of 540-nm emission when excited at the $S_1$ and aggregate bands, respectively, $\sigma_{mono,aggr}$ refers to the absorption cross sections given previously, and $N_{mono,aggr}$ is the surface number density for each species. Based on the measured emission intensities, absorption cross sections, and surface densities of 3.4 molecules/nm$^2$ for the aggregate and ≤0.013 molecules/nm$^2$ for the monomer, a lower limit estimate of ~100 is obtained. Since this ratio measures the relative effectiveness of generating 540-nm emission from excitation of the respective species, it is clear that the radiative efficiency of the monomer is much (≤100) higher. In addition, no independent emission which can be assigned to the aggregate in these structures has been observed. Thus, the only observed radiative decay channel for the aggregate is via relatively inefficient energy transfer to the monomer.

Finally, Figure 3 shows that independent excitation of these two species yields fluorescence emission spectra that are identical ($\lambda_{em}$ = 540 nm). This unusual result indicates that emission likely occurs from identical excited states, further supporting the hypothesis of energy transfer from aggregate to monomer populations. Thus, although each species is excited independently, energy migration within the aggregate and subsequent energy transfer to the monomer may result in emission solely from the monomeric species.

*Aspirated Monolayer.* Further elucidation of the robustness of the interfacial structure is accomplished by careful aspiration experiments. A stable monolayer is prepared as described previously, and the monolayer is aspirated directly from the air–water interface using a simple bulb-suction apparatus. Methanol is then added to the aspirate to form a 1:1 mixture in which the monomer is known to be soluble. The absorbance spectrum of this aspirated solution indicates the presence of only aggregate ($\lambda_{abs}$ = 340 nm), whereas a control spectrum of dye **I** in a 1:1 solvent mixture is identical to that in pure methanol ($\lambda_{abs}$ = 280 and 490 nm). The fluorescence excitation spectrum was evaluated in two geometries: in a right-angle geometry to assess the solution species and a front-face geometry to assess any species segregated to the interface. Right-angle measurements showed a small amount of monomer ($\lambda_{ex}$ = 468 nm) with no aggregate, further corroborating the lack of fluorescence from the aggregate species.

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[11] Illumination at <1 mW/cm$^2$ for more than 20 min results in no change in the 340-nm band.

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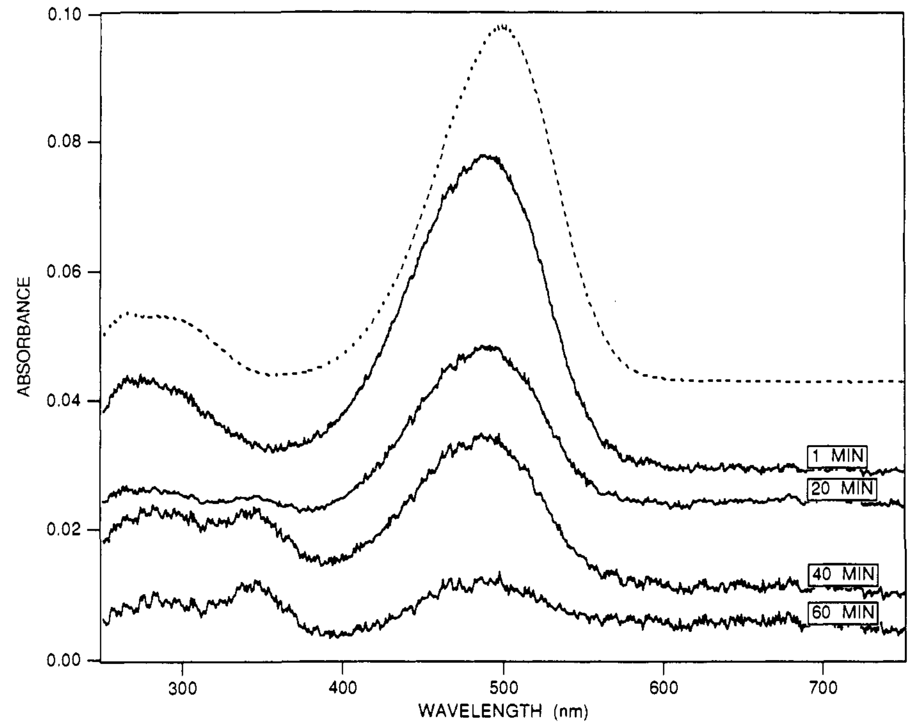

**Figure 1.** Absorbance spectra of dye I in methanol solution (- - -) and at the air–water interface (—) as a function of time from initial deposition. Conditions: $C_{init}$ = 1.1 molecules/nm$^2$, $T$ = 25 °C.

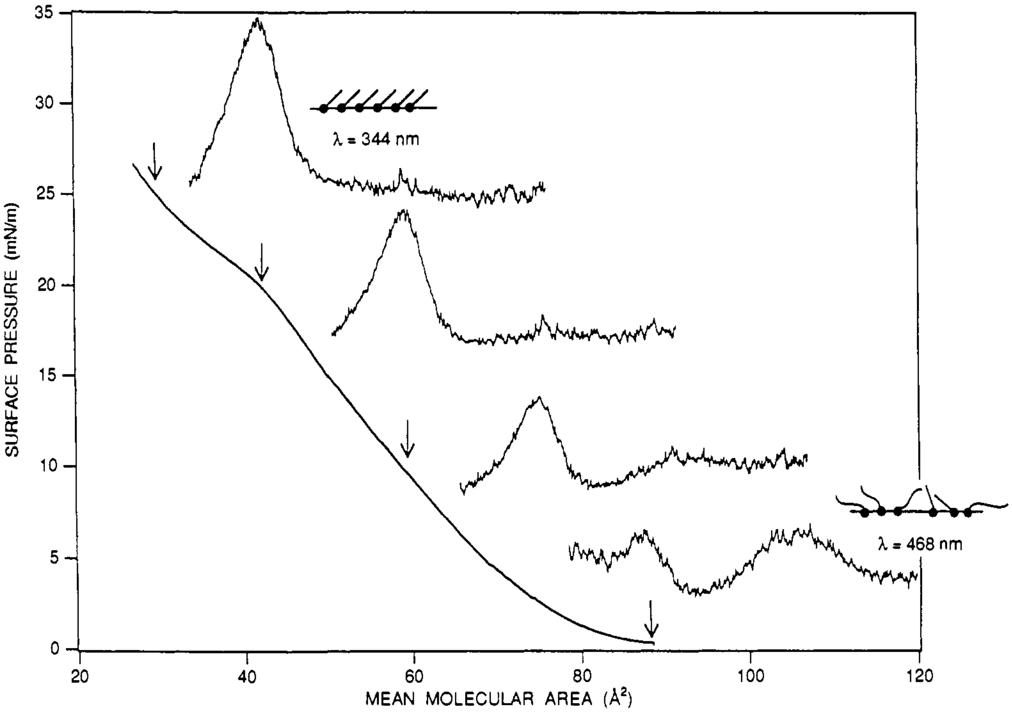

**Figure 2.** Surface pressure versus mean molecular area isotherm together with the corresponding absorbance spectra at the air–water interface. Conditions: $C_{init}$ = 1.1 molecules/nm$^2$, $T$ = 25 °C.

In contrast, the interfacial measurements show intense transitions from both monomer ($\lambda_{ex}$ = 468 nm) and aggregate ($\lambda_{ex}$ = 344 nm), consistent with results from films transferred to $SiO_2$. This result has a number of interesting implications. First, it demonstrates the significant stability of this aggregate assembly. Second, it illustrates clearly the lack of fluorescence arising from the aggregate structure itself, since emission is observed from $\lambda_{ex}$ = 344 nm only in the front-face geometry, in which a large contribution to the signal arises from material adsorbed to the front surface of the cuvette.[14] This observation is consistent with the forbidden nature of this transition (vide infra). Third, the presence of fluorescence upon excitation of the aggregate in the interfacial region confirms that energy transfer between aggregate and monomer is made possible by the close proximity (<10 nm), which is attained only at the $SiO_2$ wall. Finally, the increased fluorescence intensity from both $\lambda_{ex}$ = 344 and 468 nm in the front-face geometry indicates the selective movement of surface stable aggregate structure to the quartz-solution interface.

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[14] Independent experiments in our laboratory have shown that dye **I** readily self-assembles from methanol solution onto $SiO_2$ surfaces and that monomer slowly converts to aggregate in these self-assembled structures. Song, Q.; Bohn, P. W. Unpublished results.

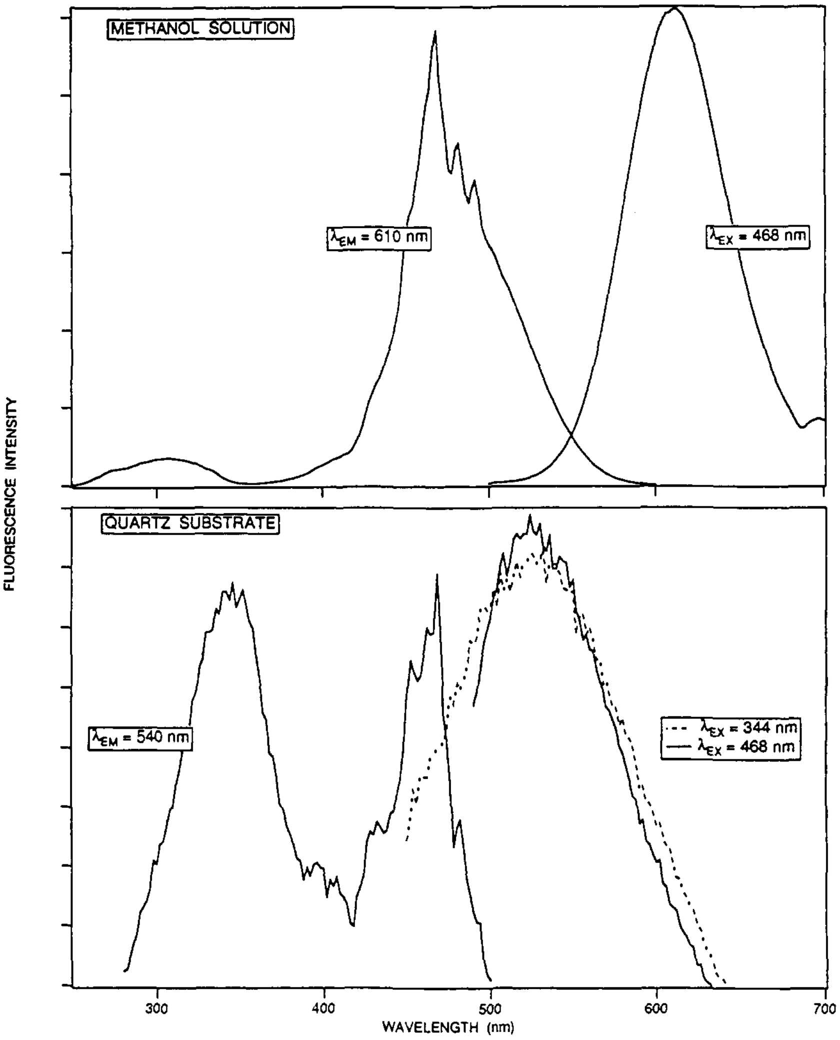


**Figure 3.** Fluorescence excitation and emission spectra of dye **I** in methanol solution (top) and on a fused-silica substrate (bottom).

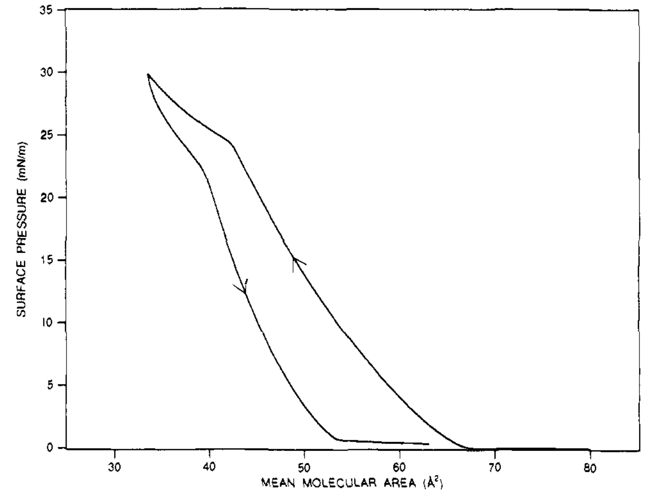


**Figure 4.** Hysteresis curve for surface-pressure/molecular-area isotherm. Forward and reverse compression rates are identical and conditions as described in Experimental Methods.

Independent observations of monolayer structures of dye **I** transferred to fused-silica substrates indicate that they may only be removed by rigorous scrubbing with $CHCl_3$ soaked swabs. Thus the film structure obtained shows remarkable stability, and it is likely that an electrostatic network is created by the zwitterion moiety, rendering the monolayer structure more stable than typical LB films.

The role of aggregation in this monolayer system is further evidenced by the considerable hysteresis in the surface-pressure/molecular-area isotherm (Figure 4). If no aggregation is present, the isotherm is expected to be completely reversible with no change in intermolecular interactions induced during the compression process. In clear contrast, the monolayer formed by dye **I** exhibits the large hysteresis predicted for aggregate formation. Thus, while self-assembly prior to compression plays an important role in the monolayer formation, further aggregation occurs during the compression process giving rise to a significant decrease in the mean molecular area.

*Proposed Models.* Two preliminary models may be evaluated with respect to these interesting results. In the first, the aggregation process forces the C–N bond connecting the tertiary amine to the ring system to rotate out of plane, causing the lone pair on the nitrogen to be inaccessible to conjugation. The transition energy, in this case, is expected to increase due to the destabilization of the excited state induced by the loss of conjugation. The transition energy increase may be estimated by measuring the effect of protonation of the tertiary amine on the absorbance spectra in solution. This measurement should emulate the loss of conjugation caused by forced rotation at the amine nitrogen. Absorbance spectra in methanol as a function of pH (Figure 5) show the expected increase in transition energy clearly. The wavelength shift is similar to that seen with aggregation in monolayer formation, providing some support for this model. However, emission spectra from the protonated ($\lambda_{ex}$ = 325 nm) and unprotonated species ($\lambda_{ex}$ = 500 nm) yield maxima at 410 and 610 nm, respectively. Thus, although the wavelength shift in the absorbance spectra is in good agreement with this

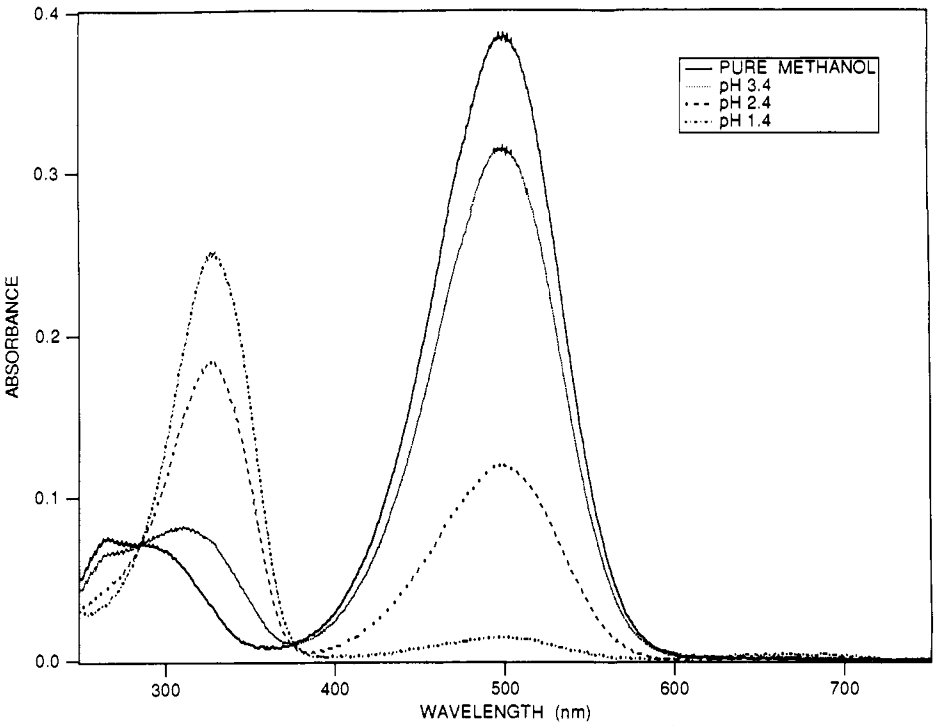
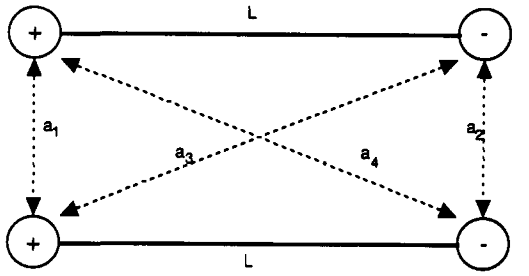


**Figure 5.** Absorbance spectra of dye I as a function of pH in methanol solution. Conditions: $C = 10^{-5}$ M, $T = 25$ °C, sulfuric acid concentration varied from 0 to 0.1% v/v.

**Scheme I**



model, the lack of fluorescence from the 340-nm transition of the aspirated monolayer in solution is not consistent with a protonated species.

In the second model, the frequency shift upon aggregation arises from transition-dipole/transition-dipole interactions resulting from the ordered alignment of molecules within the aggregate. The change in the transition energy upon aggregation may be predicted based on a molecular-exciton model.[15-17] In this model, interaction of neighboring molecules results in the excited aggregate species behaving as an array of coupled-resonant oscillators. Thus, the proximity and alignment of molecules results in excited-state resonance interactions, giving rise to a band of electronic absorption transitions. If molecules are aligned such that the transition moments form a cohesive interaction (*J* aggregate), symmetry considerations require the transition energy of the aggregate to be decreased from that of the monomer. If, however, the molecules are positioned such that the transition moments result in a repulsive interaction (*H* aggregate), symmetry considerations require the transition energy of this aggregate to be increased over the monomer. Calculation of this energy shift is accomplished by considering the interaction between transition dipoles (upon excitation of the molecular lattice) as perturbations on the energy levels within the individual molecule. Presuming an ordered, graphite-like structure, the transition energy for the aggregated species ($\Delta E_{\text{aggr}}$) is expressed as

$$\Delta E_{\text{aggr}} \approx \Delta E_{\text{mono}} \pm 6(1 - 1/N)J_{12} \qquad (2)$$

where $\Delta E_{\text{mono}}$ is the transition energy of the monomer, $N$ is the number of molecules in the aggregate structure, and $J_{12}$ is the interaction energy between adjacent molecules.[4] Based on the formation of an electrostatic network of zwitterions, the molecule of interest here is expected to orient with the transition dipoles in alignment creating an *H* aggregate. The interaction integral is determined based on the extended-dipole approximation proposed by Kuhn,[17]

$$J_{12} = (\epsilon^2/D)(1/a_1 + 1/a_2 - 1/a_3 - 1/a_4) \qquad (3)$$

where the partial charge $\epsilon$ over length $L$ is determined based on the transition moment ($M_{12}$) for the monomer species, and the dielectric constant ($D$) is estimated to be 2.5. The distances between the molecules are dependent on the structural configuration and are illustrated in Scheme I. Since the transition moment of dye I is quite large (13.5 D), yielding an electronic charge of $2.1 \times 10^{-10}$ esu, the shift in the transition energy is expected to be considerable.[18] An upper limit estimate, based on the average distance between molecules at the transfer pressure ($a_1 = a_2 = 5$ Å), results in a change in energy of 18.7 kcal/mol (6411 cm$^{-1}$) for $N > 20$ molecules. In contrast, estimates based on the spacings in the crystal structure ($a_1 = a_2 = 3.4$ Å) result in a change in energy of 27.1 kcal/mol (9442 cm$^{-1}$). The measured energy change upon aggregation of 25.7 kcal/mol (9000 cm$^{-1}$) is in much better agreement with the crystal structure estimate, indicating that the average spacing (as determined from the isotherm) and the most probable spacing differ. This observation can be reconciled by presuming that two populations are present on the surface: a loosely packed monomer at low surface concentration and a distribution of more ordered, tightly packed aggregates. This two-population monomer-aggregate model is fully consistent with all observations.

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(18) Estimation of the transition moment ($M_{12}$) is based on the calculation of the Einstein coefficient ($B_{12}$) from the monomer band profile, where $B_{12} = \int \sigma d\nu / h\nu_0$. Conversion to energy density units allows the direct determination of the transition moment from $B_{12} = |e \cdot M_{12}|^2/\hbar^2$, where $e$ is a unit vector.

Further analysis of this model is accomplished by examining the transition selection rules in aggregate systems. Momentum selection rules dictate that optical transitions must occur with $\Delta k \approx 0$, and since the ground state is formally $k = 0$, the excited state must be also. Because the $k = 0$ state for the $H$ aggregate lies at the top of the band and subsequent relaxation to the lowest energy state ($k > 0$) occurs in a time that is short compared to the excited-state lifetime, the lack of separate emission from the aggregate is explained by momentum selection rules. The only radiative decay path remaining for the aggregate involves energy transfer to the small remnant monomer population, resulting in identical spectral emission. Finally, this model explains why no aggregate-excited emission occurs in the bulk of solution from the aspirated monolayer. Because Förster transfer requires close proximity ($d < \sim 10$ nm) of the two species, this spatial condition is only attained upon readsorption onto the $SiO_2$ surface of the cuvette wall.

## Implications

Both models predict the absorbance wavelength shift upon aggregation accurately, but only the exciton model is successful in describing the remaining aspects of the observed behavior. The fluorescence behavior of the aggregate at the interface, however, appears to arise from the facile energy transfer to the residual monomer species in the aggregated layer. In this case, the monomer species is conjectured to be the sole source of emitted light, and thus identical emission profiles are expected. This proposed energy pathway is quite plausible due to the high probability of energy overlap between aggregate and monomer transitions, inferred from the fluorescence data (Figure 3), and the short distances and probable coupling interactions present in the lattice.

This result has interesting implications for the study of energy migration and trapping in all aggregated systems. In evaluating the movement and loss of excitation energy, a number of possible pathways must be considered, e.g., aggregate fluorescence/phosphorescence, energy transfer to an acceptor, exciton-phonon coupling, electron transfer, nonradiative loss (including that caused by thermal noise). In typical energy transfer studies, a small concentration of donor species is doped into a preponderance of acceptor. Based on the results presented herein, energy transfer to both the aggregated and monomeric forms of the acceptor must be considered. Ignoring this loss mechanism may lead to erroneous conclusions regarding the relative importance of energy decay pathways.

## Conclusions

The hemicyanine dye **I** is shown to form aggregate structures at the air–water interface under low surface pressure conditions. This process is not as kinetically facile as previously presumed and requires significantly more time than simple evaporation of the carrier solvent would indicate. Thus, the initial portion of the isotherm appears to be critical in determining the structure of aggregates within the final monolayer assembly. Upon transfer of the monolayer to a fused-silica substrate, no monomer species are detected by absorbance spectroscopy, but a finite population is observed by fluorescence techniques. The increased transition energy observed upon aggregation is in good agreement with both the removal of the amine lone pair from conjugation and an exciton model. Fluorescence emission behavior, however, is not consistent with either model. We propose that energy transfer between the aggregate and monomer species resulting in monomer emission is responsible for this apparent discrepancy. Thus, the acceptor and donor are of the same chemical structure, differing only in their aggregation state. This energy pathway may be more prevalent for aggregated monolayer assemblies than previously appreciated. Because the understanding of the energy migration and transfer in such monolayer systems is essential for the rational design and fabrication of chemical devices based on vectorial energy and electron transport, further investigation of this interesting energy pathway is presently underway.

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