Energy and Electron-Transfer Processes through Langmuir–Blodgett Multilayers Formed from α,ω-Diphenylpolyene Surfactants

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Received August 23, 1993. Revised Manuscript Received November 15, 1993®

Abstract: The spectral properties, as well as photoinduced electron and energy-transfer processes, of fatty acid derivatives of α,ω-diphenylpolyenes including stilbene, diphenylbutadiene, diphenylhexatriene, and various heteroatom substituted stilbene derivatives were investigated in multilayer assemblies constructed using the Langmuir–Blodgett (LB) technique. The majority of surfactant α,ω-diphenylpolyene derivatives were found to exhibit spectral properties characteristic of "H" aggregates when incorporated into multilayer assemblies. The tendency of surfactant stilbenes to form "H" aggregates was observed to be greater than that exhibited by other α,ω-diphenylpolyene surfactants studied. Multilayer assemblies containing equal molar ratios of mixed surfactant stilbene derivatives to cosurfactant show "H" aggregate spectra and aggregate intermediates absorbing between monomer and pure "H" aggregates, possibly "H" dimers. Evidently "H" aggregate formation predominates over any other type of aggregate formation in these mixed surfactant stilbene assemblies. The fluorescence from either a single stilbene fatty acid (SFA) or mixed SFA assemblies was quenched by various surfactant electron-transfer acceptors, such as surfactant viologen and cobalt complexes. While small spectral differences were observed in the absorption and emission spectra between single and mixed SFA's, large differences were observed between the excited-state behaviors of single and mixed SFA multilayer assemblies. Little if any energy migration occurred among the single SFA monolayers, whereas enhanced energy migration was observed in mixed SFA multilayer assemblies. Directional energy transfer has been demonstrated in LB assemblies containing a series of α,ω-diphenylpolyene monolayers sequentially layered in order of decreasing energy.

Introduction

Much recent effort has been focused on developing systems that provide effective transfer of energy or charge across interfaces consisting of at least one formally "insulating" component. Examples include studies of charge transport across bilayer membranes,[2,3] efforts to make effective dye–semiconductor junctions that operate vectorially,[4,5] some very elegant studies of functionalized polymers,[6,7] photoelectrochemical cells based on appropriately derivatized electrodes,[4,5,8] and numerous studies of thin films constructed by either Langmuir–Blodgett or other self-assembling techniques.[9] All of these studies in the realm of "artificial photosynthesis" have in common the assembly of potentially reactive components into an organized array in which "supramolecular" behavior uncharacteristic of the individual molecules results.[10] In many of these examples, the very high effective concentration of individual reagents leads to aggregation phenomena and often to assemblies that are not detectable in dilute condensed phases.[11,12] This can lead to complications in several cases since the aggregates may behave quite differently with regard to their photophysical behavior compared to the individual molecules.

An example from previous studies in our laboratories has been provided by the synthesis and study in Langmuir–Blodgett assemblies of the amphiphilic *trans*-stilbene derivatives whose structures and acronyms are shown in Chart 1.[13,14] In earlier studies, Mooney et al. found that these stilbene derivatives form "H" aggregates exhibiting blue shifts in their prominent absorption transitions and red-shifted long-lived fluorescence. Although such aggregates cannot be observed in dilute or even moderately concentrated organic solutions, they are the exclusive species detected in Langmuir–Blodgett (LB) assemblies formed from either pure stilbene amphiphiles or even relatively diluted (with saturated fatty acids such as arachidic acid (AA)) mixtures. The "H" aggregates have low oscillator strengths; the relatively rigid solid environment provided by the LB assembly inhibits deactivation by other pathways; consequently, the fluorescence efficiency is relatively high and the fluorescence lifetime moderately long. Earlier studies showed that, while the fluorescence from these aggregates could be quenched by energy transfer to acceptors having high oscillator strength, degenerate energy transfer between stilbene aggregates was very ineffective, and consequently, in multilayer assemblies of the stilbene aggregate, there was little or no "antenna effect" or interlayer energy transfer.[13,14]

The present paper focuses on phenomena occurring with mixed mono- and multilayers of a series of stilbene fatty acids (SFA's),

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® Abstract published in *Advance ACS Abstracts,* January 1, 1994.

[1] Taken in part from the Ph.D. Dissertation of Susan P. Spooner, University of Rochester, 1993.

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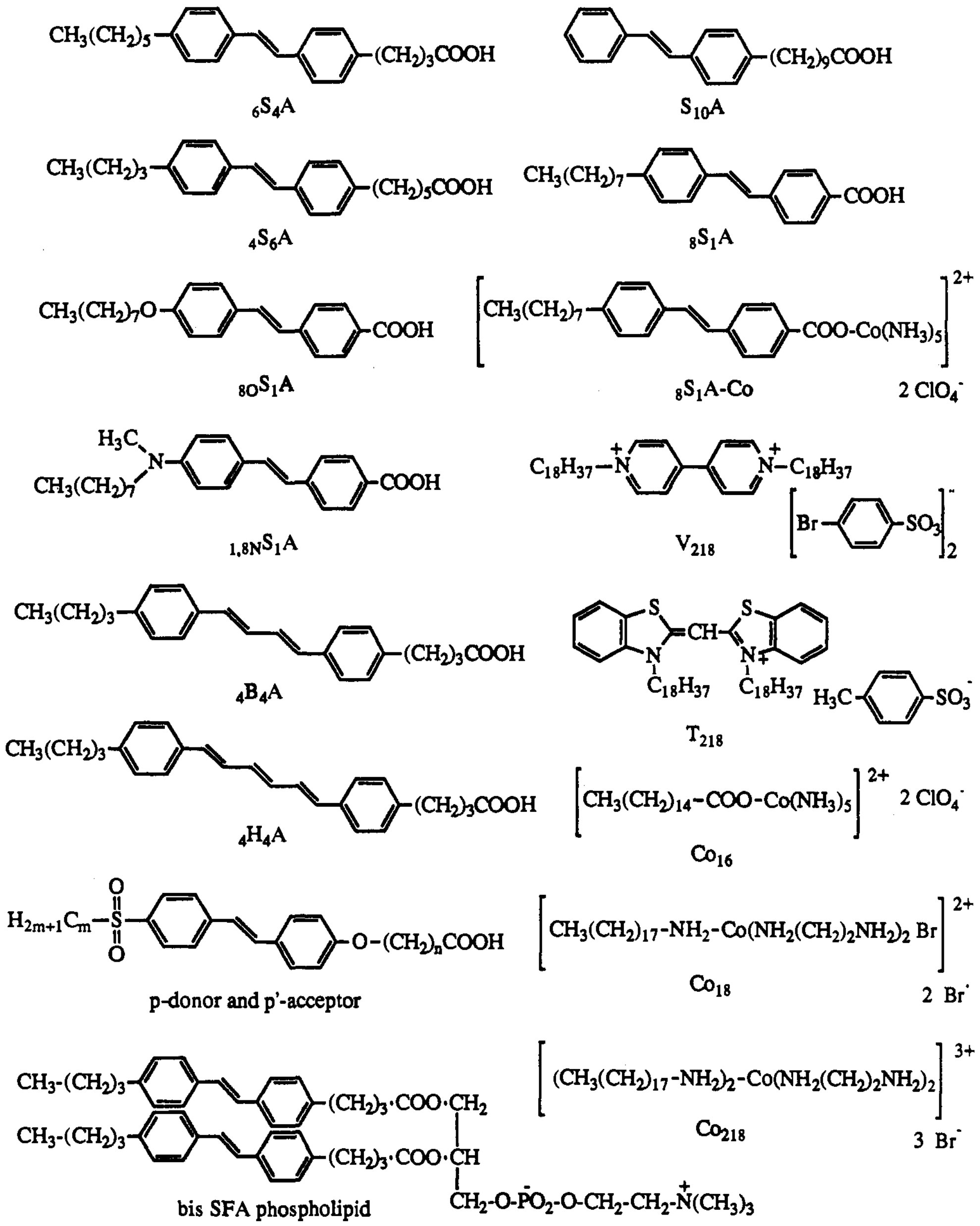
Chart 1



heteroatom substituted SFA's, and the "vinylogues" containing 1,4-diphenyl-1,3-butadiene and 1,6-diphenyl-1,3,5-hexatriene chromophores in a fatty acid backbone. We show that "H" aggregation persists in these mixed layers and is thus not simply a packing phenomenon but an energetically favorable process, probably driven by apolar association forces. Moreover, our experiments show that in mixed layers interlayer communication is enhanced, permitting an effective "antenna effect" to operate which facilitates energy migration through several multilayers and can culminate in vectorial energy and electron-transfer processes.

Experimental Section

Materials. Sodium bicarbonate (Baker Analyzed Reagent) and cadmium chloride 2-1/2 hydrate (Baker Analyzed Reagent) were used as received. Arachidic acid (Analabs, Inc.) was used as received and kept under refrigeration. Chloroform (Baker, HPLC Grade) for monolayer work was used as received. All other solvents were used as received unless otherwise specified. Langmuir–Blodgett films were formed using water deionized and polished with a Millipore purification system.

Synthesis of Surfactant α,ω-Diphenylpolyenes. The structures of the compounds used in these studies are shown in Chart 1. The synthesis of the surfactant stilbenes ($_mS_nA$) was described previously.[13] Surfactant diphenylbutadiene ($_4B_4A$) and diphenylhexatriene ($_4H_4A$) were synthesized by Miola according to reported methods.[15] The heteroatom derivatives of surfactant *trans*-stilbenecarboxylic acid including 4′-(octyloxy)-*trans*-stilbenecarboxylic acid ($_{8O}S_1A$), and 4′-(*N*-methyl-*N*-octylamino)-*trans*-stilbenecarboxylic acid ($_{1,8N}S_1A$) were synthesized by Geiger.[16] The synthesis of 4′-octyl-*trans*-stilbenecarboxylic acid ($_8S_1A$) is described below.

$_8S_1A$. Unlike the $_mS_nA$ series, this synthetic procedure utilizes a phosphonate modification of the Wittig reaction in order to obtain predominantly the *trans*-stilbenecarboxylate product.[17] α-Bromo-*p*-toluic acid (Fluka, 9 g, 4.2 mmol) was dissolved in a mixture of 100 mL of methanol and 2.5 mL of concentrated sulfuric acid. The mixture was heated to reflux for 1.5 h. The

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solvent was evaporated down to 30 mL, and 100 mL of water was added, upon which a white/yellow solid precipitated. Recrystallization of the residue from methanol/water (2×) gave 5 g (52%) of the white solid methyl α-bromo-*p*-toluate (mp 52–53 °C).

Methyl α-bromo-*p*-toluate (3.45 g, 1.51 mmol) was dissolved in 150 mL of freshly distilled dimethylformamide. Triethyl phosphite (Aldrich 2.60 μL, 1.58 mmol) was added, and the mixture was refluxed under nitrogen for 2.5 h. The reaction was cooled (0 °C), and octylbenzaldehyde (Kodak, 4.14 g, 0.019 mol) was slowly added. Sodium (Aldrich, 0.36 g, 1.58 mmol) dissolved in 15 mL of freshly distilled methanol was added dropwise, and the mixture was stirred under nitrogen at room temperature for 16 h. The reaction mixture was concentrated to 40 mL and neutralized by adding 100 mL of water and 50 mL of 10% sodium bicarbonate. The aqueous solution was extracted using chloroform (3×). The combined organic extracts were washed (saturated sodium chloride), dried (sodium sulfate), and concentrated. Recrystallization of the residue from hexane (1×) gave 2.25 g (41%) of the white crystals 4′-octyl-*trans*-stilbenecarboxylate (${}_8S_1E$) (mp 131–133 °C).

Saponification was performed by dissolving ${}_8S_1E$ (2 g, 0.57 mmol) in 50 mL of tetrahydrofuran containing four pellets of potassium hydroxide and tetrabutylammonium chloride (Sigma, 0.1 g). The mixture was refluxed for 2 h. The resulting precipitate, 4′-octyl-*trans*-stilbenecarboxylate sodium salt (${\rm Na}_8S_1A$), was filtered and washed (3×) with tetrahydrofuran. The solid was placed in 20 mL of water, and 10% HCl was added until pH < 7. The aqueous solution was extracted (3×) using ethyl ether. The combined organic extracts were dried (magnesium sulfate) and concentrated. Recrystallization of the residue (2×) from acetic acid/water gave 0.77 g (40%) of the white solid ${}_8S_1A$ (mp 251–253 °C). Anal. Calcd for $C_{23}H_{28}0_2$: C, 82.09; H, 8.40. Found: C, 82.22; H, 8.10. NMR (DMSO-d_6): $\delta = 0.82$ (t, $J = 6$ Hz, 3 H), $\delta = 1.23$ (s, 10 H), $\delta = 1.54$ (m, 2 H), $\delta = 2.55$ (t, $J = 8$ Hz, 2 H), $\delta = 7.18$ (d, $J = 8$ Hz, 1 H), $\delta = 7.24$–7.36 (dd, $J = 35$ Hz, 2 H), $\delta = 7.52$ (d, $J = 8$ Hz, 1 H), $\delta = 7.67$ (d, $J = 8$ Hz, 1 H), $\delta = 7.90$ (d, $J = 8$ Hz, 1 H).

Synthesis of Surfactant Acceptors. Dioctadecylviologen monohydrate or *N,N*′-dioctadecyl-4,4′-bipyridinium *p*-bromobenzenesulfonate monohydrate (V_{218}) was synthesized following a procedure described by Mooney.[14] *cis*-Bromo(1-octadecylamine)bis(ethylenediamine)cobalt(III) bromide (Co_{18}) was synthesized by Mooney[14] and used without further purification. The syntheses of (4′-octyl-*trans*-stilbenecarboxylato)pentaamminecobalt(III) perchlorate (${}_8S_1A$-Co) and (1-hexadecanecarboxylato)pentaamminecobalt(III) perchlorate (Co_{16}) are described below.

${}_8S_1A$-Co. Carbonatopentaamminecobalt(III) nitrate ($Co(NH_3)_5(CO_3)NO_3$) was synthesized by following a modified procedure described by Lamb and Mysels.[18] Cobalt nitrate hexahydrate (MCB, 75 g, 0.26 mmol) in 90 mL of water was slowly added to pulverized ammonium carbonate (Baker, 150 g, 1.92 mol) in 375 mL of 30% ammonium hydroxide. The solution was stirred for 48 h at room temperature under a stream of bubbled air. The solid was crudely recrystallized by heating the reaction mixture on a steam bath until all crystals dissolved in the mother liquor. The warm solution was immediately gravity filtered and cooled (0 °C) for 2 h, upon which the brick red solid precipitated. The precipitate was collected and washed with 25 mL of cold water (10×), with 50% cold ethanol (2×), with 95% cold ethanol (2×), and with 99% cold ethanol (2×). A 30-g quantity (42%) of $Co(NH_3)_5(CO_3)NO_3$ in the form of a brick red powder was obtained.

$Co(NH_3)_5(CO_3)NO_3$ was converted to aquopentaamminecobalt(III) perchlorate ($Co(NH_3)_5(H_2O)(ClO_4)_3$) by following a procedure described by Gould and Taube.[19] $Co(NH_3)_5(CO_3)NO_3$ (24 g, 0.09 mol) was dissolved in 200 mL of warm water (60 °C). Concentrated perchloric acid (Baker, 69–72%, ~ 50 mL) was added dropwise until effervescence ceased and no further precipitation was observed, upon which an additional 10 mL of perchloric acid was added. The precipitate was collected and washed (5×) with 5% perchloric acid. Recrystallizion of the residue from water gave 35 g (84%) of $Co(NH_3)_5(H_2O)(ClO_4)_3$.

(4′-Octyl-*trans*-stilbene carboxylato)pentaamminecobalt(III) perchlorate ($Co(NH_3)_5({}_8S_1A)(ClO_4)_2$) (${}_8S_1A$-Co) was prepared using a modified procedure initially developed by Vogler.[20] $Co(NH_3)_5(H_2O)(ClO_4)_3$ (1.0 g, 2.79 mmol) and ${\rm Na}_8S_1A$ (1.29 g, 2.79 mmol) were added to 45 mL of dimethylacetamide. The mixture was heated (80 °C) under nitrogen in the dark. After 3.5 h, the product was poured over 150 mL of an ice cold 5% perchloric acid solution, upon which a pink solid precipitated. After 1 h, the solution was filtered and the crude product (1.29 g) was obtained. Since recrystallization resulted in decomposition of the complex, the complex was purified by removing the starting material. The complex was added to 100 mL of water and stirred for 0.5 h. The residue was collected and rinsed with water, and the process was repeated. This procedure was repeated (2×) using anhydrous ethyl ether. The remaining pink solid product was dried and stored in a desiccator containing magnesium perchlorate. Anal. Calcd for $CoC_{23}H_{42}N_5O_{10}Cl_2$: C, 40.71; H, 6.25; N, 10.32. Found: C, 40.59; H, 6.17; N, 8.73. NMR (DMSO-d_6): $\delta = 0.82$ (bs, 3 H), $\delta = 1.22$ (s, 10 H), $\delta = 1.52$ (m, 2 H), $\delta = 2.54$ (bs, 2 H), $\delta = 2.45$ (s, 3 H), $\delta = 3.82$ (s, 12 H), $\delta = 7.18$ (d, $J = 7$ Hz, 1 H), $\delta = 7.25$–7.29 (dd, $J = 13$ Hz, 2 H), $\delta = 7.52$ (d, $J = 7$ Hz, 1 H), $\delta = 7.56$ (d, $J = 7$ Hz, 1 H), $\delta = 7.87$ (d, $J = 7$ Hz, 1 H).

Co_{16}. (1-Hexadecanecarboxylato) pentaamminecobalt(III) perchlorate (Co_{16}) ($Co(NH_3)_5(C_{16})(ClO_4)_2$ was prepared by following the previous method described for ${}_8S_1A$-Co with the following modifications: (1) ${\rm Na}_8S_1A$ was replaced by the sodium salt of palmitic acid (Aldrich). (2) The crude product was washed with chloroform (2×) instead of anhydrous ethyl ether (41% yield). Anal. Calcd for $CoC_{16}H_{46}N_5O_{10}Cl_2$: C, 32.11; H, 7.76; N, 11.70. Found: C, 32.48; H, 7.66; N, 11.13. NMR (DMSO-d_6): $\delta = 0.82$ (t, $J = 6$ Hz, 3 H), $\delta = 1.20$ (s, 26 H), $\delta = 1.39$ (m, 2 H), $\delta = 2.59$ (s, 3 H), $\delta = 3.66$ (s, 12 H).

Monolayer Film and Multilayer Deposition Studies. The general methods used for preparing Langmuir–Blodgett films and assemblies and the cleaning of the substrates were based on techniques described elsewhere.[21] Film preparations were carried out on a KSV 3000 automatic film balance. All films were transferred at a pressure of 30.0 dyn/cm. The aqueous subphase contained 3×10^{-4} M^{-1} $CdCl_2$ and 5×10^{-5} M^{-1} $NaHCO_3$ (pH = 6.6–6.8). The substrates used were Suprasil quartz purchased from Herameus Amersil Inc.

Spectra. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state fluorescence spectra were obtained using a SPEX 111 CM spectrofluorimeter containing two single beam monochromators, a 150-W Xe light sources and a thermoelectrically cooled photodetector. The slides were placed in a custom-built holder. The fluorescence was measured with the slide positioned at a 45° angle to the direction of the excitation light source. The excitation wavelength for the quenching experiments was 330 nm.

Fluorescence lifetimes of the surfactant diphenylpolyenes were measured using time-correlated single photon counting (SPC).[22] The laser system used to excite the surfactants has been described elsewhere.[23] A mode-locked frequency-doubled Nd:YAG laser

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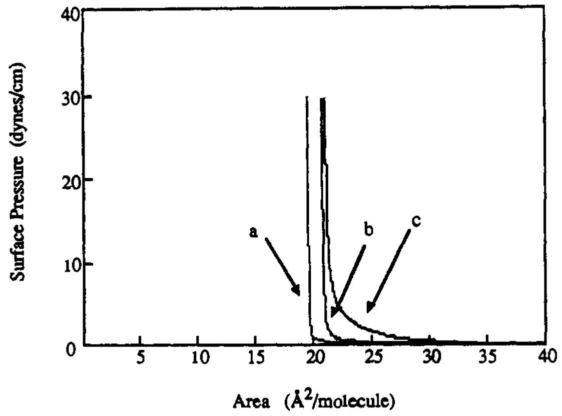

Figure 1. Isotherms of (a) AA, (b) ${}_6S_4A$/AA (1:1), and (c) mixture A (1:1:1:3).

(Quantronix Model 416) synchronously pumps a cavity-dump dye laser (Coherent, Model 703D) circulating Rhodamine-6G dye. The output of the dye laser was frequency doubled to produce a series of 5-ps pulses with a wavelength of 300 nm at a repetition rate of 38 MHz. The system had a time resolution of 10 ps which was limited by the detector. Excitation was at 290–300 nm, and the data obtained were deconvoluted using a nonlinear least-squares fitting program which could fit up to three components.

Results

Chart 1 gives structures denoting the nomenclature used for the various SFA's as well as the substituted SFA's and DPB and DPH derivatives. Also shown in Chart 1 are the structures of some surfactant potential electron acceptors which have been used as excited-state quenchers in this study.

General Multilayer Properties of SFA-Fatty Acid Mixtures. All of the SFA's and related compounds shown in Chart 1 give pressure–area isotherms generally similar to those of the corresponding chain length fatty acids such as arachidic acid (AA) over H_2O–bicarbonate–$CdCl_2$ (pH = 6.6–6.8). Figure 1 compares the isotherms of arachidic acid, an arachidate/${}_6S_4A$ (1:1) molar mixture, and mixture A consisting of a mixture of three different SFA's and arachidate (${}_4S_6A$/${}_6S_4A$/$S_{12}A$/AA 1:1:1:3)). The area per molecule of the ${}_6S_4A$ mixture and the pressure–area isotherm are consistent with a close packed structure in the compressed layer, and transfer ratios close to unity suggest that the films transferred to solid supports have a similar regular extended structure. Mixture A gives a similar limiting area per molecule but shows a larger "lift off" area (the point at which the first increase in surface pressure with reduction of area is encountered). This could be attributed to preformation of aggregates from SFA's of different chain lengths that leads to irregular mixed aggregates which must largely reassemble into "zones" of self-aggregates during the very slow compression of the films. Table 1 compares the measured cross-sectional areas per molecule for the SFA's and their vinylogues in the compressed films. It can be noted that the N-substituted SFA shows a larger area per molecule consistent with the perturbation induced by the addition of the methyl group.

All of the SFA's and their vinylogues exhibit dramatically different absorption spectra and red-shifted fluorescence in either pure or 1:1 dilution with AA in supported multilayers compared to the spectra obtained in dilute solution. Figures 2 and 3, corresponding to ${}_4S_6A$ and ${}_4H_4A$, respectively, are representative of the spectral shifts observed (see the supplementary material for additional spectra). For the SFA's, dilution up to 20-fold with AA produces relatively little change in the absorption or fluorescence spectra. Mixtures of SFA's give very similar absorption and emission spectra (Figure 4). In contrast to the SFA's, dilution of ${}_4B_4A$ or ${}_4H_4A$ with excess AA leads to absorption and fluorescence spectra resembling closely those of the monomer in dilute solution. Evidently, the tendency for the SFA's to form aggregates is greater than that exhibited by ${}_4B_4A$ or ${}_4H_4A$. Conceivably the planar nature of the *trans*-stilbene enables the SFA's to align in conformations which allow greater π orbital overlap than could be achieved by either diphenylbutadiene or diphenylhexatriene since these molecules are not as planar. These spectroscopic changes are clearly due to a physical effect rather than to a chemical reaction since recovery of the sample by dissolving the multilayer in an organic solvent such as chloroform is quantitative and reveals no net chemical change. Although the substituted SFA's such as ${}_8S_1A$, ${}_{8O}S_1A$ show solution absorption and fluorescence rather different from the simple "dialkyl" SFA's, the absorption spectra in the supported multilayers are quite similar, while the fluorescence obtained often shows variation either in wavelength or in structure. This has

Table 1. Typical Area per Molecule for α,ω-Diphenylpolyene Surfactants[a]

compound	area per molecule (Å²)
AA	20
${}_4S_6A$, ${}_6S_4A$, or $S_{12}A$	22
mixture A	24
${}_8S_1A$	22
${}_{8O}S_1A$	22
${}_{1,8N}S_1A$	38
${}_4B_4A$	26
${}_4H_4A$	27

[a] All monolayer films consisted of a 1:1 molar ratio of surfactant to AA, assuming ideal mixing of the two components. The area per molecule of each α,ω-diphenylpolyene surfactant was calculated by extrapolating to zero pressure.

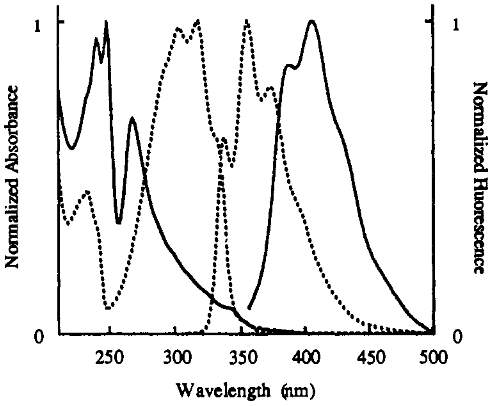

Figure 2. Normalized absorbance and fluorescence spectra of ${}_4S_6A$ in cyclohexane (···) and in a multilayer assembly (—) consisting of a 1:1 molar ratio of ${}_4S_6A$/AA.

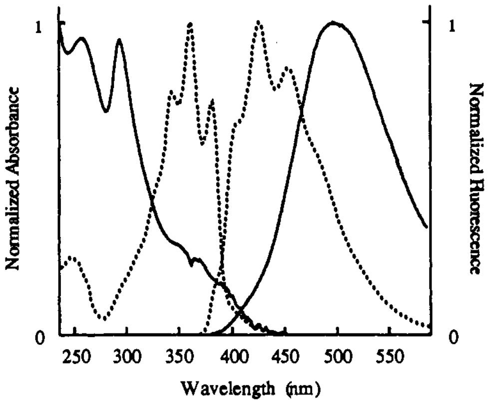

Figure 3. Normalized absorbance and fluorescence spectra of ${}_4H_4A$ in cyclohexane (···) and in a multilayer assembly (—) consisting of a 1:1 molar ratio of ${}_4H_4A$/AA.

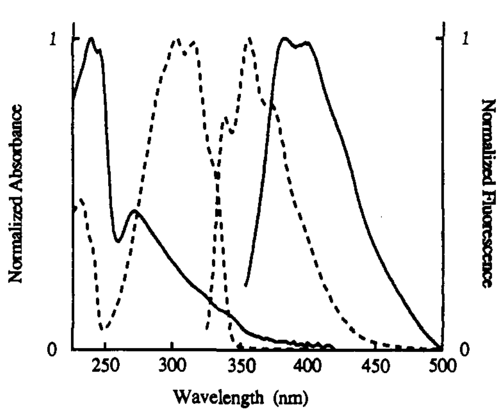

Figure 4. Normalized absorbance and fluorescence spectra of mixture A (1:1:1:7) in cyclohexane solution (- - -) and in a multilayer assembly (—).

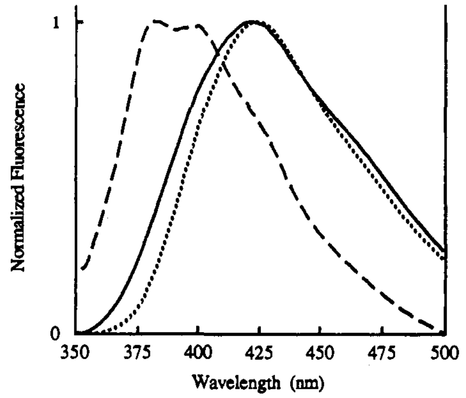

Figure 5. Normalized fluorescence spectra of mixture A (-) mixture A′ (- - -), and a 1:1 molar ratio of ${}_8S_1A$ and AA (—).

Table 2. Fluorescence Lifetime Data Obtained for Various Molar Ratios of α,ω-Diphenylpolyene Surfactants to AA in Multilayer Assemblies

mixture A (1:1:1:3)[a]		${}_4B_4A$/AA (1:1)[b]		${}_4H_4A$/AA (1:1)[c]	
lifetime	relative quanta	lifetime	relative quanta	lifetime	relative quanta
10.5	0.30	9.9	0.42	18.3	0.43
2.0	0.37	2.8	0.39	4.1	0.35
0.4	0.33	0.6	0.19	0.9	0.22

[a] Excitation and emission were monitored at 291 and 400 nm, respectively. CHISQ = 1.08. [b] Excitation and emission were monitored at 291 and 435 nm, respectively. CHISQ = 1.07. [c] Excitation and emission were monitored at 291 and 500 nm, respectively. CHISQ = 1.03.

also been found with surfactant *trans*-stilbene derivatives substituted with *p*-donor and *p*′-acceptor substituents.[24] Mixture A′ (containing ${}_8S_1A$) (${}_4S_6A/{}_6S_4A/S_{12}A/{}_8S_1A$/AA (1:1:1:1:4)) shows absorption spectra very similar to those of either a single SFA/AA mixture or mixture A; however, the fluorescence from the mixture is nearly identical to the fluorescence observed for ${}_8S_1A$/AA mixtures (Figure 5). Fluorescence lifetimes determined by nanosecond laser single photon counting techniques are invariably multiexponential and difficult to fit cleanly even with three exponentials. Table 2 lists several representative data sets for different LB assemblies examined.

Dilution and Mixing Effects for SFA Multilayers. As discussed above, "diluting" the surfactant butadiene and hexatriene derivatives with excess AA leads to the appearance of monomer-like absorption and emission spectra in supported LB assemblies while the SFA's exhibit only small spectral changes in the same dilution range. As will be discussed below, the changes are attributed to aggregation effects in the supported multilayers, and it is instructive to compare the less dramatic changes that are observed when a single SFA or mixture of SFA's is studied with varying dilutions with AA. For a single SFA, ${}_6S_4A$, it is found that, while dilution with AA produces little change in the absorption or fluorescence activation spectrum, there is a small but significant blue shift in the fluorescence (Figure 6) accompanying dilution together with changes in the lifetimes and lifetime distribution of the fluorescence (Table 3). The difference spectrum obtained by subtraction of the two fluorescence spectra gives a slightly structured blue shifted spectrum which is quite red shifted from the solution monomer fluorescence (Figure 7) but significantly different from that of the "pure aggregate" (*vide infra*).

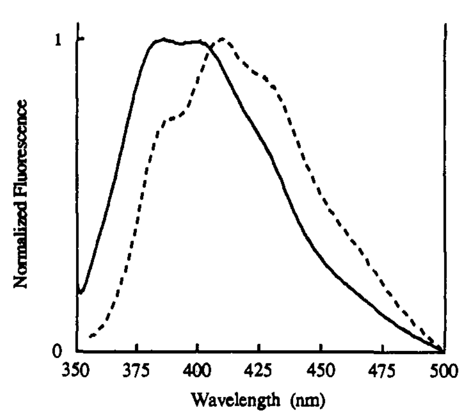

Figure 6. Normalized fluorescence spectra of multilayer assemblies containing a 3:7 molar ratio of ${}_6S_4A$/AA (- - -) and a 1:9 molar ratio of ${}_6S_4A$/AA (—).

Table 3. Fluorescence Lifetime Data for Various Molar Ratios of ${}_6S_4A$/AA

1:1 molar ratio of ${}_6S_4A$/AA[a]		1:9 molar ratio of ${}_6S_4A$/AA[b]	
lifetime	relative quanta	lifetime	relative quanta
15.5	0.26	8.2	0.37
2.6	0.48	2.7	0.45
0.6	0.26	0.8	0.18

[a] Excitation and emission were monitored at 291 and 400 nm, respectively. CHISQ = 1.08. [b] Excitation and emission were monitored at 291 and 400 nm, respectively. CHISQ = 1.08.

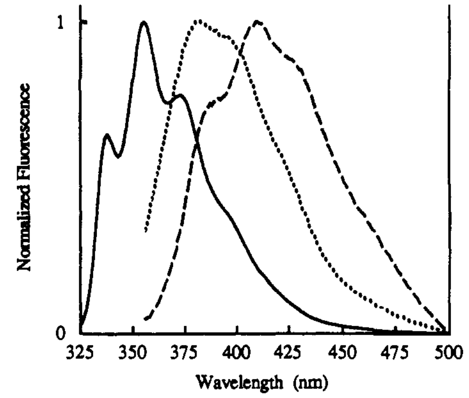

Figure 7. Normalized fluorescence spectra of ${}_6S_4A$ in cyclohexane (—), the "H" aggregate multilayer spectrum of ${}_6S_4A$/AA (3:7) (- - -), and the spectrum obtained upon the subtraction of the multilayer spectra of ${}_6S_4A$/AA (3:7) from ${}_6S_4A$/AA (1:9) (···).

As described above, LB assemblies of mixture A and mixture B (consisting of ${}_4S_6A/{}_6S_4A/S_{10}A/S_{12}A/S_{16}A$/AA (1:1:1:1:1:5)) were also investigated. Both mixtures show generally similar behavior and properties. The more extensively studied mixture A exhibits absorption, fluorescence activation, and fluorescence spectra somewhat different from those of a single SFA at the

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(24) Furman, I.; Whitten, D. G.; Penner, T. L.; Ulman, A. Submitted for publication.

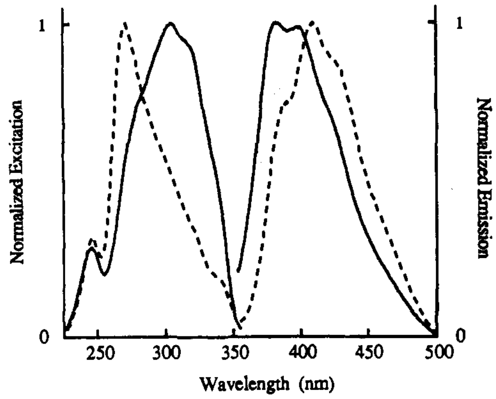


Figure 8. Normalized excitation and emission spectra of multilayer assemblies containing a 3:7 molar ratios of ${}_6S_4A/AA$ (- - -) and mixture A (1:1:1:7) (—).

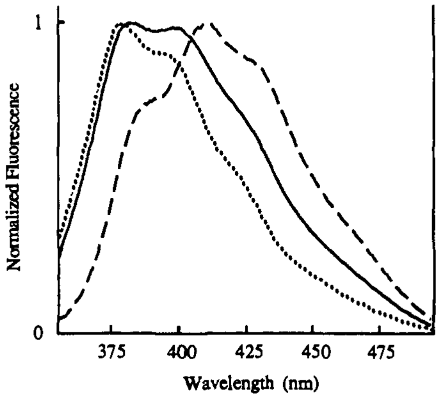
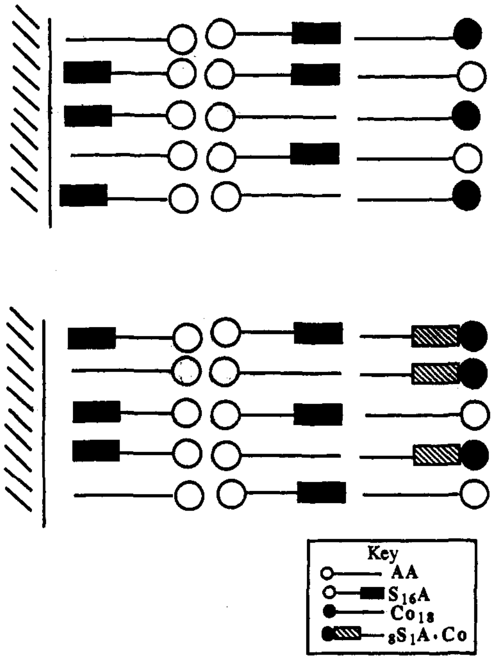


Figure 9. Normalized fluorescence spectra of a multilayer assembly containing mixture A (1:1:1:7) (—) and ${}_6S_4A/AA$ (3:7) (- - -) and the "H" dimer-like spectrum (···) resulting from the subtraction of the ${}_6S_4A/AA$ (3:7) spectrum from the mixture A (1:1:1:7) spectrum.

same dilution (Figure 8). The difference spectrum between that of a single SFA (${}_6S_4A$) and mixture A (Figure 9) is quite different from that of a SFA monomer in solution but relatively similar to that obtained by diluting a single SFA within an LB assembly (Figure 7). The fluorescence of LB assemblies of mixture A can be very closely matched with LB assemblies formed from a mixture of ${}_6S_4A$ with AA in a 1:9 molar ratio.

Energy and Electron-Transfer Quenching of Surfactant Stilbene and Diphenylpolyene Fluorescence in Multilayer Assemblies. In previous studies we employed the potential electron acceptors V_{218}, Co_{18}, and Co_{218} as quenchers for the fluorescence of assembly-incorporated SFA's.[14,25,26] In the present study we have used these acceptors and in addition the surfactant acceptors ${}_8S_1A$-Co and Co_{16}, whose structures are shown in Chart 1. Previous studies with the singlet energy acceptor T_{218} showed that, while energy transfer from SFA to T_{218} could occur over relatively long distances, SFA-to-SFA energy transfer was very ineffective with layers of a single SFA mixed with AA.[14] The cobalt complex of ${}_8S_1A$ shows an absorption spectrum in both solution and supported multilayers very similar to that of the uncomplexed carboxylate; however, the cobalt complex shows no fluorescence in either solution or the LB assemblies. The cobalt complex shows photoreactivity in solution similar to that of the nonsurfactant (*trans*-stilbenecarboxylato)cobalt complex; this reactivity has been associated with an intramolecular stilbene–cobalt electron transfer following photoexcitation and is accompanied by what is evidently a mechanistically complicated oxidation of the stilbene to an aldehyde and reduction of the Co^{3+} to Co^{2+}.[20,27] Although the surfactant cobalt complex is nonfluorescent in supported LB assemblies, little or no photodecomposition is observed on prolonged irradiation into the stilbene transitions. Quite reasonably it appears that, for this complex in LB assemblies where little or no diffusive separation of initial electron-transfer photoproducts can occur, return electron transfer is the primary path for decay of the initial intramolecular electron transfer photoproduct; however, we cannot rule out a very fast nonradiative decay of the excited state via a path not involving specific electron transfer.

Scheme 1. Schematic Representation of a Multilayer Assembly[a]



[a] A bilayer of $S_{16}A/AA$ (1:1) in contact with a monolayer of Co_{18} (1:2) and (b) a bilayer of $S_{16}A/AA$ (1:1) in contact with a monolayer of ${}_8S_1A$-Co/AA (1:2).

${}_8S_1A$-Co was found to be an effective quencher of the fluorescence from assemblies containing either a single or mixed SFA layered with AA. For example, the SFA fluorescence in the three-layer assemblies shown in Scheme 1 shows little or no quenching when Co_{18} is in the third layer (part a) while substitution of an equivalent molar concentration of ${}_8S_1A$-Co results in 45% quenching (part b). As will be discussed below, the extent of quenching is consistent with a combination of energy-transfer and electron-transfer quenching whereby the excitation from a SFA aggregate can migrate over distances on the order of 25–40 Å to a receptor ${}_8S_1A$ chromophore and intramolecular stilbene–cobalt electron transfer can result in fluorescence quenching.

While previous studies of assemblies constructed from single SFA/AA mixtures showed that there was insignificant quenching of fluorescence from SFA/AA layers not in hydrophilic contact (head-to-head) with the layers containing the aforementioned quenchers, we find that multilayers of mixture A or mixture B show significant quenching by all of the potential electron acceptors. For example, comparison of the quenching of a three-layer assembly formed from two layers of mixture B in contact with a layer containing the same concentration of ${}_8S_1A$-Co (Scheme 1) indicates about 70% quenching compared to the 45% for the single SFA ($S_{16}A$). More impressive differences are encountered when multilayers such as the six-layer assembly

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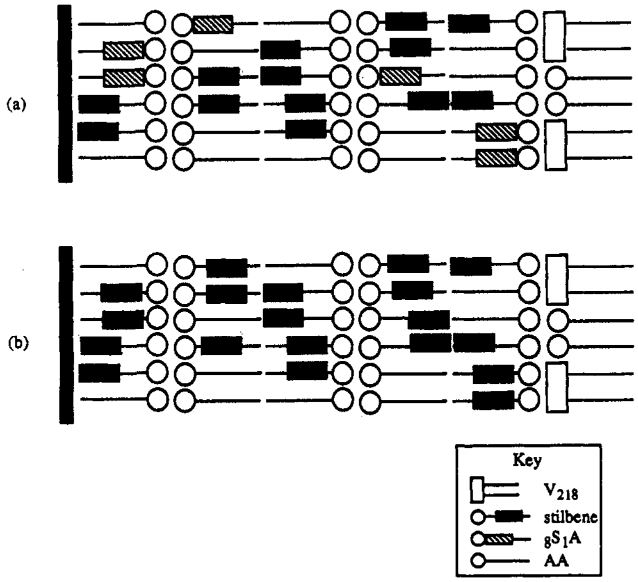
(25) Spooner, S. P.; Whitten, D. G. *Proc. Soc. Photo-Opt. Instrum. Eng.* **1991**, *1436*, 82.

(26) The general features of the spectra and degree of quenching are quite reproducible from sample to sample. As reported in previous studies[12-14,25] of SFA's in LB multilayers, irradiation of the aggregates from either a single SFA or a mixture in the presence or absence of "quenchers" results in little photoreaction of the SFA. Only a very slow photobleaching to produce as yet unidentified products is observed upon prolonged irradiation. The films appear to be indefinitely (months) stable in the dark.

(27) Vogler, A.; Kern, A. *Z. Naturforsch.* **1979**, *34b*, 271.

Scheme 2. Schematic Representation of a Multilayer Assembly[a]



[a] (a) Five layers of a mixture A′ and (b) five layers of a mixture A, in contact with a layer of V_{218}.

Table 4. Percentage of Fluorescence Quenching of Stilbene Multilayer Assemblies

	quencher		
stilbene assembly[a]	V_{218}	$_{8}S_{1}A$-Co	Co_{16}
mixture A	41	41	38
$_{6}S_{4}A$	5	11	
$S_{12}A$	7	9	5

[a] Five-layer multilayer assembly containing a 1:1 molar ratio of surfactant stilbene to AA.

shown in Scheme 2 are compared. For three different acceptor–quenchers (V_{218}, $_{8}S_{1}A$-Co, and Co_{16}), there is appreciable quenching of the five layer assembly formed from mixture A but very little quenching when the mixture is replaced by single SFA/AA mixtures (either $_{6}S_{4}A$ or $S_{12}A$) (Table 4).

While the fluorescence of assemblies formed from the mixtures of SFA's with AA (either mixture A or mixture B) is strongly quenched even for multilayers, addition of 1 molar equiv of $_{8}S_{1}A$ (for example mixture A′ (containing $_{8}S_{1}A$) ($_{4}S_{6}A/_{6}S_{4}A/S_{12}A/_{8}S_{1}A/AA$ (1:1:1:1:4)) results in an attenuation of the "long-range" quenching. As indicated above, the fluorescence of these mixtures (see Figure 10) is dominated by that of $_{8}S_{1}A$; for a mixture having the structure shown in Scheme 1 with $_{8}S_{1}A$-Co as quencher the fluorescence is 60% quenched compared to the 70% quenching in mixture A. Similarly, when multilayers such as the six-layer assembly show in Scheme 2 contain $_{8}S_{1}A$, the quenching is reduced to 29–35% compared to the 38–41% quenching with the same quenchers and mixture A.

The finding that fluorescence from mixed multilayers can be effectively quenched by several electron acceptors suggested that the use of modified stilbene-like surfactants might provide directional or vectorial energy or electron transfer or a combination thereof.[28] Since the butadiene and hexatriene surfactants have fluorescence at lower energies than the SFA aggregates or $_{8}S_{1}A$, it would be expected that both intralayer and interlayer energy migration from SFA to butadiene or hexatriene should occur. Experiments with $_{4}H_{4}A$ and mixture or individual SFA's within a single layer showed that the assembly fluorescence was prominently that from the hexatriene. Similar results were obtained with mixtures of SFA and $_{4}B_{4}A$. While a number of multilayers have been investigated, a representative one is shown in Scheme 3 where a four-layer assembly of diphenylpolyene surfactants of decreasing excitation energy—mixture A, mixture A′, $_{4}B_{4}A$ + AA, $_{4}H_{4}A$ + AA—is sandwiched between layers containing either pure AA or AA + Co_{18} (2:1). As shown in Figure 10, the fluorescence from the unquenched multilayer appears to have contributions from all of the fluorescent components but predominantly $_{4}H_{4}A$ and $_{4}B_{4}A$. Addition of the quencher only at the interface with the layer of mixture A leads to little quenching and only to the short wavelength portion of the fluorescence. In contrast, addition of the quencher-containing layer to the multilayer in contact with the layer of $_{4}H_{4}A$/AA results in significant fluorescence quenching and some selective reduction of the long wavelength component.

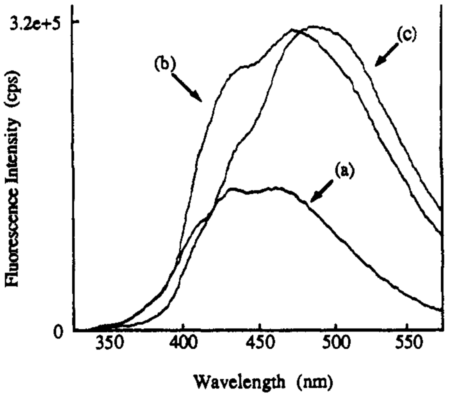
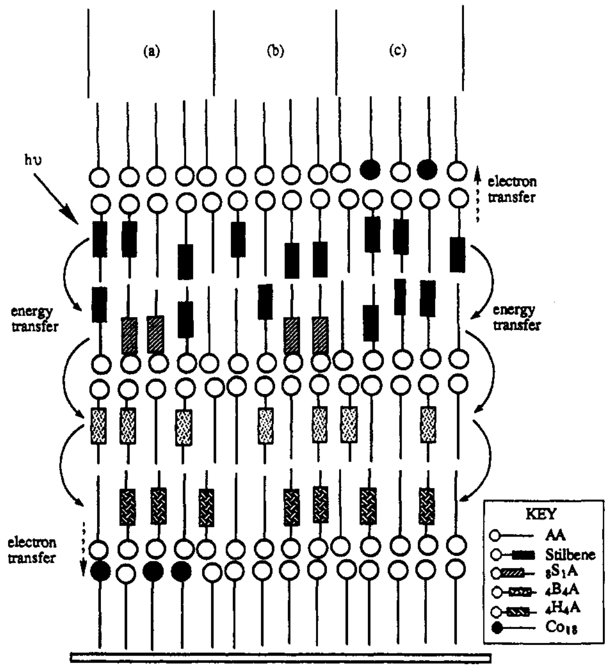


Figure 10. Resulting fluorescence spectra of a multilayer assembly constructed from surfactant diphenylpolyene monolayers in order of decreasing energy in which (a) the quencher is in contact with the $_{4}H_{4}A$ layer, (b) no quencher is present, and (c) the quencher is in contact with the mixed stilbene layer.

Scheme 3. Schematic Representation of a Multilayer Assembly[a]



[a] (a) The quencher is in contact with the $_{4}H_{4}A$ layer, (b) no quencher is present, and (c) the quencher is in contact with the mixture A layer.

Discussion

The behavior of supported LB assemblies formed from mixtures of SFA's appears similar in several ways to that of assemblies formed from a single SFA or SFA–fatty acid mixture; yet there

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(28) Fox, M. A.; Kamat, P. V.; Fatiadi, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 1191. Torres, W.; Fox, M. A. *Chem. Mater.* **1992**, *4*, 146.

are some significant and instructive differences. The main features that need to be considered in some detail include the persistence of relatively sharp spectra associated with the "H" aggregate of a single SFA in the absorption spectra of even mixtures containing as many as five different SFA's in equimolar amounts, the similarity of absorption (and to a lesser extent emission) spectra of different SFA's, functionalized and heteroatom-substituted SFA's, and SFA "vinylogues" in LB assemblies, and the rather large differences in energy migration in multilayers formed from SFA mixtures compared to those constructed from a single SFA or single SFA–fatty acid mixture.

In our previous investigations it was assumed that the "H" aggregate was formed due to a combination of physical compression of the individual surfactant molecules into a semicrystalline extended conformation with the high effective molar concentration of the SFA in the pure or concentrated SFA–fatty acid mixed films. The fact that the "H" aggregate is not detectable in solutions of the SFA's in organic or aqueous micellar media[29] together with its absence in the solid state of SFA's or other substituted stilbene derivatives suggests that there is little or no tendency for the stilbene chromophore to associate in such an aggregate structure in the absence of external forces. However, our findings detailed in this study of "H" aggregate formation with such a variety of structures containing the *trans*-stilbene chromophore and the persistence of the "H" aggregate as the prominent species present even in cases of fairly high dilution suggest that the "H" aggregate may well be an energy minimum in aqueous environments for the stilbene chromophore, perhaps favored under these conditions by apolar association forces such as have been proposed in a number of somewhat related studies.[30-35] This is reinforced by other studies in which we have found very similar aggregation absorption spectra and behavior from even substituted SFA's such as those shown in Chart 1 which have strong *p*-donor and *p'*-acceptor substituents and monomer absorption and fluorescence spectra very different from *trans*-stilbene or dialkyl-*trans*-stilbene derivatives.[24] Also in related studies we have found that the bis SFA phospholipids such as the structure shown in Chart 1 give nearly identical ("H" aggregate) absorption and emission spectra to those obtained for SFA's in monolayers when dispersed in aqueous buffer under conditions favoring bilayer vesicle formation.[35] The finding that the diphenylbutadiene and diphenylhexatriene surfactants give similar "H" aggregate absorption in LB assemblies formed from "concentrated" films but are more easily diluted to give assemblies showing "monomer" properties suggests that the apolar association forces that drive "H" aggregation may be weaker for these compounds, a not too surprising result in view of the relatively less extensive aromatic portion of the extended π system.

The preponderance of sharp "H" aggregate spectra for mixtures of SFA's in which the *trans*-stilbene chromophore is situated in different positions in the fatty acid chain coupled with nearly identical pressure–area isotherms for the mixtures compared to those for individual SFA's suggests that there must be a "molecular sorting" process that occurs during the compression of these mixtures at the air–water interface. The possibility that there may be some association into "H" aggregates at very low compression may be indicated by the slightly earlier "lift-off" at larger areas per molecule in the mixed films. A more exaggerated example of this phenomenon has been observed for the *p*-donor–*p'*-acceptor stilbene acids shown in Chart 1. Here we observed very different behavior on the first and second compression of mixed films at the air–water interface, yet transferred films showed only pure "H" aggregate as indicated by absorption spectra, even for pairs having quite different chromophore positions.[24] That the mixed layers consist largely of zones or domains of essentially pure "H" aggregate of a single species is perhaps most clearly indicated by our studies of fluorescence of the SFA mixture to which 12.5 mol % of $_8S_1A$ has been added (Figure 5). The difference in the fluorescence of the $_8S_1A$ aggregate from that of the simple SFA aggregates is clearly seen in the figure. The presence of nearly pure $_8S_1A$ aggregate fluorescence in these assemblies shows both that the $_8S_1A$ aggregate is present and that energy transfer to this aggregate occurs with reasonable efficiency.

It was originally thought that the mixtures of SFA's of different structure might lead to the presence of "heteroaggregates" which might be characterized by different absorption and emission spectra. To date we have seen very little evidence for such structures. The small differences between the fluorescence measured for dilute and concentrated layers suggest that there may be species having slightly structured fluorescence occurring at wavelengths between those for the (solution) monomer and the "H" aggregate (Figure 7). Comparison of the fluorescence spectra for the three-component mixture and fatty acid diluted single SFA shows similarities (compare Figures 9 and 6); this suggests that the same or similar species having intermediate fluorescence maxima may occur in both dilute layers of a single SFA or in SFA mixtures. A reasonable assignment of this species as an "H" dimer is reinforced by our finding that bis SFA phospholipids show somewhat similar spectra when dispersed in mixtures with excess (100 fold) saturated fatty acid phospholipid.[36] It appears from all of the compositions examined to date that the spectra (both absorption and emission) obtained can be accounted for in terms of the monomer, the intermediate species which we would assign as an "H" dimer, and the "limiting" "H" aggregate.

The rather large general difference in fluorescence quenching between the single or multiple layers of SFA mixtures compared to those containing only a single SFA and arachidate indicates that energy migration in the former assemblies is much more efficient and extensive than in the latter. There are at least three plausible explanations (or a combination thereof) which could account for the substantial differences in quenching illustrated by Scheme 2 and Table 4. As we have discussed above, it was originally anticipated that the presence of SFA's in the mixture having the stilbene chromophore at different positions in the fatty acid backbone could lead to mixed aggregates, possibly having some "J" character and hence greater oscillator strength. If these were present they could facilitate energy transfer through multilayers and enhance long-range quenching efficiencies. However to date we have seen no evidence for the occurrence of such species even though it would seem certain that the high concentrations of individual SFA's in mixtures A and B should favor their occurrence. Their presence, even in very low—perhaps undetectable—concentrations, remains a viable explanation. Alternatively the strong evidence that the layers of the mixed SFA's are composed largely of zones of individual SFA "H" aggregates suggests that energy transfer through the mixed SFA multilayers could be facilitated by aggregate to aggregate migration within a single layer which could in turn enhance layer to layer migration. The observation that addition of $_8S_1A$ to the mixtures results in exclusively its fluorescence suggests that intralayer migration in the mixed layers is efficient. The fact that the interlayer distance between aggregate zones in the SFA mixture layers is much smaller than the aggregate separation

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(36) Geiger, C.; Richard, W. G.; Furman, I.; Whitten, D. G. Unpublished result.

between multilayers of a single SFA suggests then that this might account for the enhanced efficiency of migration in the mixture multilayers. Finally a third possibility is that the multilayers formed from mixtures A and B seem to have higher concentrations of the monomer and the "H" dimer than layers containing the same total concentration of a single SFA. Both the monomer and the "H" dimer have a stronger low-energy transition and are better suited to serve as antenna for enhancing degenerate energy migration. Thus it would be expected that the presence of these species could enhance energy migration even when the emission spectra of these assemblies is dominated by the low-energy "H" aggregate fluorescence. With the data presently available, it is hard to distinguish whether any one or a combination of these explanations can explain quantitatively the observed results. However, there is clear experimental evidence favoring the second and third explanations while the first must be regarded as at best speculative at this time. The question as to whether "mixed" aggregates can be formed with the SFA's remains an interesting one which we are examining through specific synthesis and study of phospholipids containing the same or different SFA's in the two adjacent chains.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9211586) for support of this research. We also thank Cristina Geiger for the synthesis of the heteroatom substituted surfactant stilbene derivatives.

Supplementary Material Available: Normalized absorbance and fluorescence spectra of ${}_4B_4A$, ${}_8S_1A$, ${}_{8O}S_1A$, and ${}_{1,8N}S_1A$ in solution and in multilayer assemblies (spectra similar to those shown in Figures 2 and 3) (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.