energy, as is similarly found for retinal.[12]

An increase in the number of methyl groups attached to the ring also correlated with a rise of proton translocation activity (retinal **4** 7.5%, retinal **3** 24%, retinal **2** 45% of the value found for retinal (**1**); the data are taken from the measurements under saturating illumination). An explanation for this strong influence of the methyl groups can be given. Flash photolysis of the BR analogue containing the acetylenic retinal **3** showed the appearance of a blue-shifted intermediate with an absorption around 390 nm, comparable to the M intermediate in BR. This decayed with a $t_{1/2}$ value of ca. 6 ms and gave rise to a red-shifted intermediate around 590 nm, which took 200 ms for full decay. This slower photocycle, compared to that of BR, can lower the proton translocation efficiency.

The increasing lability of chromoproteins with decreasing numbers of methyl groups cannot be used as an explanation for the decreasing activity, because the measurements shown in Figure 6 were reproducible also after application to the highest irradiance. The proton translocation measurements were always carried out with cell vesicles in the presence of tetraphenylphosphonium cations, thus preventing the establishment of a membrane potential. In contrast, the photophosphorylation experiments, which were carried out with living cells, showed an even lower activity (6.7% instead of 24% for retinal **3**. Here, the developing membrane potential could play a role by destabilizing several intermediates of the photocycle of that BR analogue.

By comparison of the experiments performed with opsin to those with BO the following conclusions can be drawn: In opsin two binding sites exist, which in the case of retinal supplement each other. In the case of analogue retinals with different geometric arrangements of ring and side chain, association and thereby covalent binding are complicated or even prevented.

BO interacts predominantly with the carbonyl end group of retinal; competition studies of the BR reconstitution reaction by the use of cyclocitral or β-ionone gave no indication for the existence of a β-ionone binding site comparable to that found in opsin.[17] However, interactions of the cyclohexene ring with BO must exist and are enhanced by the presence of the methyl groups at the positions 1 and 5. These interactions have a considerable influence on the function of BR as a light-driven proton pump.

Acknowledgment. We are greatly indebted to Dr. L. Ernst (GBF Stöckheim) for the measurement of the 400-MHz ^{1}H NMR spectra. We thank Dr. P. Tavan for MNDOC calculations to elucidate the ground-state structures of retinals shown in Figure 8 and Dr. J. Deisenhofer for assistance with the computergraphics of that figure.

Registry No. *all-trans*-**2**, 91365-73-0; 13-*cis*-**2**, 91422-74-1; 9,13-*cis,cis*-**2**, 91422-75-2; 9-*cis*-**2**, 91422-76-3; 11-*cis*-**2**, 91422-77-4; *all-trans*-**3**, 91365-74-1; 13-*cis*-**3**, 91365-75-2; 9,13-*cis,cis*-**3**, 91365-76-3; 9-*cis*-**3**, 91365-77-4; *all-trans*-**4**, 91365-78-5; 13-*cis*-**4**, 91365-79-6; 9,13-*cis,cis*-**4**, 91365-80-9; 9-*cis*-**4**, 91365-81-0; **5**, 74193-14-9; **6**, 91365-82-1; **7**, 583-60-8; **8**, 1193-47-1; **9**, 91365-83-2; **10**, 91365-84-3; **11**, 91365-85-4; **12**, 91365-86-5; **13**, 91365-87-6; **14**, 91365-88-7; **15**, 78-27-3; $(EtO)_2P(O)CH_2CN$, 2537-48-6; $(EtO)_2P(O)CH_2C(CH_3)=CHCN$, 87549-50-6.

Photochemistry and Photophysics of Surfactant *trans*-Stilbenes in Supported Multilayers and Films at the Air–Water Interface[1]

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Abstract: The synthesis and study of several surfactant *trans*-stilbene derivatives are described. Both compounds containing the *trans*-stilbene at the hydrophobic terminal of a surfactant chain and those containing an intrachain stilbene chromophore have been studied. These molecules form stable films at the air–water interface which can be transferred sequentially to give quartz-supported multilayers. The stilbenes in the multilayer assemblies show very low photoreactivity and specifically little photoisomerization. Strong fluorescence is observed from all of the stilbenes studied; the fluorescence shows similar vibronic structure to the molecular fluorescence of *trans*-stilbene in solution. However, the fluorescence is substantially red-shifted and the fluorescent lifetime is greatly increased over that in solution. The observed changes in absorption and fluorescence can be explained by a "cardpack" exciton model in which the excitation is shared by clusters of closely packed stilbene units and in which considerable migration and delocalization of excitation energy occurs.

Introduction

The properties and reactivity of molecules incorporated into films or attached to solid surfaces have been the subject of numerous recent investigations.[4-15] There has been particular interest in the "interfacial" behavior of such molecules and their interaction with other molecules incorporated into the same film or molecular assembly due to widespread potential applications including the development of photosensitive devices giving reso-

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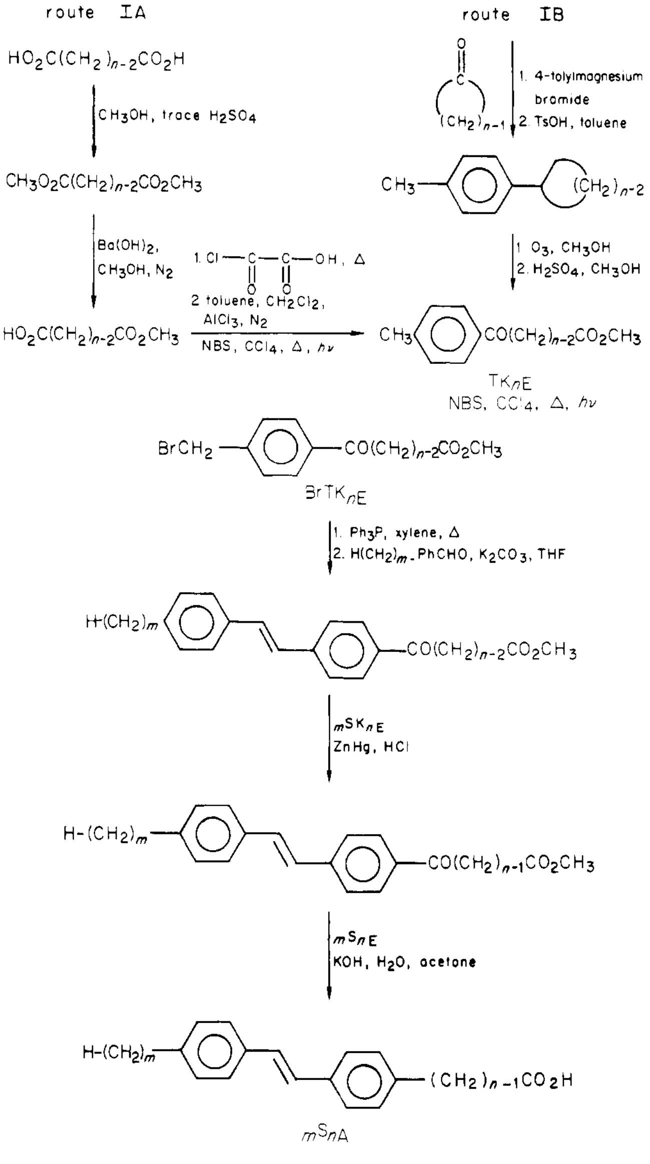
lution at or near molecular levels.[10-15] The question of excited-state energy migration or delocalization in assemblies has also been a topic of considerable investigation.[8,9,15] In this paper we report the synthesis and study of a number of surfactant molecules containing the *trans*-stilbene chromophore as a component of the hydrophobic hydrocarbon backbone. These molecules were designed as probes for the hydrophobic regions of molecular assemblies formed from self-aggregation of amphiphilic molecules. Since the stilbene chromophore is rod-like and has a reasonably small cross-sectional area, it appeared attractive from the point of being a readily detectable probe with good photochemical and photophysical properties for interrogating the "environment"[16,17] while simultaneously producing a minimum of structural perturbations. We have already reported results of studies of some of the stilbenes in micelles and other aqueous surfactant assemblies.[18-20] In the present study we report on their behavior in quartz-supported multilayers. The results of this study are interesting in that in contrast to the other assemblies examined, where molecular excited states are the exclusive species encountered, the multilayer assemblies show strong evidence of "supermolecular" or excitonic behavior of all of the stilbenes examined. Results obtained in this study, including the observation of a structured, red-shifted fluorescence with a relatively long lifetime, suggest that the stilbene exciton in multilayer assemblies can extend over several molecules and result in extensive energy migration within the assembly.

Scheme I. Synthesis of Surfactant Stilbenes $_mS_{nA}$



Experimental Section

Materials. *trans*-Stilbene (Eastman) was recrystallized from ethanol. Arachidic acid and methyl arachidate were used as received from Analabs, Inc., and kept under refrigeration. Dimethyl sulfoxide (Fisher) was predried over Drierite and then distilled under vacuum from calcium hydride between 45 and 70 °C. Chloroform (Fisher Certified) for monolayer work was used as received. Water for monolayer work was triply distilled (once from alkaline permanganate and once from sulfuric acid) as previously described.[21]

Synthesis of Surfactant Stilbenes. The surfactant stilbenes S_{10A}, S_{12A}, S_{16A}, $_4S_{6A}$, and $_2S_{8A}$ were synthesized by the routes outlined in Scheme I. For S_{10A} the acid chloride monomethyl ester was easily prepared, making the acylation route (IA) the obvious choice. S_{16A} was also initially prepared by this route.[18] For the others, the cyclic ketones have been used as starting materials (IB) and the toluene ketoester intermediates were prepared via the Grignard–dehydration–ozonolysis route. While this route involves more steps than the acylation route, the amount of time and overall yields are comparable. The synthesis of $_4S_{6A}$ is described below in detail with yields, melting points, and analytical data given for the other homologues.

$_4S_{6A}$. A solution of 4-bromotoluene (Aldrich, 15 g, 0.088 mol) dissolved in 50 mL of tetrahydrofuran was added slowly to crushed magnesium turnings (Mallinckrodt, 2.34 g, 0.096 mol) in 40 mL of tetrahydrofuran in a carefully dried flask under nitrogen purging. After a third of the addition was complete, the mixture was heated to reflux and the addition of the bromide solution completed. Refluxing continued for a total of 2 h. To this mixture was added over a period of 10 min, cyclohexanone (Aldrich, 9.5, 0.097 mol), and the solution was refluxed 30 min. White crystals began to form on the edge of the flask after which cold water and 10% hydrochloric acid were added to quench the reaction. The tetrahydrofuran was removed by evaporation and the remaining mixture was extracted from the aqueous phase with 3 × 80 mL of diethyl ether. The ether layers were combined and extracted with saturated sodium chloride solution. The ether was removed by evaporation and replaced with 180 mL of toluene and 100 mg of toluenesulfonic acid. The toluene was distilled down to 50 mL, replaced with 150 mL of toluene, and again distilled down to 50 mL. TLC, using hexane as eluent, indicated that this liquid had completely converted to the styrene. The product was purified by passing through a silica column using a solvent mixture of 20% chloroform in hexane. The solvent was removed by evaporation, yielding cyclic styrene (13.09 g, 0.063 mol, 72%) in the form of a colorless liquid. Preparation of the analogous cyclic styrenes for the other surfactant stilbenes also gave colorless oils in 65–72% yields.

The cyclic styrene was next ozonolyzed by use of a Welsbach Model T-816 ozonator. The voltage was set at 90 V and the pressures at 9 psi of pure O_2 input and 1 psi in the output. The reaction vessel containing the cyclic styrene (3.0 g, 0.017 mol) dissolved in methanol was cooled in an ice bath with stirring. The mixture was ozonolyzed about 20 min after which TLC indicated complete reaction using methylene chloride as eluent. The cyclic styrene appeared at R_f 0.8 and the product at R_f 0. To the mixture was added 7 mL of sulfuric acid over a 30-min period with refluxing. The volume was reduced to about 30 mL by evaporation. The ozonolysis procedure was repeated twice using 3.0 g (0.017 mol) and 6.0 g (0.034 mol) of cyclic styrene, and all of the products were combined and extracted between diethyl ether and water. The ether was washed with sodium carbonate solution and dried with saturated sodium chloride solution and anhydrous sodium sulfate. The ether was evaporated, leaving an oil which crystallized on ice. The product was recrystallized from hexane yielding white crystals of the toluene keto esters (TK_{6E}) (8.2 g, 0.035 mol, 51.5%), mp 46–48 °C. The corresponding keto esters were obtained in the same manner: TK_{12E}, mp 73 °C, 64.1%; TK_{8E}, 36 °C, 45.7%.

TK_{6E} was brominated with *N*-bromosuccinimide as follows. TK_{6E} (3.8 g, 0.016 mol) was added to *N*-bromosuccinimide (Fisher, 2.84 g, 0.016 mol; recrystallized from 10 times its weight in water and dried under vacuum), and a total of 250 mL chloroform (dried for several hours over anhydrous sodium sulfate) was dropped in until the mixture dissolved. This was refluxed until the chloroform was boiling under N_2 atmosphere

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about 5 min. A sunlamp was used to initiate the reaction. After 20 min, the colorless liquid became yellow from Br_2 formation. Subsequently the liquid suddenly became colorless, indicating completion of reaction. The lamp was removed and the flask slowly cooled to room temperature with succinimide floating on the surface. The bromide product is soluble in chloroform, so the liquid was filtered and evaporated; a residue of greenish crystals remained. Hexane was added and the mixture heated to dissolve the crystals. A dark green oil formed and the light yellow liquid was poured into another flask in which crystals began to form. The bromination step was repeated and all crystals were recrystallized in hexane, yielding $BrTK_{6E}$ (3.0 g, 0.0096 mol, 60%), mp 89 °C. Similar preparations afforded $BrTK_{12E}$ (mp 73 °C, 48%) and $BrTK_{10E}$ (mp 65–66 °C, 59%).

The Wittig reaction was carried out by dissolving $BrTK_{6E}$ (2.8 g, 0.0089 mol) and triphenylphosphine (2.33 g, 0.0089 mol) in xylene (150 mL). The solution was heated with stirring for 1 h. Afterwards the solution was cooled and filtered (gravity); the xylene solution was then reheated for ca. 1 h. The xylene solution was then concentrated under reduced pressure; the crystals that formed upon cooling were collected by filtration and combined with the first crop collected. The solids were recrystallized from benzene and dried under vacuum. The resulting crystals were dissolved in a mixture of 50 mL of methylene chloride and 80 mL of tetrahydrofurn. To this solution are added 4-butylbenzaldehyde (Sigma, 5.5 g, 0.034 mol) and potassium carbonate (4 g, 0.029 mol); the mixture was refluxed under N_2, the reaction being checked by TLC using chloroform as eluent. The liquid was poured off, leaving potassium carbonate behind. The liquid was evaporated and run through a silica column using a chloroform as eluent, leaving triphenylphosphine impurity on top of the column.

TLC was used to indicate which collections contained the impurity in them by observing a TLC spot at $R_f = 0$. These collections were recrystallized in hexane and again put through the silica column. The collections contained product $_4SK_{6E}$ (R_f 0.5) and were brightly fluorescent. The solvent was evaporated and the product was recrystallized in hexane, yielding $_4SK_{6E}$ (1.25 g, 0.0033 mol, 38%), white crystals, mp 107–108 °C. Similar procedures afforded SK_{12E} (mp 114.5 °C, 39%) and SK_{10E} (mp 115 °C, 32%).

Reduction of the ketone was accomplished by Clemmensen reduction. Zinc (Mallinckrodt, 0.54 g, 0.0083 mol, 20 mesh) was washed with 2 mL of 10% hydrochloric acid for 1 min followed by two washings in distilled water. To the zinc was added 2 mL of amalgamating solution (contains 5 mL of concentrated hydrochloric acid, 50 mL of water, and 5 g of mercuric chloride), and the mixture was agitated for 1 min. The zinc was washed four times with distilled water and placed in a flask containing 2 mL of 25% hydrochloric acid, followed by the addition of $_4SK_{6E}$ (0.101 g) and 4 mL of toluene. The mixture was refluxed with stirring. TLC, eluting with methylene chloride, indicated complete disappearance of strating material (brightly fluorescent spot at R_f 0.7. The reaction was repeated three more times, and the toluene layers were collected and dried with anhydrous sodium sulfate. The solvent was removed by evaporation and the product passed through a silica column using 20% chloroform/hexane. The solvent was evaporated from the fractions containing product $_4S_{6E}$. In an analogous manner S_{12E} (mp 76 °C, 22%) and S_{10E} (mp 70 °C, 28%) were obtained.

Saponification to give the surfactant stilbene $_4S_{6A}$ was carried out by adding the solid $_4S_{6E}$ to a mixture of 5 mL of water and 10 mL of acetone containing three pellets of potassium hydroxide. This mixture was refluxed for 2 h. As the acetone was removed, water was added to keep the volume constant. Hydrochloric acid (10%) was added until the solution was acidic to pH paper. When the mixture was cooled to room temperature, a precipitate formed. The solution was extracted with diethyl ether. The ether was evaporated off and the crystals were purified in acetone/water, yielding $_4S_{6A}$ (0.15 g, 0.004 mol, 14% from $_4SK_{6E}$), mp 132–133 °C. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.90; H, 8.48. Calcd for S_{10A}: C, 82.24; H, 8.63. Found: C, 82.00; H, 8.67. Calcd for S_{12A}: C, 82.49; H, 9.05. Found: C, 82.15; H, 9.06.

Monolayer Film and Multilayer Deposition Studies. The general methods used for preparing films and assemblies have been described elsewhere.[21] Most studies employed a double-barrier roung trough of the type designed and described by Fromherz.[22] Virtually all monolayer films were spread on a subphase of triply distilled water (with a typical conductivity of 1–2 μohms) to which had been added cadmium chloride (3×10^{-4} M) and sodium bicarbonate (5×10^{-5} M), giving it a pH 5.5–6.0 (aerated). The addition of cadmium promotes formation of superior long-chain carboxylic acid films.[21] In fact, under these conditions, the majority of acid film has been converted to the corresponding cadmium salt.[23]

Monolayer assemblies were constructed by Langmuir-Blodgett[24] molecular assembly[21] techniques on 12 mm × 35 mm × 1 mm Suprasil quartz slides obtained from Heraeus-Amersil, Inc. Unlike typical glass slides, these slides had virtually no absorbance in the 200–700-nm region and gave very little fluorescence in the 300–500-nm region. All slides were precoated with five layers of cadmium arachidate (CdAA) on a rectangular trough; all other depositions of assemblies were performed on a multicompartment circular Teflon trough equipped with feedback electronics described by Fromherz.[22] A Wilhelmy balance was used to measure relative surface pressure, and surface pressure–area isotherms were output to a Hewlett-Packard 7015B XY recorder. During construction of multilayer assemblies of different films, the round trough was also equipped with a simple subphase reservoir which smoothly replenished subphase volume during aspiration of the spread film over a submerged slide. The stilbenes and arachidic acid were dissolved in a CH_3Cl solution. Typically 20 μL of a mixture of $_mS_{nA}$ and AA as spread dropwise from a microliter syringe over 30–60 s. This and all subsequent operations were performed in dim red light. The uncompressed layer was allowed to rest for at least 1 min before slow compression (at a rate of 27 cm^2/min. or ca. 9.0×10^{-2} Å^2/s·molecule) was started. When the surface pressure reached ca. 1 dyn/cm, the compression rate was slowed to 8 cm^2/min (ca. 3.0×10^{-2} Å^2/s·molecul). The film was then compressed to a pressure of 30.0 ± 0.5 dyn/cm and held there in the constant-pressure mode. The isotherm was then checked to see if it was satisfactory. This was an important empirical evaluation which was refined over multiple experiments. It involved achieving and recognizing reproducible isotherm "sharpness" or slope and a reasonable, limiting molecular area. In many cases during compression, the film area would decrease by only 2–3 cm^2 between 4 and 30 dyn/cm. The film would also be checked initially for stability using the most sensitive area setting, a magnification of 10. At constant pressure, we have found that a "stable" film should lose less than 0.5 cm^2/min. Ideally, no area loss should occur within the first 5 min.

If the compressed film was satisfactorily stable, then coating of slides was commenced. Coating speeds were 70–80 s/cm (or 0.0133 cm/s). Quality of coating was routinely checked by three means: (1) integrity of menisci (hydrophobic on downstroke, hydrophilic on upstroke, strong and even during both), (2) proximity to unity of transfer ratio, and (3) uniformity of slide fluorescence (as checked by UV handlamp and/or fluorimeter when appropriate). If the spread film was to be aspirated off with the slide submerged so a new surfactant could be spread, the flow from the subphase reservoir was regulated to offset the volume loss from aspiration, thus closely maintaining the initial subphase level and surface pressure (ideally between +0.5 and −1.5 dyn/cm). Often the hydrophobic meniscus could be retained intact. The next film could then be spread and compressed as usual, and coating would resume. The slide/assembly typically remained submerged for 10 min or less prior to coating on the upstroke.

Spectra. All steady-state fluorescence measurements were performed on a SLM 8000S digital, photon-counting spectrofluorimeter equipped with Glan-Thompson prism polarizers and an Osram 450W "zone-free" Xe excitation source. The instrument was supplied with internal programs which corrected emission spectra for polarizer absorption and photomultiplier tube response. All fluorescence spectra were taken in the photon-counting mode. The excitation and emission channel polarizers were set at "0°" unless polarization of emission was being investigated. Excitation spectra were obtained by a two-channel ("double-beam") ratiometric procedure[25] involving the reference channel B. A 9.5×10^{-5} M Rhodamine B solution in ethylene glycol was used as a quantum counter.[25,26] For economy and convenience, a conventional square fluorescence cell with no reference channel filter was employed instead of the manufacturer-suggested triangular cell and RG630 filter. Results indicated that these modifications caused no significant errors in spectral accuracy.

Monolayer and multilayer assembly spectra were obtained by positioning the quartz slide in a standard, 1.00-cm fluorescence cuvette at about 45° to the direction of excitation propagation. This orientation reflected most nonabsorbed excitation light away from the emission monochromator. The 45° orientation of the slide did not produce the greatest fluorescence intensity, but is afforded a satisfactory intensity along with good, convenient reproducibility of intensity. All $_mS_{nA}$ mon-

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olayer for spectroscopic measurements contained 30 mol % of the S_{nA} except in cases where dilution effects were investigated. This concentration was chosen to ensure good film stability by including a sufficient concentration of arachidic acid, to provide enough sample so that monolayer fluorescence could be observed easily, and for convenience. Spectra were very reproducible in terms of maxima and minima, and good to ±10% regarding intensity. Other mole fractions within 10% of this give virtually the same shape fluorescence spectra with the anticipated intensity change, although intensity of emission often seemed to be nonlinear with concentration (though it was monotonic). When dilutions down to 1–5% were used, the background fluorescence/light scattering became troublesome and a good signal became hard to extract. Nonetheless, it appeared that no major changes in fluorescence band maximum or shape arose down to the instrumental limit. Ultraviolet spectra were recorded on a Perkin-Elmer Model 576ST double-beam spectrophotometer. Photolyses were carried out with a Schoeffel Model LPS-255 1000W Hg-Xe arc lamp equipped with a Bausch and Lomb high intensity monochromator. Single photon counting lifetimes were obtained with a Photochemical Research Associates system.[27]

Results

The several surfactant stilbenes used in this study all form stable, well-behaved films at the air–water interface either pure or in 1:2 mixtures with arachidic acid.[28] Because of the pH used (6.8) and the presence of Cd^{2+} in the aqueous subphase, the films and transferred layers contain the carboxylate head groups as their cadmium salts. Typical isotherms are obtained for S_{16A}, $_4S_{6A}$, and arachidic acid ($C_{20}H_{40}O_2$) films and various mixed films. The isotherms are similar in the 0–20 dyn/cm surface pressure domain and suggest that the *trans*-stilbene chromophore has a similar cross-sectional area to a polymethylene chain (ca. 20 Å^2/molecule) and that the packing of the stilbene surfactants does not disturb the film extensively.[16,21] The isotherms for a 1:2 molar ratio of surfactant stilbene to arachidic acid are superior to those for pure stilbene surfactant, and since these films give better transfer ratios, they were used in the subsequently described studies. Transfer ratios for the mixed films (from water to hydrophobic cadmium arachidate coated quartz slides) were typically 0.92 ± 0.05 on the downstroke coating to hydrophobic surface) and 0.97 ± 0.05 on the upstroke (coated surface hydrophilic). Transferred multilayer assemblies can be formed with up to 30 layers per side without difficult for both the S_{nA} and $_mS_{nA}$ surfactants in 1:2 molar ratio mixtures with arachidic acid.

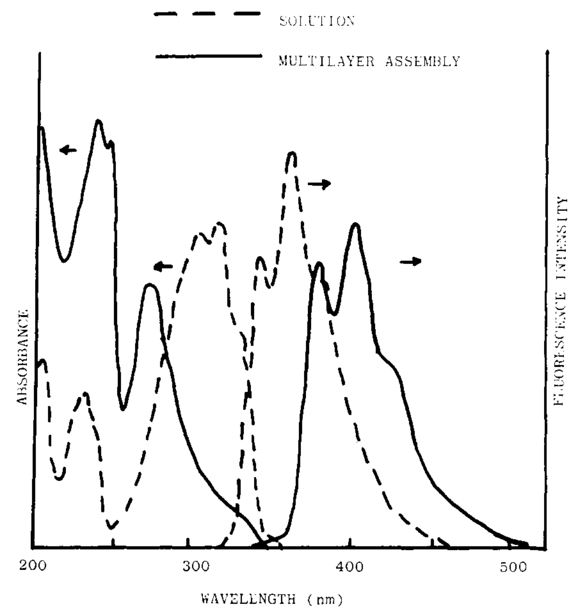

Figure 1. Comparison of solution and multilayer assembly spectra for $_4S_{6A}$: fluorescence excited at 310 nm for solution, 330 nm for multilayer.

Table I. Observed Bandshifts for Some Stilbenes on Going from Solution to the Solid State

	solution absorption		monolayer absorption[a]		
compd	λ_{max} (nm)[b]	λ_{max} (cm^{-1})	λ_{max} (nm)[b]	λ_{max} (cm^{-1})	bandshift (cm^{-1})
tS	201.5	49 630			
	228.5*	43 765	331	30 200[a]	
	283 (sh)	35 335			
	294.1*	34 000	337	29 700[a]	ca. −4300
	306.9	32 585			
	320.5 (sh)	31 200			
$4^{S}6A$	211	47 395	234 (sh)	42 735	
	227 (sh)	44 055	241	41 495	
	233*	42 920	249	40 160	−2760
	290 (sh)	34 485			
	304	32 895			
	317*	31 545	272*	36 765	+5220
	331 (sh)	30 210	295 (sh)	33 900	

[a] Data for tS from solid-state spectra according to ref 30. [b] An * denotes relative maximum.

Table II. Observed Bandshifts for Some Stilbenes on Going from Solution to the Solid State

	solution fluorescence		monolayer fluorescence[a]		
compd	λ_{max} (nm)[b]	λ_{max} (cm^{-1})	λ_{max} (nm)	λ_{max} (cm^{-1})	bandshift (cm^{-1})
tS	334	29 940	364	27 475[a]	
	349*	28 655	381	26 26 245[a]	−2410
	370 (sh)	27 030	403 (sh)	24 815[a]	
			435 (sh)	22 990	
$4^{S}6A$	358	27 935	376	26 595	
	362*	27 625	398	25 125	−2500
	380 (sh)	26 315	417 (sh)	23 980	
$^{S}10A$	340	29 410	376	26 595	
	357*	28 010	394	25 380	−2630
	375 (sh)	26 665	420 (sh)	23 810	

[a] Data for tS from solid-state spectra according to ref 30. [b] An * denotes relative maximum.

Supported multilayers containing the various surfactant stilbenes with arachidic acid all show strong fluorescence which shows little or no spectral variation with change in the molar ratio stilbene:arachidate or with chromophore location in the surfactant "frame".[29] In this study the stilbenes S_{16A}, S_{12A}, S_{10A}, $_4S_{6A}$, and $_2S_{8A}$ were all examined; since there were only small differences noted in their spectroscopic behaviors intensive investigations were confined to S_{16A}, S_{12A}, S_{10A}, and $_4S_{6A}$. For most of these studies the monolayer film used in preparing the quartz-supported assemblies contained 30 mol % of the stilbene. The solution absorption and fluorescence of the surfactant *trans*-stilbenes are very similar to that of *trans*-stilbene (tS) with similar absorptivity coefficients and fluorescence intensities but with small red shifts in both absorption and fluorescence with increasing alkyl substitution ($\lambda_{_4S_{6A}} > \lambda_{S_{10A}}$). Incorporation into a supported multilayer produces dramatic changes in both the absorption and fluorescence spectra of the surfactant stilbenes. These changes are completely reversible since washing of the assembly from the slide gives solutions having the characteristic spectra of tS as noted above. Slides containing supported multilayers gave the same results in terms of fluorescence behavior and reversibility whether studied in sealed, evacuated chambers or open to the air. Although there is a slow photobleaching on long exposure which may be in part oxidative, this poses no problems under the experimental procedures employed. Figure 1 compares spectra of $_4S_{6A}$ in quartz-supported multilayers and in solution. At first inspection, the absorption spectrum in multilayers appears strongly blue-shifted while the fluorescence is shifted markedly (ca. 20–30 nm) to the red. Tables I and II tabulate absorption and fluorescence maxima

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(27) We thank Drs. G. S. Cox and D. Condirston for assistance in performing some of the lifetime measurements.

(28) Surfactant stilbenes with fewer than eight methylene groups do not form stable insoluble films.

(29) The lack of variation is attributed to lack of microscopic homogeneity in the films. Such behavior, which is often encountered in mixed films, appears in all of the stilbene–arachidata films, regardless of the spreading techniques we have used with the molar ratios employed. Under a microscope the films are clear and show no evidence of macroscopic inhomogeneity.

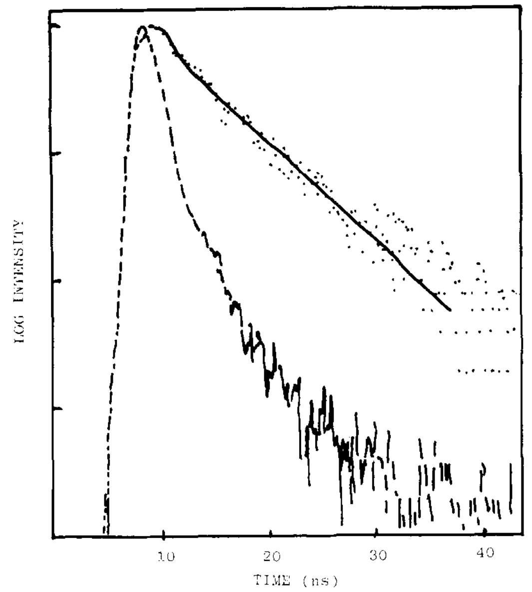

Figure 2. Fluorescence excitation spectrum of S_{10A} assembly monitored emission at 400 nm.

in nm and cm^{-1} for tS in solid and solution and for $_4S_{6A}$ and S_{10A} in multilayers and solution. The fluorescence spectra of the multilayer-incorporated surfactant stilbenes show similar structure and band separation to those of the same stilbenes in solution; however, the bands are shifted ca. 2500 cm^{-1} to lower energy. The structured, red-shifted fluorescence spectra observed for the surfactant stilbenes in multilayers are similar to that of tS in the crystalline state as can be seen in Table II.[30]

The changes in the absorption spectra of the surfactant stilbenes are quite pronounced in that the characteristic intense absorption centered near 300 nm is essentially missing; the major bands now appear near 230 nm with a weaker peak near 270 nm. The fluorescence excitation spectrum of $_4S_{6A}$ shows a weak peak near 340 nm (Figure 2) which may correspond to a "hidden" band in the multilayer absorption spectrum. Previous studies have shown that crystalline tS has a red-shifted absorption spectrum[30,31] while substituted stilbenes exhibit a variety of absorption and fluorescence types depending upon the crystal structure.[32,33]

In contrast to the solution behavior of the stilbenes, for all of the multilayer-incorporated surfactant stilbenes fluorescence is the most prominent of the various photophysical and photochemical pathways available. The fluorescence intensities of all of the surfactant stilbenes are considerably higher in the quartz-supported multilayers. The quantum yield for S_{16A} is 0.38 ± 0.05; using this as a reference we estimate identical values for S_{10A} and S_{12A} and a slightly lower value, $\phi_f = 0.27$, for $_4S_{6A}$. Compared to solutions, the supported multilayers are relatively stable to photoisomerization. For example, it was found that the quantum yield for photobleaching of the trans isomer of a 30-layer assembly containing 50 mol % S_{16A} at 254 nm is 0.02, more than 10-fold below its reactivity in most organic solvents. The photoisomerization yield is significantly lower; although it is difficult to estimate the precise quantum yield (ϕ_{t-c}) owing to the rapid conversion of the cis isomer to the corresponding phenanthrene, an upper limit of 1.6×10^{-3} can be established for the *initial* isomerization in multilayers. The rate of disappearance of the *trans*-stilbene chromophore on irradiation in the multilayers generally decreases with time. The results obtained in studies of several samples suggest that most photobleaching and certainly the photoisomerization occur in "defect sites" and that most of the assembly-incorporated stilbene chromophores are photostable. The rapid conversion of the small amount of cis isomer formed to the corresponding phenanthrene is probably consistent with location of those molecules in a somewhat disordered region of the assembly in which more molecular motion is possible.

Table III. Single-Photon Counting Lifetimes of $_mS_{nA}$ in Assemblies

stilbene measured	lifetime[a] (ns)	medium	ref
tS	0.84 ± 0.17	solution	29
$_4S_{6A}$	3.3	multilayer	27
S_{10A}	4.7	multilayer	27
S_{12A}	4.6	multilayer	27
S_{16A}	4.7	multilayer	27

[a] The lifetime of the major component; in several cases a minor short-lived component is also observed (see text).

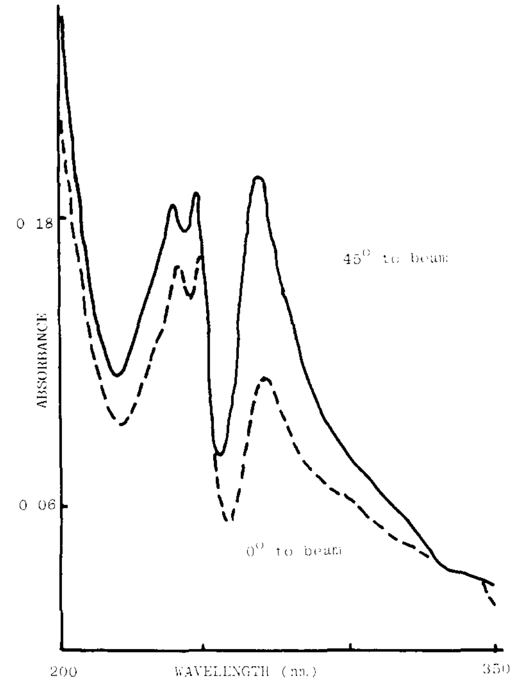

Figure 3. Single photon counting lifetime of S_{10A} in S_{10A}/AA assembly biexponential decay.

Fluorescence lifetimes for several of the assembly-incorporated *trans*-stilbenes were measured by single photon counting techniques; in each case the major fluorescence lifetime component was found to be on the order of 3–5 ns (Table III, Figure 3). This represents an approximately 50-fold increase over the fluorescence lifetimes of tS and the surfactant derivatives in homogeneous solutions of low viscosity. Furthermore, these lifetimes exceed the "true" radiative lifetime of tS by a factor of ca. 2–3. The increases in lifetime together with the spectral shifts provide strong evidence that the *trans*-stilbene chromophore in the mulilayer assemblies cannot be described as an isolated molecule, but must be interacting with one or more neighboring stilbene units.

To determine the type of interaction which occurs in the multilayer assemblies containing the surfactant stilbenes, it would be necessary to know the orientation of the chromophores. Most directly for the films, the compressibility, stability, and homogeneity can be deduced from pressure–area isotherm data. As described above, the mixed films of S_{16A}, S_{12A}, S_{10A}, and $_4S_{6A}$ with arachidic acid are stable and show good isotherm packing to a limiting area close to 20 Å^2/molecule. The isotherms of the mixed films are slightly different from pure arachidic acid implying that the mixed films are relatively homogeneous.[21,24] These observations suggest that there is no gross bending or collapse of the stilbene surfactants in the assemblies such that the stilbene chromophore chould be oriented roughly perpendicular to the mean plane of the spread film. The finding that transfer ratios are close to unity suggests that similar orientation should be obtained in the supported multilayers.

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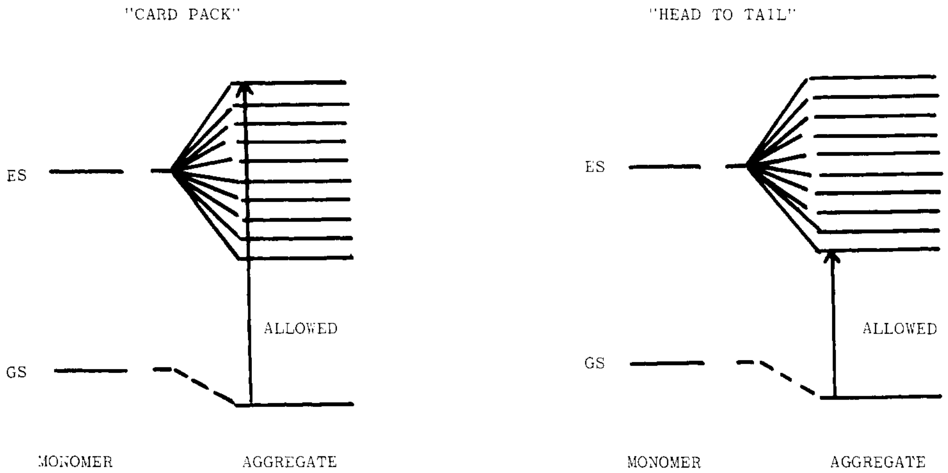

Figure 4. Effect of slide orientation on absorption spectrum of ${}_4S_{6A}$ assembly.

The spectral data obtained from the assemblies strongly imply that the stilbene chromophores are oriented with the long molecular axis perpendicular to the layer (support) plane. The absorption and fluorescence spectra all exhibit good reproducibility of maxima and band shape indicating that the molecular organization can be replicated with consistency. Polarized absorption spectra, which could indicate the orientation with certainty, could not be obtained in these studies because of the location of the bands in the ultraviolet. Nonetheless, supporting evidence concerning the chromophore orientation can be attained by examining the absorption spectral changes induced by varying the orientation of the assembly with respect to the incident light in a conventional spectrophotometer. Figure 4 compares spectra of an assembly of ${}_4S_{6A}$ with the slide normal and at 45° to the light beam. When the slide is normal to the beam there are two transitions, one at i250 nm and a weaker one at 270 nm. The same two transitions appear when the slide is at 45°; both transitions increase since there is more sample exposed to the light but the ratio of the 270 nm band to the 250 band strongly increases as well. In solution the lower energy band of tS is long-axis polarized; the changes in the monolayer spectra are consistent with the band at 270 nm also being long-axis polarized and that a change in the orientation facilitates absorption by increasing the integral of the electric vector with the light beam. The reason for the "residual" intensity at 270 nm when the assembly is normal to the beam is not clear; though a hidden transition[34,35] could contribute this residual absorption, a more reasonable explanation is that the chromophores are tilted away from the normal to the layer plane. Such behavior has previously been noted.[36,37] The fluorescence spectra of S_{12A} in quartz-supported multilayers are polarized nearly perpendicular to the support; this suggests the stilbene chromophore is in a similar alignment since the fluorescence of tS is long-axis polarized.[35,38-40]

Discussion

The results obtained with assemblies of the several different surfactant stilbenes show very similar behavior with regard to their photochemistry and photophysics. They clearly indicate that the great majority of the stilbene chromophores in the assemblies are in a rigid, restricted environment which is probably quite ordered and, interestingly, that there is strong interchromophoric interaction within the assemblies. That the multilayer-incorporated stilbenes should show low photoisomerization efficiences is not surprising in view of previous studies of other olefins in multilayers[33,41] and the finding that the same surfactant stilbenes show reduced photoisomerization efficiencies in much less restrictive environments such as micelles, vesicles, and amylose inclusion complexes.[18-20] As mentioned in the Results, the small amount of photoisomerization occurring appears attributable to reaction of a few chromophores located in "defect" sites, and it is clear that overall the assembly-incorporated *trans*-stilbene units are for the most part photostable.

Probably the most interesting aspect of the study is the finding that strong interaction between the stilbene chromophores occurs in the assemblies, resulting in a strong, structured fluorescence with an excited-state lifetime much longer than the radiative lifetime of *trans*-stilbene. To put the present results in perspective and to understand the type of interaction occurring, it is worthwhile to review other cases in which there is strong interchromophoric interaction as well as previous studies on *trans*-stilbene and related molecules in the crystalline state.

Extensive studies of assemblies containing closely packed chromophores have been carried out by Kuhn, Möbius, and their co-workers.[4,21,42-44] Many of these studies have focused on dialkyl-substituted cyanine dyes in which the chromophores' long axes are aligned parallel to the layer plane; for these dyes several types of aggregates have been observed including those with sharp, intense low-energy bands (J aggregates) and other with broad, higher energy bands nH aggregates). Evidence for broad excitonic interaction or "molecular cooperativity" has been shown convincingly in several of these studies; especially interesting is the finding that excited aggregates serve as effective antennae for rather widely spaced traps compared to localized excited states.[4,21,42-44]

Although many molecules with hydrophilic chromophores oriented parallel to the layer plane have been studied and found to show the aforementioned aggregates, relatively few systems have been studied when the chromophore is in a hydrophobic site or oriented perpendicular to the layer plane. A notable exception to this was the molecule quinquethienyl and a series of p-donor, p′-acceptor substituted stilbenes and azobenzenes recently described by Heesemann.[45,46] The latter clearly show evidence of some interaction through absorption spectra and polarization behavior. In each case, however, the absorption spectra are relatively broad and there is apparently little or no fluorescence. Heeseman presents evidence that the predominant species are

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"H-aggregates";[45,46] however, to some extent there is difficulty in interpreting these spectra because of their breadth and the fact that the charge-transfer transitions occurring are extremely sensitive to solvent effects[47,48] or nearby polar molecules. Fukuda and co-workers[49] have also studied azobenzene surfactants in which the position of the azobenzene chromophore relative to the assembly plane varied; again some evidence for interchromophoric interaction is present but the lack of fluorescence allows relatively little to be determined about the excited states occurring.

Recently Vincent and Barlow[50] and Matsuki and Fukutome[51] have studied surfactant anthracene derivatives which can be incorporated into supported multilayers. In the first study the anthracene was built into the surfactant unit by 9,10 substitution of the chromophore; the anthracene long axis would thus be anticipated to be perpendicular to the alkyl chain and parallel to the layer plane. Through isotherms, absorption, fluorescence spectra, and X-ray crystallography, it can be seen that the anthracene nuclei are tilted in the layers and show an anomalous interpenetration of alkyl chains. The short-axis polarized absorption band is slightly red-shifted and the emission appears best described as an excimer type.[50]

In the studies of Matsuki and Fukutome[51] the surfactant molecule has an anthracene appended to a hydrocarbon chain via a carboxy ester group affixed to the 9 position of the anthracene. Thus here the long axis should lie parallel to the surfactant chain. Assemblies formed from these surfactant anthracenes show clear evidence of an excitonic excited state with a blue-shifted spectrum, but in each case there exists a strong absorption due to monomeric anthracene. Clearly for these surfactants the packing allows an appreciable fraction of the anthracenes to remain dispersed.[51]

The structured and long-lived fluorescence observed for all of the surfactant stilbenes in the present study appear unique for monolayers or multilayer assemblies; however, the fluorescence observed is somewhat similar to that observed for crystals of *trans*-stilbene.[29,30] Early work showed that both absorption and fluorescence are red-shifted in the crystal by 2000–3000 cm^{-1}.[30] Subsequent investigations by Hochstrasser[30a] showed that the red-shifted fluorescence is little affected by temperature from 77 to 300 K. It was suggested that emission occurs from "defect centers" that are lower in energy than the "free exciton" state. Doping the crystal with 10^{-4}–10^{-5} mol % tetracene leads to an inordinately enhanced fluorescence of the impurity, suggesting that long-range energy migration occurs in the crystal.[29] While *trans*-stilbene gives a structured red-shifted fluorescence, some substituted stilbenes such as *trans*-2,4-dichlorostilbene[32] and *N*-octadecyl-4-stilbazole[33] give a broad structureless "excimer-type" fluorescence shifted considerably (5000 cm^{-1}) to the red compared to the solution monomer fluorescence. Unlike crystalline *trans*-stilbene, the derivatives giving excimer-type fluorescence in the crystal also form solid-state photodimers.[32,33]

The crystal structure of *trans*-stilbene is monoclinic with four molecules/unit cell.[52] Two types of molecular sites occur, with the long axes of the stilbenes being roughly perpendicular to one another.[52] Thus, relatively little electronic overlap occurs and the lack of photodimerization can be understood. Each molecule in a type "A" or "B" site has other nearest neighbors; although these can be as close as 3–4 Å, the transition moments are nonaligned so relatively little electronic interaction occurs.[52] Nonetheless, at these distances the oppourtunity for dipole–dipole interaction is good, and this is the type of interaction which produces excited-state coupling; thus an excitonic excited state results. The similarity between the fluorescence of the stilbene chromophore in the assemblies and pure crystal does not seem to carry over to the absorption spectra so it is not clear how close an analogy should be drawn.

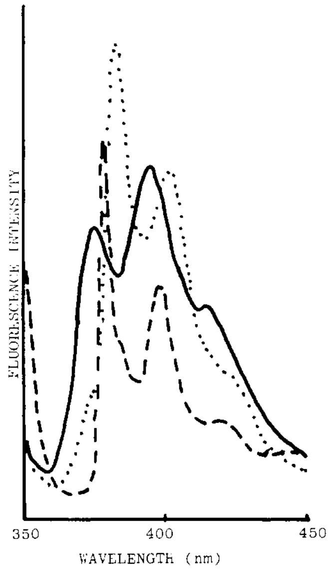

Figure 5. "Card pack" and "head-to-tail" models for surfactant stilbene aggregate excitons in monolayers and multilayers.

To define both qualitatively and quantitatively the behavior of the *trans*-stilbene chromophores in the multilayer assemblies it is useful to apply an exciton treatment: an exciton is defined as "a quantum of electronic excitation energy traveling in a periodic structure, whose motion is characterized by a wave sector" called k.[53] It is thus a quasi-particle/wave, responsible for propagating a collective excited state in solids, transferring energy among the molecules in a periodic aggregate. The Frenkel or "tight-binding" exciton is a type indigenous to molecular crystals for which each molecule in the aggregate essentially retains its ground-state electronic integrity and no intermolecular transfer of charge occurs in the excited state. The exciton concept can be pursued on exceptionally quantitative, mathematical levels;[53-56] it is useful to give a qualitatively correct account of some specifics followed by a simple quantitative approach, for developing an understanding of the present results.

Specific spectroscopic excited-state traits of a molecular aggregate depend on the configuration of the aggregate as well as the orientations of the transition moment dipoles in each molecule.[57,58] We can develop an ideal case which might correspond to that of a ${}_mS_{nA}$ monolayer, the H-aggregated "pincushion" arrangement (see ref 57 and 58), by starting with the spectroscopic properties of the monomers and building from there. First, several points can be established as initially summarized by Kasha:[57,58]

(1) The transition moments of the lowest energy ${}_mS_{nA}$ absorption (the A band) will all be parallel in the pincushion but perpendicular to the layer plane, while the higher energy transition moments (the B band) will be parallel to each other and to the layer plane in more of a "head-to-tail" arrangement. This should lead to marked splitting of the excited state into N bands, where N is the number of monomers in the aggregate. However, in the first order, the ground state should not be split because these wave functions are not coupled by a dipole Hamiltonian.[53,59]

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(2) Because of the regular transition moment alignments, we can predict what transitions will be allowed or forbidden. As shown in Figure 5, the "pincushion" or "card-pack" aggregate of the long-axis transition moments formally has one dipole-allowed transition, that being to the topmost energy level of the exciton band. Transitions to or from any lower level are forbidden. On the other hand, the "head-to-tail" aggregate picture should suit the arrangement of the short-axis transition moments (perpendicularly polarized B band), implying again that only one dipole-allowed transition should occur. Now, though, that transition should be to the lowest level of the exciton band, the rest being forbidden.

(3) Using the predictions from 2, we would expect that the low-energy absorption of *trans*-stilbene should be blue-shifted (a weak forbidden absorption from this band should be red-shifted, but the intense, readily observable band should be blue-shifted), the high-energy absorption band should be red-shifted, and the fluorescence should be red-shifted, all with magnitudes proportional to the strength of the interaction among their respective transition moments.

(4) In addition, because of forbiddenness of the fluorescence which should originate from the lowest level of the exciton band after rapid "internal conversion" from the highest level, we would expect a significantly increased fluorescence lifetime.

(5) The increased residence time in the lowest singlet excited state could enhance the chance of intersystem crossing and therefore the probability of phosphorescence.

(6) Because of long-range energetic communication in the aggregate, doping the lattice with even small concentrations of a lower energy fluorophore should produce observable impurity emission.

In dealing with so many types of molecular aggregate and their spectroscopic properties, Kuhn and co-workers[60] developed a quantum-mechanical treatment for calculating absorption spectral bandshifts for a variety of chromophore configurations. We have applied this method, with some modification, to our $_mS_{nA}$ assembly systems. The method and calculations are detailed as supplementary material. For a $_4S_{6A}$/AA assembly with 30 mol % $_4S_{6A}$, we observed a bandshift of 45 nm (5200 cm^{-1}). Using this method, and assuming a "pincushion" arrangement of $n > 50$ or so monomers and an interchromophore distance of 3.4 Å, we calculate a bandshift of 44 nm. From this we draw several conclusions.

(1) The $_mS_{nA}$ must basically be in a "pincushion" configuration, although they could be inclined from the normal to the layer plane and still give comparable results.[37,51,57,58]

(2) The $_mS_{nA}$ must be aggregating in small patches of at least 25 monomers within the film, to the partial local exclusion of AA, in order to approach one another to 3.4 Å.

(3) This aggregation must be a dominant feature of the assembly, leaving relatively few "free" monomers and producing a strong exciton state.

Other data corroborate these conclusions as well. The above qualitative predictions of bandshift directions for particular transition moments match our observations. Doping studies using 4 mol % of a surfactant pyrene derivative in S_{16A} assemblies display a great transfer of excitation energy to the impurity, despite its low concentration (Figure 6). Other studies demonstrate that $_mS_{nA}$ in multilayers can communicate through energy transfer over many layers. Single photon counting lifetimes (Table III) show that the primary lumophore in the assemblies decays at a markedly slow rate slower by nearly a factor of 3 than tS in a glass at 77 K. However, this rate is still orders of magnitude faster than those observed for triplet luminescence in tS crystals by Ern and co-workers.[61]

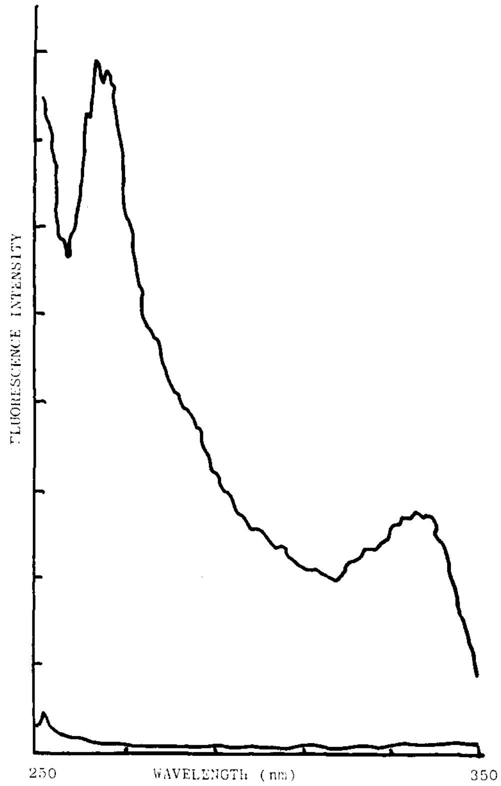

Figure 6. Fluorescence spectra of assemblies with an without surfactant pyrene as dopant: (—) S_{16}A:arachidate 1:1 (- - -) Py$_{16}$A:arachidate 1:1, (· · ·) S_{16}A:arachidate 1:1 with 4% Py$_{16}$A.

The physical data from monolayer work and the spectral/excitonic characteristics mutually reinforce a picture of the $_mS_{nA}$ assemblies: these are uniform (though not rigorously homogeneous), well-constructed multilayers in which the $_mS_{nA}$ cluster to form extended arrays of near-parallel transition moments. These moments couple in the excited state through a dipole interaction, giving rise to a collective excited state which propagates rapidly and extensively by singlet exciton migration. The long-axis transition moments appear to be coupled more strongly than the short-axis moments, judging from the size of their respective bandshifts. Although the long-axis moments probably deviate somewhat from the normal to the layer plane, they apparently remain close enough to it (and each other) to manifest the expected polarization of absorption, molecular area, and "pincushion" exciton bandshift. The cylindrical symmetry of the chromophore about the long-axis transition moment increases the "degrees of freedom" for molecular rotation which still provide a strong coupling. Conversely, the observed polarization behavior and the lesser magnitude of the bandshift for the short-axis transition reflect at least a partial randomization of the transition moments in the aggregate in a plane which parallels the layer plane (Tables I and II).

Finally, the increased fluorescence lifetime, strong "impurity" (pyrene) fluorescence, and fluorescence red-shift all corroborate our conception of an H-aggregate band structure and singlet exciton migration. There is no clear-cut explanation for the unexpectedly small fluorescence shift (about 2500 cm^{-1} rather than 5000 cm^{-1}); however, this could be an example of "defect center" emission noted by previous researchers.[29,30] The monomer vibronic structure of the fluorescence implies two points: first, the deexcitation must occur to a monomer-like ground state;[62] second, the emission is decidely not of an excimer nature.[32,63] This must mean either that the molecules lie in an unfavorable orientation for excimer emission, or that the rate of excimer formation cannot compete well with "defect" fluorescence or energy transfer. If it could, the expected lower energy excimer luminescence would certainly be seen. We also have no notion of how much or in what

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direction the ground-state energy of the $_mS_{nA}$ is displaced by the dielectric changes brought about by the exciton.

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Registry No. p-BrC$_6$H$_4$CH$_3$, 106-38-7; p-BuC$_6$H$_4$CHO, 1200-14-2; S$_{10A}$, 77824-98-7; S$_{12A}$, 77814-49-4; S$_{16A}$, 74392-06-6; $_4$S$_{6A}$, 91202-35-6; $_2$S$_{8A}$, 91202-36-7; TK$_{6E}$, 91202-39-0; TK$_{8E}$, 91202-40-3; TK$_{12E}$, 85554-56-9; BrTK$_{6E}$, 91202-41-4; BrTK$_{10E}$, 91202-43-6; BrTK$_{12E}$, 91202-42-5; $_4$SK$_{6E}$, 91202-44-7; SK$_{10E}$, 91202-46-9; SK$_{12E}$, 91202-45-8; $_4$S$_{6E}$, 91202-47-0; S$_{10E}$, 91202-49-2; S$_{12E}$, 91202-48-1; tS, 103-30-0; cyclohexanone, 108-94-1; 1-(1-cyclohexen-1-yl)-4-methylbenzene, 1821-23-4; 1-(4-methylphenyl)cyclooctene, 91202-37-8; 1-(4-methylphenyl)cyclododecene, 91202-38-9.

Supplementary Material Available: Method and calculations of exciton bandshifts of $_mS_{nA}$ assembly systems (6 pages). Ordering information is given on any current masthead page.

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Aminolysis of Maleic Anhydride. Kinetics and Thermodynamics of Amide Formation

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Abstract: The rates of reaction of maleic anhydride with a series of a primary straight-chain amines were measured for solutions at pH 4, 25 and 15 °C. The series was selected to minimize complications due to steric and hydrophobic effects. The second-order rate constants for production of N-alkylmaleamic acids at 25 °C range from 3×10^2 to 1×10^5 M^{-1} s^{-1}. The rate constants follow a nonlinear Brønsted relationship (log k vs. pK_a of the conjugate acid of the nucleophile) and conform to the expression $1/k = 10^{-0.95\mathrm{p}K_a+3.03} + 10^{-0.23\mathrm{p}K_a-2.52}$. The data fit the rate law for a process in which a change in rate-determining step in a single mechanism causes a change in slope from 0.95 to 0.23, with equal rates for the two steps for the case of an amine with a conjugate acid of pK_a = 7.7. The results are interpreted in terms of a mechanism in which proton transfer in the zwitterionic tetrahedral intermediate is the rate-determining step for amines whose conjugate acids have pK_a values less than 7.7. The reactions of more basic amines involve rate-determining formation of the tetrahedral intermediate. These results contrast with those for aminolysis reactions in which acylammonium compounds are produced and which do not involve proton-transfer steps. The equilibrium constants for formation of amides from maleic anhydride and the amines at 50 °C were determined by combining these data with the rates of the reverse reaction. The equilibria fit the expression log K = 0.44pK_a + 4.7. The free energies of hydrolysis of the maleamic acids are estimated to range from 7.6 to 11 kcal/mol.

The detailed mechanism of addition of nucleophiles to reactive carbonyl compounds is a problem of continuing interest. The reaction of primary amines with anhydrides is a common and practical approach to the formation of amides. There have been very few studies in this system, and the most complete have been complicated by steric effects.[1,2] The addition of pyridines to acetic anhydride has been studied, but in that case, since the nucleophile is a tertiary amine, the product is an unstable acylpyridinium salt.[3] The reactions of primary and secondary amines with anhydrides lead to stable neutral amides since proton loss occurs.

Detailed mechanistic analysis of a reaction is assisted by information from studies of the reverse reaction. Acylolysis of amides, the reverse of the aminolysis reaction, is observed for aqueous solutions only in the case of intramolecular reactions. The intramolecular carboxyl-assisted hydrolysis of amides proceeds via intermediary formation of an anhydride along with expulsion of the amine.[4] This class of reaction has been studied in detail and is the reverse of the aminolysis of a cyclic anhydride.[5,6] We have now examined the aminolysis of maleic anhydride, a reaction whose reverse has earlier been subject to kinetic analysis. The kinetic results enhance the mechanistic analysis and provide information about aminolysis reactions in general.

Experimental Section

Materials. All amines except 2,2-difluoroethylamine were purchased from the Aldrich Chemical Co. All liquid amines were distilled prior to use. Hydrochloride salts were purified as reported by Kertes.[7] Maleic anhydride and spectrophotometric grade acetonitrile were purchased from the Aldrich Chemical Co. and were used without further purification. Reagent grade inorganic materials and organic reagents were obtained from Fisher Scientific.

***N*-(2,2,2-Trifluoroethyl)maleisoimide.** Dicyclohexylcarbodiimide (DCC, 45 mmol in 50 mL of dichloromethane) was added over 10 min to 45 mmol of N-(2,2,2-trifluoroethyl)maleamic acid in 50 mL of dichloromethane. N,N'-Dicyclohexylurea began to precipitate before the addition of DCC was complete. The solution was refluxed for 1 h. The urea derivative was removed by filtration and the solvent evaporated from the filtrate. The product was distilled under high vacuum. The maleisoimide is an oil at room temperature. Proton NMR (chloroform-d, in ppm from internal tetramethylsilane reference, Varian T-60 spectrometer): 6.90 (d, J = 7 Hz), 6.20 (d, J = 7 Hz), 3.66 (q, J = 9 Hz).

Kinetics. Rate data were obtained with a Varian Cary 210 spectrophotometer to measure the change of absorbance at 255 nm. Data were collected through a microprocessor-controlled interface (built by Comspec Ltd., Downsview, Ontario, Canada). The data were stored in a

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