12616 *J. Phys. Chem.* **1996,** *100,* 12616−12623

Enhanced Aggregation of Derivatized Tolan Surfactants through Donor−Acceptor Interactions at the Air−Water Interface and in Langmuir−Blodgett Films

Catie Weiss Farahat,[†] Thomas L. Penner,*[,‡] Abraham Ulman,*[,§] and David G. Whitten*[,†]

Center for Photoinduced Charge Transfer, Hutchison Hall, University of Rochester,
Rochester, New York 14627

Received: February 26, 1996; In Final Form: April 25, 1996[⊗]

Control of aggregation behavior of derivatized surfactants by moderately polar functional groups as well as the role of charge-transfer interactions governing photophysical phenomena was studied using surfactants incorporating the diphenylacetylene (tolan) chromophore (TFAs) modified with either a sulfone or an ether group (sTA or oTA, respectively). H aggregation is prevalent in these systems as monitored by the spectral shifts of absorption and emission. Packing of surfactants and aggregation were found to be strongly influenced by the presence of bivalent metal cations, Cd^{2+}, in the subphase, as demonstrated by molecular area and chain orientation measurements. The nature of the aggregates formed from sTA surfactants is directly affected by complexation of the acid headgroup; in contrast, the associated oTA chromophore aggregation is unaffected by subphase modifications, despite the altered packing of surfactant chains. The photophysical behavior of aggregated TFAs in monolayer systems was followed at the air−water interface as well as with supported films on quartz, and conclusions can be made of the surfactant arrangements' stability. A unique mixed aggregate was formed when both the ether- and sulfone-derivatized TFAs were incorporated into a single phosphatidylcholine molecule (mixed PC) and deposited as an LB film. This monolayer exhibits additional enhancement in aggregation properties attributed to donor−acceptor interactions between the tolan chromophores that are distinct from a statistically mixed LB sample prepared from a mixture of TFAs. The current results are viewed in terms of general principles governing aggregation for a family of chromophore-derivatized surfactants in LB film.

Introduction

The assembly of derivatized surfactants in two-dimensional matrices using Langmuir−Blodgett techniques has been of great interest in recent years.[1−5] A number of systems have been designed and synthesized in which a chromophore is embedded within an amphiphilic chain in order to study the aggregation of the extended π systems in conjunction with the assembly properties of the surfactant itself. Chromophore aggregation is frequently characterized by distinct photophysical behavior associated with the coupling of the π systems in particular molecular arrangements governed by hydrophobic, hydrophilic, and van der Waals forces. The wide range of applications of this two-dimensional ordering of molecular systems includes studies of energy transfer,[6] long-range electron transfer,[7] and nonlinear optical devices,[8] as well as a determination of fundamental forces controlling molecular aggregate formation under specific boundary constraints.[9]

Kuhn and co-workers have studied aggregation for a number of configurations of clustered dye molecules, using an extended dipole model which relates spectral energy shifts between aggregate and monomer to the orientation and distance between dye molecules.[3,10] In an extension of this model, contributions due to the angular distribution of chromophores about the surface normal have been incorporated in order to predict spectral shifts upon aggregation.[5] The orientation of chain axes and chromophore transition moments have been found to be further directed by the presence of bivalent cations necessary for the formation of a soap monolayer at the air−water interface, and many studies have focused on the role played by the surfactant headgroup in the packing of molecules in LB assemblies.[11] Experimental techniques such as surface reflectance,[12] FTIR-ATR spectroscopy,[11,13] and linear dichroism,[14] as well as computer simulation[9] methods are increasingly used to probe the organization of a large family of derivatized surfactants.

Incorporation of *trans*-stilbene within fatty acid chains (SFAs) has been studied extensively in micelles, bilayer vesicles, and LB films.[4] The observed changes in the absorption and fluorescence upon aggregation in such systems can be explained by a modified "card-pack" exciton model in which the excitation energy is delocalized across an array of transition moments of the individual stilbene molecules.[4,10] Further investigations have revealed the structure of spectroscopically similar H aggregates in vesicles formed from *trans*-stilbene-derivatized phospholipids, and recent results suggest there is a unit size for the aggregate from which the extended assembly is built.[15] Indeed, the tendency to form small aggregates of a specific size (*e.g.*, four chromophore units) strongly governs the packing behavior of the entire surfactant system and may be considered a general model for the behavior of several types of chromophores.[15c,16] In general, H aggregation appears to predominate over other types of aggregation in a wide variety of modified stilbene systems, even those specifically designed to exhibit altered (*i.e.*, J aggregation) behavior.[4b,17]

Directional energy transfer has been demonstrated between types of aggregate clusters in heterogeneous media.[4,17] Extensive studies performed in our lab have involved mixtures of surfactants derivatized with stilbene units at different positions along the hydrophobic chain that show self-aggregation does occur, resulting in discrete domains within LB film samples. Energy transfer is observed between aggregated clusters across

---

* To whom correspondence should be addressed.

[†] Present address: Department of Chemistry, University of Rochester.

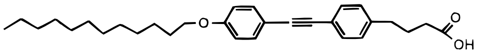
[‡] Present address: Eastman Kodak Company, Rochester, NY 14650.

[§] Present address: Department of Chemistry, Polytechnic University, Brooklyn, NY 11201.

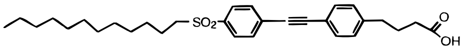
[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

layers to low-energy aggregate traps in the system. Additional studies have involved the arrangement of donor−acceptor-substituted stilbene surfactants in a supported monolayer and the effect of substitution on aggregation behavior.[4] Both charge-transfer interactions between modified chromophore units[4] as well as trapping of the excitation energy of aggregate systems by a small residual population of monomers[5] have been proposed as mechanisms that explain the complex spectral observations when polar chromophores have been studied in LB films. A broader knowledge of the influences of polar substituents on the photophysical properties and aggregation behavior of various chromophore-derivatized amphiphiles is necessary to understand the general controlling influences of chromophore-substituted surfactants in different heterogeneous media.[18]

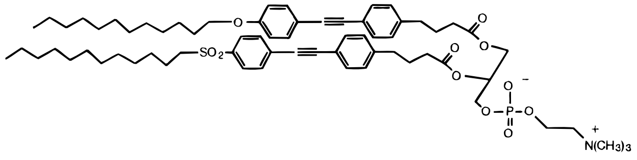
In the present work, representative derivatized surfactants incorporating the rodlike diphenylacetylenic (tolan) chromophore (TFAs) were studied. The tolan moiety in this series was modified with either a sulfone or an ether group (sTA or oTA, respectively) between the aromatic ring and a 12-carbon hydrophobic chain in order to study the role of moderately polar functional groups on the aggregation and photophysical behavior of tolan-modified surfactants in LB film. The tolan-derivatized fatty acids oTA and sTA were found to exhibit blue-shifted absorption and red-shifted fluorescence emission upon assembly in Langmuir film at the air−water interface and in deposited LB films, spectral behavior that is characteristic of H aggregation of chromophores in restricted media similar to that of stilbene-modified surfactants (SFAs). Unlike the SFAs,[19] however, the packing of surfactants was found to be strongly dependent on the presence of the bivalent metal cation Cd^{2+} in the subphase; thus, for TFAs, the complexation of the acid headgroup appears to exert direct influence on the nature of aggregates formed in some cases. A unique mixed aggregate was formed when both ether- and sulfone-derivatized TFAs were incorporated into a single phosphatidylcholine molecule (mixed PC) and deposited as an LB film. This monolayer sample exhibits photophysical properties distinct from a statistically mixed LB film sample prepared from oTA and sTA, in a ratio of 1:1.



oTA



sTA

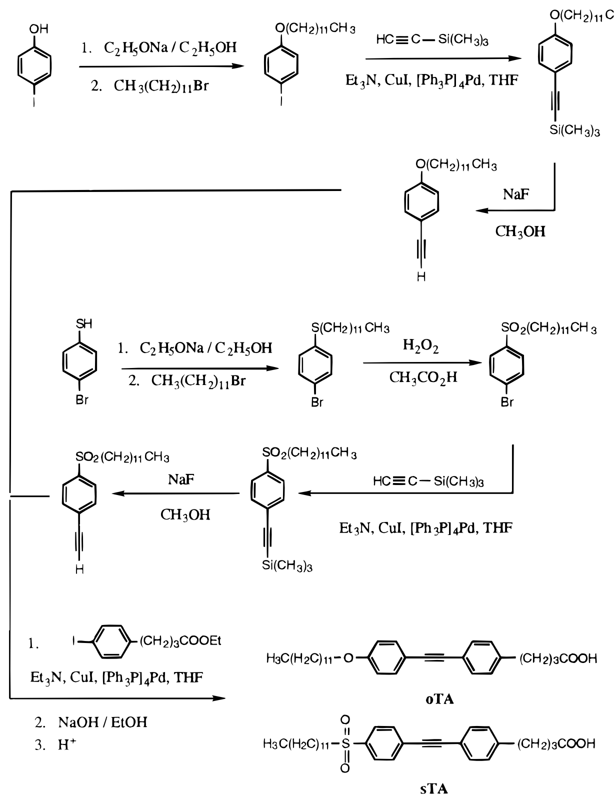


mixed PC

Experimental Section

Materials. The derivatized fatty acids, oTa and sTA, were synthesized[20] in a multistep synthesis by palladium-catalyzed coupling of the corresponding acetylene and iodobenzene derivatives as described in Scheme 1 and crystallized from isopropyl alcohol/heptane before use. The derivatized mixed phosphatidylcholine (mixed PC) was synthesized by the method described by Radhakrisman *et al.* and Bligh and Dyer from the corresponding TFAs.[21] The product mixed PC was purified by preparative TLC. The TFAs and mixed PC derivative were found to be pure by TLC and ^1H NMR, and the fast atom bombardment (FAB) mass spectra obtained show the M^+ ions associated with the parent compounds. Lignoceryl acid was purchased from Avanti Polar Lipids Inc. and used as received. Chloroform and methylene chloride used in all spectroscopic and LB work were HPLC-grade, pentene-stabilized solvents (Fisher). Milli-Q filtered house-deionized water was used for all measurements in an aqueous medium. Quartz glass slides, 1 × 5 cm were cleaned sequentially in chloroform and detergent and followed by “piranha” solution cleaning (30% H_2O_2/H_2SO_4) for 30 min.[22] The quartz substrates were rinsed thoroughly in Milli-Q water and dried before use in the Langmuir−Blodgett assembly.

SCHEME 1



Langmuir−Blodgett Film Preparation. An aliquot of tolan fatty acid or phospholipid in $CHCl_3$ (∼1 mM stock solution) was spread onto an aqueous subphase at 20 °C; unless otherwise noted, the subphase was composed of $CdCl_2$, 3.0×10^{-4} M, and buffered with 5.2×10^{-4} M $NaHCO_3$ (pH 6.8). The organic solvent was allowed to evaporate from the surface for at least 15 min before a compression/expansion cycle was carried out to a maximum surface pressure of 40 mN/m. A film compression in which the isotherm was recorded preceded deposition of the monolayer onto quartz in the upstroke of the substrate through the subphase. The transfer ratios obtained for single monolayers deposited were 1.0 ± 0.1 in all samples prepared. Steady-state measurements were the result of averaged 2−3 separate slide samples.

Absorption and Fluorescence. Routine absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Monolayer samples were oriented perpendicular to the incident light source, and no variation in absorption values was observed upon rotation of the sample ± 45°. Steady-state emission was measured using a SPEX Fluorolog spectrofluorometer with a 300-nm cutoff filter. All emission and excitation spectra were corrected for instrumental response. Film samples were oriented 45° relative to the incident light and detected at a 30° angle from incidence. Fluorescence quantum yields for solutions were determined by comparing with a standard *trans*-stilbene in *n*-pentane ($\phi_f = 0.0435$).[23]

Fluorescence Lifetime Measurements. Time-correlated single-photon-counting (TCSPC) experiments were carried out on an instrument consisting of a mode-locked Nd:YLF laser (Quantronix 4000 Series) operating at 76 MHz as the primary laser source. The second harmonic (KTP crystal) of the Nd:YLF laser was used to synchronously pump a dye laser (Coherent 700) circulating Rhodamine 6G in ethylene glycol as the gain medium. The pulse width of the dye laser was typically 8 ps, as determined by autocorrelation, and was cavity dumped at a rate of 1.9 MHz. The dye laser was tuned to the desired wavelength and frequency doubled in a β-barium borate (BBO) crystal for sample excitation (~295 nm). Emission from the sample was collected by two convex lenses and focused at the entrance slit of a Spex 1681 monochromator (0.22 m) and was detected by a red-sensitive multichannel plate (MCP) detector (Hamamatsu R3809U-01). The single-photon pulses from the MCP detector were amplified and used as the stop signal for a time-to-amplitude converter (TAC, EG&G Ortec), while the signal from a photodiode, detecting a small fraction of the dye laser output, was used as the start signal for the TAC. The start and stop signals for the TAC were conditioned before entering the TAC by passing through two separate channels of a constant fraction discriminator (CFD, Tennelec TC 454). The output of the TAC was connected to a multichannel analyzer (MCA) interface board (Norland 5000) installed inside a 486DX2 personal computer. The MCA was controlled by software from Edinburgh Instruments (Edinburgh, UK). The same software was used to carry out the deconvolution of the data and exponential fitting using the nonlinear least-squares method. The nonexponential fluorescence decays were analyzed using the distribution of lifetimes method provided as part of a commercial software package by Edinburgh Instruments.[24]

Polarization Spectroscopy. Absorption spectra for polarization measurements were recorded on a Perkin-Elmer Lambda 19 DM scanning spectrometer. Supported monolayers on quartz substrate (one side) were investigated in terms of preferential absorption of the p and s linear polarized light components using a film polarizer. Evaluation of molecular orientation was accomplished by considering a four-phase system and assuming uniaxial orientation of the transition moment from the surface normal with an angle θ,[25] Figure 1. The ratio of p- and s-polarized intensities are related to θ as follows:

$$\frac{A_p}{A_s} = \frac{n_1 \cos i + n_3 \cos r}{n_1 \cos r + n_3 \cos i}\left(\cos i \cos r + \frac{2 n_1^{\ 3} n_3 \sin^2 i}{n_2^{\ 4} \tan^2 \theta}\right) \quad (1)$$

where $n_1 = 1.00$ (air), $n_2 = 1.50$ (assumed for LB film), $n_3 = 1.49$ (300 nm) (quartz),[26] $i = 45°$ (angle of incidence at the air−LB film interface), and r = angle of refraction at the LB film−substrate interface:

$$r = \sin^{-1}\left[\frac{n_1}{n_3} \sin i\right] = 28°$$

Surface Reflectance Spectroscopy. Reflectance spectra of spread monolayers on the surface of the subphase were recorded using an Ocean Optics spectrometer equipped with optical fibers and detector. Both excitation (D_2 lamp source) and detection fibers were situated above the surface so that the reflected beams enter the horizontal plane of the optical fibers. Reference spectra were obtained from the pure subphase surface without a spread film. Relative reflectivity (Rf) was calculated from intensity measurements in the dark, I_D, and on the subphase surface, I_R:

$$\mathrm{Rf} = -\left[\log\left(\frac{I_{Rf} - I_D}{I_R - I_D}\right)\right] \quad (2)$$

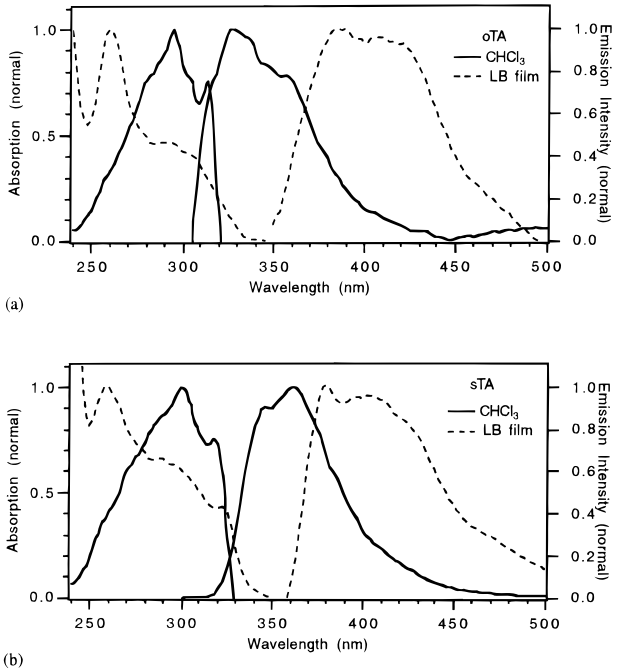


Figure 1. Absorption and fluorescence spectra for (a) oTA and (b) sTA in $CHCl_3$ and LB film. Excitation wavelengths for emission spectra were 290 nm ($CHCl_3$) and 260 nm (LB film).

Results and Discussion

Pure TFAs in Organic Solution and LB Film. The tolan-derivatized acids oTA and sTA are soluble in relatively nonpolar organic solvents ($CHCl_3$, CH_2Cl_2), and the observed absorption and emission spectra are attributed to the monomeric form of the chromophores in dilute solution.[27c] The complex structure of the derivatized tolan absorption spectra can be better understood in relation to the photophysical properties of tolan in solution. In brief, the absorption of tolan is due to three energetically close-lying excited singlet states. Emission occurs from both the lowest excited singlet associated with the ground-state equilibrium geometry and S_2, associated with the equilibrium geometry of the excited state.[27c] The absorption and emission of the supported monolayers of pure oTA or sTA Cd^{2+} salts on quartz are compared with those from $CHCl_3$ solutions in Figure 1a,b. LB films of oTA and sTA exhibit altered absorption spectra (blue-shifted ~ 4700 cm^{-1} relative to $CHCl_3$ solutions), and upon excitation, emission is red-shifted 1000−3000 cm^{-1} from that observed for the monomers in $CHCl_3$. The spectral behavior of TFAs, like that of stilbene fatty acids, is attributed to the formation of H aggregates of the tolan chromophores in LB films in which the transition moments along the long tolan axis are roughly aligned in a head−head arrangement such that a splitting of exciton levels occurs in the excited state. The photophysics associated with the exciton model are depicted in Figure 2. Similarly, dilution of the TFAs with saturated fatty acids of the same extended length (*e.g.*, lignoceryl acid, C_{24}) in LB films up to a molar ratio of 1:10 results in aggregated chromophore systems that display photophysical properties essentially identical to the pure samples; this

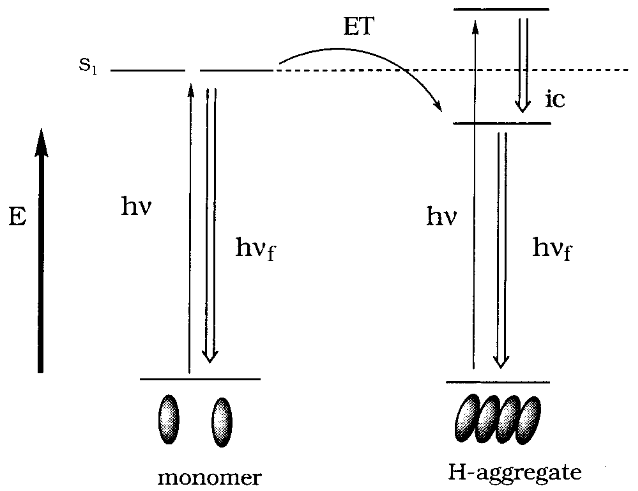


Figure 2. Depiction of exciton splitting of energy levels upon aggregation and associated photophysics.

TABLE 1: Fluorescence Quantum Yields and Lifetimes in $CHCl_3$

	ϕ_f	τ,[a] ns
oTA	0.0033	<0.02
sTA	0.16	0.35
mixed PC	0.018	0.05, 0.28

[a] Lifetimes obtained from the fit of the data to mono- or biexponential decay kinetics.

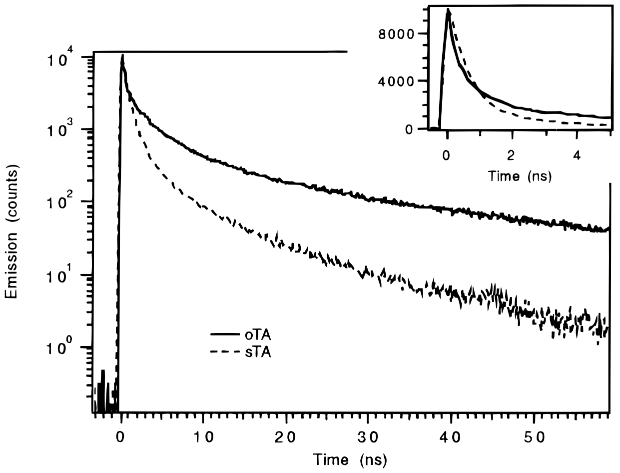


Figure 3. Fluorescence decay kinetics ($\lambda_{exc} = 296$ nm, $\lambda_{mon} = 390$ nm) for pure oTA and sTA LB film samples. Inset: Comparison of TFA decay kinetics during the first 5 ns after pulse, linear scale.

suggests that the mosaic-like clusters of aggregates cannot be readily disrupted upon "dilution" by surfactant molecules.[28] Simple monoexponential decay was measured for the fluorescence of oTA and sTA surfactants in $CHCl_3$, Table 1. The decay kinetics associated with the LB film samples are significantly longer than for the organic solutions (Figure 3); the highly nonexponential fluorescence decay of the LB films persists over nanoseconds, as compared with the picosecond measurements obtained for $CHCl_3$ solutions of TFAs, Table 1. The natural lifetimes of the monomers in solution are calculated to be ca. 1 ns for the individual chromophores; therefore, the observed photophysics of the LB films are attributed to emission from the lower forbidden state, as depicted in Figure 2 for the excitonic splitting of energy levels for an H-aggregated system.

Mixed PC in Organic Solution. The tendency to form a mixed aggregate composed of ether- and sulfone-derivatized tolans was explored using the mixed PC. Unlike other bis-chromophore PCs investigated (*e.g.*, bis(stilbene)PC), where no association was detected in the ground state or excited state for dilute organic solutions, the moderately strong electron donor and acceptor functionalities of oTA and sTA, respectively, were expected to alter the observed photophysics of the system in restricted media through increased charge-transfer interactions.[4b] In Figure 4, the absorption and emission of the mixed PC in $CHCl_3$ are compared with those of the individual TFAs in solution, as well as a dilute (1:1) acid mixture, revealing the altered mixed PC absorption that is distinct from the simple spectral addition of the two acid samples. At first glance, the dominance of emission by the feature virtually identical with that of sTA emission alone is surprising. However, the emission spectrum of mixed PC can be understood upon consideration of the 50-fold difference in quantum yields, ϕ_f, between oTA and sTA in $CHCl_3$ (Table 1). If the two chromophores in the mixed PC are in fact remote from one another, then the emission is expected to be dominated by sTA fluorescence. On the other hand, if there is some close interaction between the ether- and sulfone-tolans of the mixed PC in solution, as suggested by the distinctive absorption spectrum (Figure 4b), then another explanation for the emission features is plausible: possibly an equilibrium exists between an open (remote chromophores) form and a closed (interacting chromophores) form such that the fraction of the population adopting the open form acts as a Förster energy trap for the entire system, giving rise to emission associated with monomeric sTA, Figure 2.

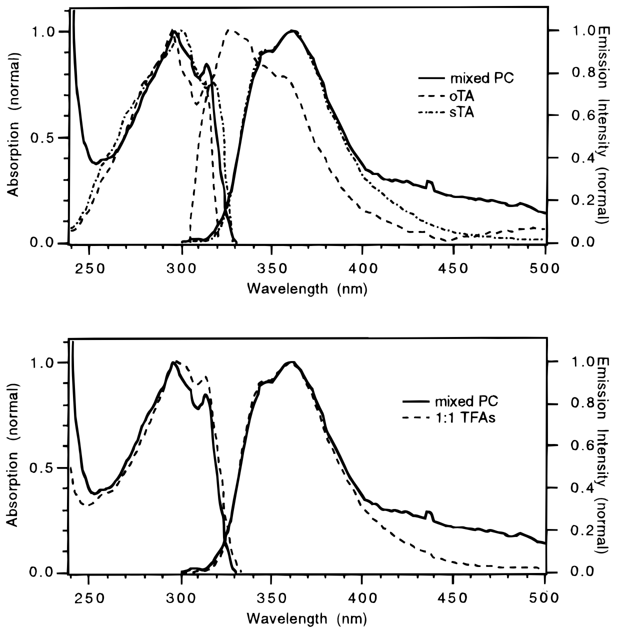


Figure 4. Absorption and fluorescence spectra for oTA, sTA, and mixed PC solutions in $CHCl_3$ (2×10^{-5} M); $\lambda_{exc} = 290$ nm, 25 °C.

$$\begin{array}{lcll} & & \text{closed} \longrightarrow & \text{open} \\ & & \text{closed} \xrightarrow{h\nu} & \text{*closed} \\ \text{*closed} & + & \text{open} \xrightarrow{\text{ET}} & \text{closed} + \text{*open} \\ & & \text{*open} \xrightarrow{\text{flr}} & \text{open} + h\nu \end{array}$$

From a biexponential fit of the decay kinetics for the mixed PC in $CHCl_3$, two lifetime components were obtained, 50 and 300 ps, suggesting two remote TFAs in solution. However, the value of ϕ_f for the mixed PC is not an average of those associated with the individual oTA and sTA fluorophores. Clearly, some pathway for depopulating the excited state(s) of the mixed PC is available, giving rise to a quantum yield

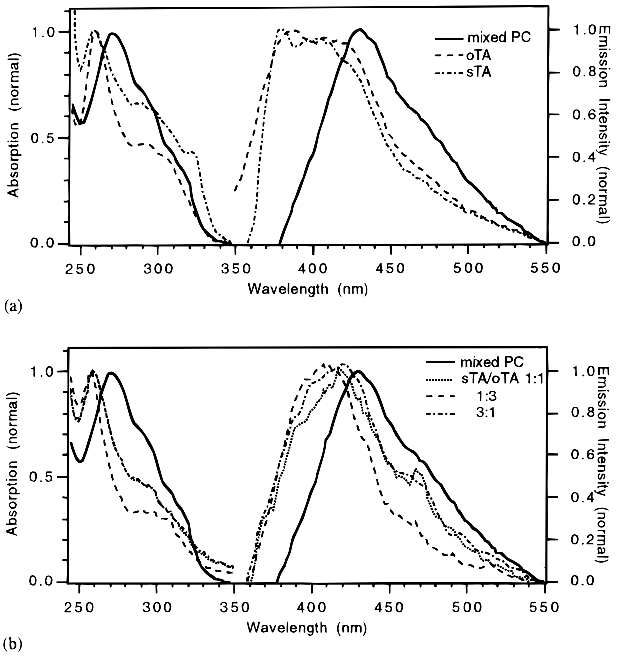


Figure 5. Absorption and fluorescence for LB films of (a) mixed PC compared with pure oTA and sTA films; (b) mixed PC compared with films composed of mixtures of TFAs in various ratios, as noted.

significantly lower than the one expected for remote fluorophores in organic solution.[29]

Mixed PC in LB Film. When an LB film is prepared from the mixed PC on quartz substrate, the absorption and emission are characteristic of an H-aggregated chromophore system, Figure 5a. Absorption and emission are shifted to the blue and red, respectively, similar to the behavior of stilbene-derivatized surfactants. However, the spectral features of the mixed PC LB film are distinct from pure TFA LB films as observed from the narrow absorption absorption and emission of the mixed PC appearing at lower energies relative to the pure TFAs' LB film bands. Accordingly, LB films of mixtures of oTA and sTA in various ratios were prepared, and their spectra are compared with the mixed PC in Figure 5b. These results demonstrate that the steady-state spectra for the mixed PC are not additive with respect to the individual chromophores in restricted media, but rather, a unique aggregate is formed between the derivatized tolans in the mixed PC that is not readily adopted in the mixed TFA samples. It must be noted that some narrowing of emission bands occurs in the mixture LB films that is distinct from pure TFA LB films, indicative of some degree of enhanced interactions between chromophores. The red-shifted absorption spectrum of the mixed PC (relative to pure TFAs) is then attributed to a population of "heterodimers" as opposed to the mixed TFAs in LB films which appear to contain predominantly zones of like aggregates with some residual interactions between different chromophores. No modification of spectral features was observed with dilute $CHCl_3$ solutions of TFA mixtures; Beer's law is obeyed, and absorption and emission appear to represent simple mixtures of unassociated TFAs. Absorption and fluorescence spectra for samples of mixed PC diluted with lignoceroyl acid (LA) (1:7) display the same spectral shifts associated with aggregate formation, suggesting the heterodimer is responsible for these observations. In Figure 6a, fluorescence decay kinetics for LB film samples of the mixed PC and pure TFAs as well as the 1:1 mixed acid sample are compared, demonstrating the long-lived nonexponential fluorescence decay of the mixed PC in LB film. For qualitative comparison of the fluorescence decay kinetics for LB film samples presented in Figure 6a, a distribution analysis was utilized to show the overall relative contributions of various fluorescent components. It must be mentioned that reasonable analyses are expected from decay kinetics of 10 000 counts for systems in the absence of any energy transfer or spectral shifts during the lifetime of the excited state,[24] and therefore, interpretation of the individual lifetime clusters must be done with care. Nevertheless, some comparison between sample profiles is useful. Figure 6b depicts the relative intensities of lifetimes components for the four LB film samples subjected to this analysis. On inspection of the lifetime distribution comparison, one finds that a significant portion of fluorescence emission of the mixed PC LB film system is due to very long-lived (>20 ns) emissive species that are virtually absent in pure TFA samples and present to a much smaller degree in the 1:1 TFA mixture LB sample.

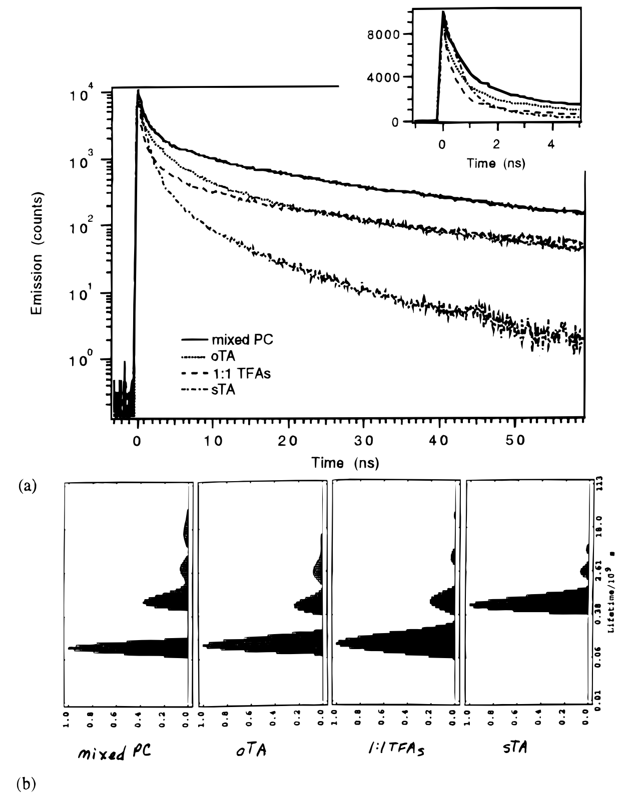


Figure 6. (a) Fluorescence decay kinetics of LB film samples compared with representative kinetics for $CHCl_3$ solution, as noted; (b) distribution of lifetimes associated with kinetics.

Influence of Cd^{2+} Complexation on TFAs' Aggregation Behavior. It is common practice to prepare Langmuir films on an aqueous subphase that contains bivalent metal cations, such as Cd^{2+}, in order to form stable monolayer soaps of the complexed surfactants that are insoluble in the aqueous phase.[2] In the previously discussed studies, Cd^{2+} was consistently employed in this manner to prepare monolayers for investigation. Monolayers formed upon aqueous solutions containing no metal cations are expected to be of comparable overall stability but composed of surfactants (and associated chromophores) arranged differently, due to the larger molecular area adopted by the surfactants under these conditions. Cd^{2+} complexation is known to alter the molecular area of arachidic acid, for example, at the subphase surface, in addition to causing a shift in the molecular orientation of the fatty acid chains from 25°, relative to the surface normal, to a near-perpendicular orientation.[25] Nevertheless, we were surprised to find that some aggregation and photophysical behavior of the TFAs is dramatically altered when monolayers are prepared in the absence of Cd^{2+} cations. In the present studies, UV surface absorption (relative reflec-

TABLE 2: Molecular Areas from Isotherms and Tilt Angles from Polarization Spectra

tolan/subphase	molecular area,[a] Å^2	θ, deg
sTA/CdCl$_2$	22	12
oTA/water	26	15
oTA/CdCl$_2$	30	16
sTA/water	34	18

[a] Measured from surface pressure−area isotherm extrapolated to 0 compression (±5% molecular area). [b] θ calculated from polarized absorption spectra, as described in the text (±10% angle).

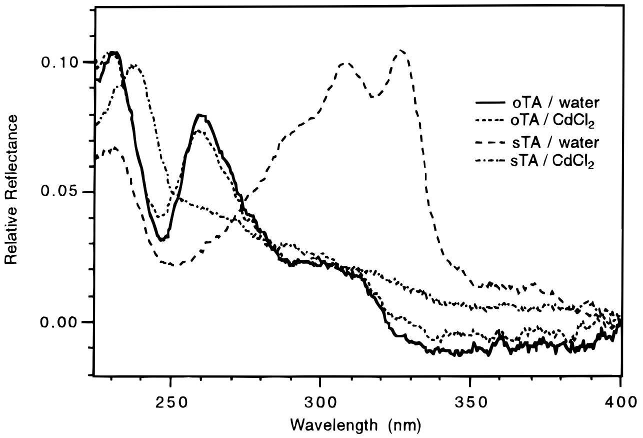


Figure 7. Absorption spectra (relative reflectance) for TFA monolayers at the air−water interface, within 30 min of film compression to 40 mN/m; subphase as noted.

tance) was used to probe the aggregation behavior of tolan-functionalized fatty acids at the air−water interface in the presence and absence of Cd^{2+} ions in buffered (pH 6.8) aqueous subphase. While surface pressure−area isotherms monitored during compression for oTA and sTA on either buffered water or buffered Cd^{2+}-containing subphase display similar shapes, the molecular areas obtained for the TFAs at 40 mN/m were found to be significantly different between oTA and sTA, as well as between those obtained on different subphases, Table 2. Indeed, a trend reversal was observed, for oTA exhibits a slightly larger molecular area when complexed with Cd^{2+} than in water and the sTA/Cd^{2+} system exhibits a smaller molecular area than does sTA on water. Notably, reflectance spectra obtained at the air−water interface compared for the four systems reveal the marked difference between sTA on water (λ_{abs} = 300−330 nm) and on Cd^{2+}-containing subphase (λ_{abs} < 240 nm) (Figure 7), while oTA and the mixed PC absorption spectra are virtually indistinguishable in both subphase compositions and when monitored as a function of time. In order to determine more precisely the arrangement of tolan chromophores that are aggregated under the two subphase conditions discussed, the two-dimensional density (molecular area) and the photophysical properties are considered.[30]

First, a comparison was made between UV absorption spectra of quartz-supported monolayers and air−water interface films, to monitor if the integrity of film aggregation was maintained upon transfer to solid support, Figure 8. The broad absorption (300−330 nm) of sTA monolayer formed at the air−water interface of a water subphase was observed for the supported film from the same subphase conditions; however, one notable difference was observed between absorption for sTA/Cd^{2+} at the air−water interface (λ < 240 nm) and the supported film (λ = 260 nm). Some explanation for the sTA spectral variations observed can be made in light of the UV polarization measurements and the present experimental technique (*vide infra*). No distinguishable spectral differences were observed between oTA deposited from different subphase conditions. All fluorescence spectra of the supported monolayers prepared from Cd^{2+} subphase show broad emission at 380−420 nm; however, emission at lower energy (λ_{em} = 430 nm) resulted only upon excitation of sTA deposited from the water subphase. An important comparison is made of the absorption and emission of sTA in CHCl$_3$ solution and the LB films of sTA prepared on both water and Cd^{2+}-containing subphase, revealing absorption of the LB film from water that is broadened and more structured than the CHCl$_3$ solution, yet only slightly perturbed in energy, Figure 9, in contrast with the blue-shifted absorption of sTA/Cd^{2+}. The red-shifted emission from the sTA/water LB film is also compared with fluorescence associated with other samples. These results strongly support a model in which an arrangement is adopted of compressed sTA chromophores on the water subphase that may not form an extended H-aggregated array to the same extent as with Cd^{2+} complexation.

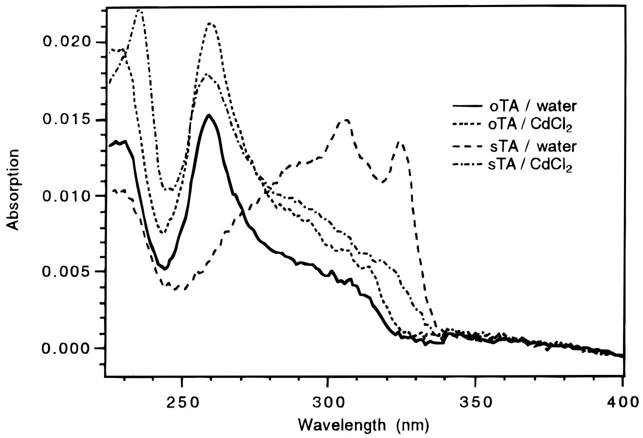


Figure 8. Absorption spectra for LB films on quartz transferred from subphase as noted.

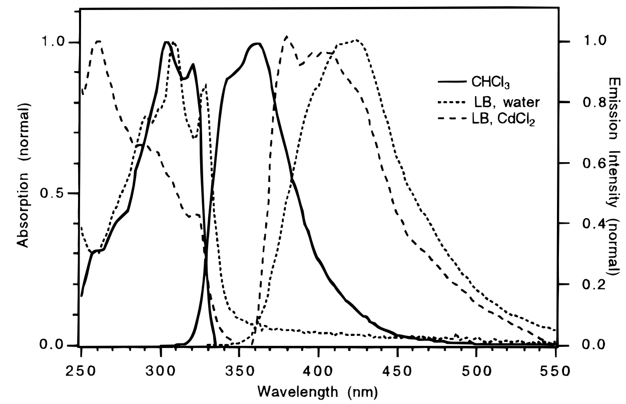


Figure 9. Absorption and fluorescence spectra for sTA on quartz, transferred from subphase, compared with CHCl$_3$ solution as noted; λ_{exc} = 260 nm (CdCl$_2$), λ_{exc} = 300 nm (water, CHCl$_3$).

In a second investigation, an attempt was made to shift the arrangement of sTA on water that gives rise to the unique photophysical features compared in Figure 9 to that of sTA on Cd^{2+}-containing subphase by simply injecting an appropriate volume of CdCl$_2$ stock solution into the subphase to reproduce the Cd^{2+}-containing subphase conditions. Upon diffusion of Cd^{2+} ions throughout the bulk subphase under the formed film, the spectral feature of the film was expected to shift toward that associated with sTA/Cd^{2+} at the air−water interface. Surprisingly, no such spectral shift took place after 24 h, even after repeated expansion and compression cycles of the film in addition to thorough mixing of the subphase below the formed

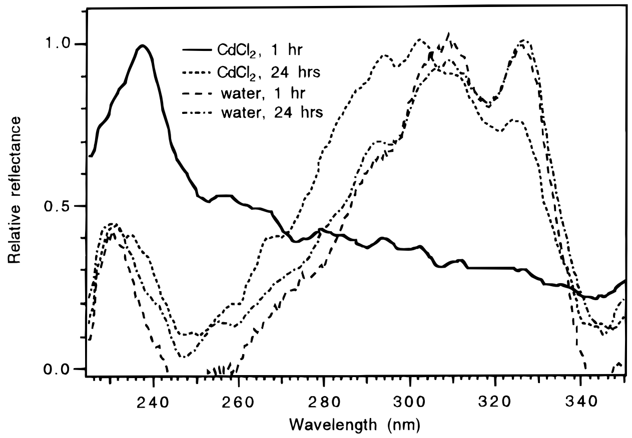


Figure 10. Comparison of absorption spectra for sTA film at the air−water interface, in subphase as noted, 1 and 24 h after compression at 40 mN/m.

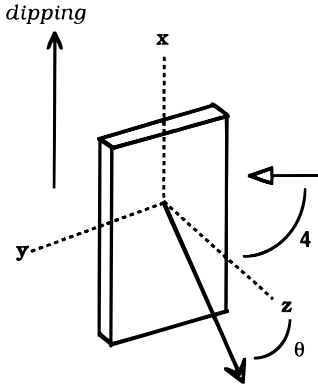


Figure 11. Depiction of transition moment orientation with respect to quartz surface normal and s- and p-polarized light components.

film. This behavior suggests that the original structure is ordered and that a sort of annealing process takes place that starts from grain boundaries and penetrates into the cluster. That repeated expansion−compression did not affect the order is not surprising since the expansion probably gives small ordered clusters. A control experiment revealed the stability and preference for the *expanded* orientation of an sTA film formed on either subphase; when sTA is spread on a Cd^{2+}-containing subphase, initially, the spectral features include absorption below 240 nm, which appears stable over ~8 h. Maintenance of the film at a stable surface pressure (40 mN/m) over 24 h results in a surface absorption that has shifted to 300−320 nm and is significantly broadened, Figure 10. This resultant spectrum is similar to that of sTA on the water surface and appears to represent the stable arrangement of aggregated sTA in the monolayer.

Linear Dichroism of TFA-Supported Monolayers. Polarized absorption spectra of single monolayer films of TFAs, prepared from aqueous or Cd^{2+}-containing subphase supported on quartz slides, were compared in the UV region. From an analysis of the ratio of p- and s-linearly polarized components of a spectrum, a value for the tilt angle, θ, of the long axis associated with the $\pi-\pi^*$ transition was estimated from eq 1 (Figure 11). These tilt angles are compared in Table 2, along with the molecular areas obtained from the isotherms of spread monolayers immediately after compression. The trend of molecular tilt angles of the TFAs from the surface normal is consistent with that observed for molecular areas obtained from surface pressure−area isotherms. It is important to note that because of the inhomogeneity of chromophore arrangements in the supported LB films, the tilt angles of an assumed uniaxial sample of long-chain molecules need to be broadly interpreted as those representing an *average* tilt adopted by the chromophore population. With the orientation of chromophores in mind, it is of particular interest to compare the absorption spectrum for sTA/Cd^{2+} on quartz with that of the monolayer on the subphase surface. The lowest energy absorption band at 260 nm is virtually absent in the spectrum taken at the air−water interface, while it is present for the quartz-supported system. It is proposed that because of the small average tilt angle associated with the sTA/Cd^{2+} system in the LB film, a similar angle of chains (perpendicular to the subphase surface) is adopted and the interaction of the p-polarized light with the molecules' transition moments is minimized due to the orientation of the horizontal plane of the fiber optics parallel with the surface plane.[31] In contrast, the relatively large average tilt angle of sTA/water is expected to allow interaction of both p and s components of the electric field with the chromophores to occur. No oblique reflection setup is possible with the present system in order to probe further this phenomenon.

Conclusions

Novel ground-state aggregation is observed for amphiphilic tolan derivatives in spread monolayers at the air−water interface and in LB films. In agreement with our understanding of the aggregation properties of stilbene-derivatized surfactants, a model of H aggregation serves to explain some of the photophysical observations for the LB films of tolan derivatives, prepared on Cd^{2+}-containing subphase, depicted by the exciton splitting model (Figure 2). However, the simple H-aggregate model for arrangement of aggregated chromophores is not sufficient to completely explain all of the current results. The behavior of sTA on a water subphase suggests a more expanded matrix of surfactants is formed, in which both chain packing and tolan aggregation occur to a smaller degree than with Cd^{2+} complexation. Nevertheless, the appearance of red-shifted fluorescence emission is indicative of an aggregated sTA sample in which emission occurs from the forbidden energy level. The comparable ground-state absorption spectra of oTA, independent of subphase composition, suggest the extended H aggregation of chromophores occurs to a similar extent under both subphase conditions.

The unusual photophysical behavior of the sTA/water system may be understood by considering the following plausible models: (1) The emission that is observed for sTA/water LB films is excimer-like, implying that the sTA molecules have no significant ground-state interactions that would significantly alter their absorption spectra, yet the emission is clearly shifted from that associated with the monomer. The likelihood for formation of a complex between one excited sTA molecule and a ground-state sTA in a restricted medium such as an LB film during the lifetime of the excited state is small, and therefore, other explanations are sought. (2) Only residual emissive aggregates may exist (<1%) amidst nonaggregated sTA, and these aggregates act as energy traps (*vide supra*).[5,32] The microheterogeneous nature of the aggregated tolans is established by the wavelength dependence of the steady-state fluorescence and excitation spectra, as well as the highly nonexponential nature of the fluorescence intensity decays. Red-shifted fluorescence spectra for tolan derivatives exhibit excited-state lifetimes that are 40−500 times longer than those of monomeric species in solution. The observed lifetimes are also several times longer than the natural radiative lifetime of the monomeric species and can be attributed to emission from the lowest (forbidden) excitonic level of particular aggregates. Moreover, the degree of aggregation in LB films appears dependent on both tolan substituents and subphase composition.

Given the nonexponential nature of the fluorescence decay kinetics, which do not easily fit into a simple model with few components, the existence of both aggregates and monomers in varying percentages is likely. While any fluorescence rise for this system cannot be detected within 20 ps, the limit of the instrumentation, energy transfer cannot be ruled out as a mechanism for the trapping of excitation energy in a small percentage of aggregates. (3) Ground state H dimers of sTA on water may be formed in which the absorption appears close to that of the organic solution. Conceivably, there may be both blue-shifted absorption occurring associated with H aggregation as well as red-shifted absorption due to charge-transfer behavior, resulting in the absorption that is close in energy to that of the monomer. Furthermore, the emission expected from such a system should be red-shifted relative to the monomeric spectrum, as is presently observed. For a related system in which charge transfer plays a crucial role in the photophysics of polar-substituted stilbene surfactants, see ref 4b. Current work in our laboratory is continuing to address the issues involved with the aggregation behavior of the tolan series.

H-type aggregation is observed for the covalently linked ether/sulfone-derivatized tolan phospholipid, mixed PC. Indeed, some interaction between the covalently linked ether and sulfone is even observed in dilute organic solutions of the mixed PC. Upon consideration of ϕ_f values for oTA and sTA, the spectral shape of the emission is not expected to vary significantly from that of one close to pure sTA in $CHCl_3$, yet the low fluorescence quantum yield of the mixed PC in $CHCl_3$ can be explained by a mechanism of an enhanced nonradiative decay pathway available to the molecule in solution due to the close proximity of ether and sulfone tolans in a single molecule. Furthermore, while the pure sTA or oTA LB films exhibit distributions of several lifetime components, which point to the inhomogeneous nature of TFA aggregates in the supported film, both the degree of red-shifted emission associated with the mixed PC aggregate in LB film and the very long fluorescence decay time indicate a unique aggregated form of the ether- and sulfone-modified tolans is achieved when they are constrained in the PC, in contrast to a simple 1:1 distribution of the individual acids in LB film. This effect is attributed to an enhancement of H aggregation between ether- and sulfone-derivatized tolans due to charge-transfer interactions that are favorable when donor and acceptor species are closely aligned.

Acknowledgment. We gratefully acknowledge the National Science Foundation for a Science and Technology Center Grant (CHE-9120001).

References and Notes

(1) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic: Boston, 1991.

(2) Roberts, G. *Langmuir Blodgett Films*; Plenum: New York, 1990 and references therein.

(3) (a) Czikkely, V.; Försterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 11. (b) Czikkely, V.; Försterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 207.

(4) (a) Mooney, W. F., III; Brown, P. E.; Russell, J. C.; Costa, S. B.; Pederson, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5659. (b) Furman, I.; Geiger, H. C.; Whitten, D. G.; Penner, T. L.; Ulman, A. *Langmuir* **1994**, *10*, 837.

(5) (a) Evans, C. E.; Song, Q.; Bohn, P. W. *J. Phys. Chem.* **1993**, *97*, 12302. (b) Song, Q.; Evans, C. E.; Bohn, P. W. *J. Phys. Chem.* **1993**, *97*, 13736. (c) Evans, C. E.; Bohn, P. W. *J. Am. Chem. Soc.* **1993**, *115*, 3306.

(6) (a) Bohn, P. W. *Annu. Rev. Phys. Chem.* **1993**, *44*, 37. (b) Penner, T. L. *Thin Solid Films* **1988**, *160*, 241.

(7) (a) Kuhn, H. *J. Photochem.* **1979**, *10*, 111. (b) Hsu, Y.; Penner, T. L.; Whitten, D. G. *J. Phys. Chem.* **1992**, *96*, 2790.

(8) Penner, T. L.; Willand, C. S.; Robello, D. R.; Schildkraut, J. S.; Ulman, A. *Proc. SPIE* **1991**, *1436*, 169.

(9) Perlstein, J. *J. Am. Chem. Soc.* **1994**, *116*, 11420.

(10) (a) Kuhn, H.; Möbius, D.; Bucher, H. In *Techniques of Chemistry*; Weissberger, A., Rositer, B. W., Eds.; Wiley: New York, 1973; Vol. 1, Part 3B. (b) Kuhn, H.; Möbius, D. *Angew. Chem.* **1971**, *83*, 672. (c) Kuhn, H.; Möbius, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *10*, 620.

(11) Ahn, D. J.; Franses, E. I. *J. Phys. Chem.* **1992**, *96*, 9952.

(12) Gruniger, H.; Möbius, D.; Meyer, H. J. *J. Chem. Phys.* **1983**, *79*, 3701.

(13) Takenaka, T.; Nogami, K.; Gotoh, H.; Gotoh, R. *J. Colloid Interface Sci.* **1971**, *35*, 395.

(14) (a) Chollet, P.-A. *Thin Solid Films* **1978**, *52*, 343. (b) Vandevyver, M.; Barraud, A.; Daudel-Teixier, A.; Maillard, P.; Gianotti, C. *J. Colloid Interface Sci.* **1982**, *85*, 571.

(15) (a) Chen, H.; Farahat, M. S.; Law, K.-Y.; Whitten, D. G. *J. Am. Chem. Soc.*, in press. (b) Song, X.; Geiger, C.; Furman, I.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 4103. (c) Song, X.; Geiger, C.; Leinhos, U.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 10340.

(16) Preliminary results involving phospholipids of tolan derivatives in aqueous solution suggest a unit size composed of six chromophores: Farahat, C. W. Unpublished results.

(17) Spooner, S. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 1240.

(18) Chen, H.; Farahat, C. W.; Farahat, M. S.; Geiger, H. C.; Leinhos, U. W.; Liang, K.; Song, X.; Penner, T. L.; Ulman, A.; Perlman, J.; Law, K.-Y.; Whitten, D. G. *Mater. Res. Bull.* **1995**, *6*, 39.

(19) Farahat, C. W. Unpublished results.

(20) Ulman, A. Unpublished results.

(21) (a) Radhakrishman, R.; Robson, R. J.; Takagaki, Y.; Khorana, H. G. *Methods in Enzymology*; Academic: New York, 1982; Vol. 72, Chapter 29. (b) Bligh, D.; Dyer, W. J. *Can. J. Biochem. Physiol.* **1959**, *37*, 911.

(22) Pintchovski, F.; Pricw, J. B.; Tobin, P. J.; Peavey, J.; Kobold, K. *J. Electrochem. Soc.* **1979**, *126*, 1428.

(23) Saltiel, J.; Marinari, A.; Chang, D. W.-L.; Mitchener, J.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

(24) Gakamsky, D. M.; Goldin, A. A.; Petrov, E. P.; Rubinov, A. N. *Biophys. Chem.* **1992**, *44*, 47.

(25) (a) Chollet, P.-A. *Thin Solid Films* **1978**, *52*, 343. (b) Vandevyver, M.; Barraud, A.; Daudel-Teixier, A.; Maillard, P.; Gianotti, C. *J. Colloid Interface Sci.* **1982**, *85*, 571.

(26) *CRC Handbook of Chemistry and Physics*, 71st ed.; CRC: Boca Raton, FL, 1990.

(27) (a) Tanizaki, Y.; Inoue, H.; Hoshi, T.; Shiraishi, J. *Z. Phys. Chem. (Munich)* **1971**, *74*, 45. (b) Hirata, Y.; Okada, T.; Mataga, N.; Nomoto, T. *J. Phys. Chem.* **1992**, *96*, 6559. (c) Ferrante, C.; Kensy, U.; Dick, B. *J. Phys. Chem.* **1993**, *97*, 13457.

(28) This phenomenon of aggregate clusters forming amidst a high concentration of fatty acid "dilution" molecules in LB film occurs commonly with a variety of chromophores such as stilbene- and squaraine-derivatized surfactants; see refs 4b and 15.

(29) The fluorescence "tail" observed for the mixed PC in the red region of the spectrum (410−500 nm) was analyzed by distribution of lifetimes with identical results, compared with the 360-nm emission maximum. This spectral feature may be due to emission from the **closed* state of the system, referred to in the text.

(30) The values of molecular areas obtained from isotherms compare well with those obtained for saturated fatty acids under the same subphase and surface pressure conditions, between 20 and 35 Å^2 (ref 2). While the formation of multilayers or collapsed domains at the air−water interface cannot be ruled out before microscopy techniques are utilized (*e.g.*, Brewster angle, fluorescence), the stability of films under the present conditions suggest only monolayers are formed.

(31) Orrit, M.; Möbius, D.; Lehmann, U.; Meyer, H. *J. Chem. Phys.* **1986**, *85*, 4966.

(32) This mechanism of energy trapping is being further probed with *trans*-stilbene-derivatized surfactant systems: Farahat, M. S. Unpublished results.

JP960579G