

Photochemistry and Photophysics of *trans*-Stilbene and Related Alkenes in Surfactant Assemblies

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Introduction

During the last 20 years there has been extraordinary interest and development in the study of microphases formed by self-assembly of monomeric units ranging from amphiphile or surfactant organic molecules to inorganic ions.¹⁻¹⁰ A major focus emerging has been the observation of modified reactivity or properties of "guests" entrapped within or otherwise associated with these microphases.^{2,4,11-15} This modified reactivity has been used in some cases as a structural probe and in others as a potentially useful end itself. In parallel developments, the study of host-guest chemistry in which clays, zeolites, cyclodextrins, or crown ethers are used to entrap smaller molecules within restricted sites has resulted in a similar development of new chemical reactivity.¹⁶⁻²² Many of these phenomena involve organic substrates in aqueous or mixed aqueous-organic solutions. A number of investigations have outlined the role that solvent-solvent and solvent-solute interactions play in controlling or organizing the formation of the "supramolecular" assemblies that are central in all of this work.^{9,23-28} In this Account we review the reactivity of a relatively simple yet versatile chromophore molecule—*trans*-stilbene—which has several attractive features: medium-sensitive and easily monitored photophysics and photochemical reactivity, synthetic accessibility and facile structural modulation, and the possibility of undergoing both intramolecular and intermolecular interactions. Although several facets of modified reactivity in surfactant assemblies will be discussed, we will focus on some of our most recent work, which illustrates the interesting and important ability of these organic chromophores to form aggregates of regular and controllable structure. These assemblies can have extended and highly anisotropic "conjugation", and they point the way to exciting prospects for the design and construction of novel materials and assemblies.

trans-Stilbene was one of the earliest studied molecules during the development of so-called molecular photochemistry during the early 1960s,²⁹⁻³² although

the *cis*-*trans* photoisomerization of stilbene and related alkenes had been observed much earlier.³³⁻³⁵ Much of the work in the 1960s focused on the triplet path for photoisomerization and the role of energy transfer to and from sensitizer triplets.²⁹⁻³³ For a number of years, there was considerable controversy as to the role of the triplet stilbene in the direct photochemistry of the stilbenes; however, it is now generally accepted that there are discrete singlet and triplet paths for photoisomerization and little direct population of triplet states for *trans*- and *cis*-stilbene under direct irradiation.^{32,36} A schematic representation of the energy surfaces for the ground and excited singlet states of the stilbenes is shown in Figure 1; a key feature for the excited singlet state is the existence of minima corresponding to *transoid* (t) and *perpendicular* (p) geometries with a small barrier between these two states. Although the studies described above focused on the intramolecular photoreactions of the stilbenes, namely *cis*-*trans* photoisomerization and photocyclization of the *cis* isomer, other intermolecular photoreactions of the stilbenes, such as [2 + 2] photocycloaddition reactions leading to dimers or adducts, have also been observed.³⁷ In more recent work, a variety of other photoaddition reactions have been observed, which in many cases can be attributed to initiation by single-electron-transfer (SET) reactions of the stilbene (or other molecule) excited states.³⁸

David G. Whitten was born in Washington, DC, in 1938. He received the A.B. degree in Chemistry in 1959 and the M.A. and Ph.D. degrees in 1961 and 1963, respectively, from the Johns Hopkins University. Following military service, involving research in the space program at Caltech's Jet Propulsion Laboratory, he spent a postdoctoral year (1965-66) with George Hammond at the California Institute of Technology. He joined the faculty of the University of North Carolina at Chapel Hill in 1966 and rose to the rank of M. A. Smith Professor in the Department of Chemistry. In 1983, he assumed his present position as C. E. Kenneth Mees Professor of Chemistry at the University of Rochester, where he is also Director of the NSF Center for Photoinduced Charge Transfer. The present paper is based on his award address on receiving the 1992 ACS Award in colloid or surface chemistry at the ACS Meeting in San Francisco in April 1992. His research interests include fundamental studies of photochemical reactivity, including electron-transfer reactions, and reactivity and properties of molecules incorporated into microheterogeneous media.

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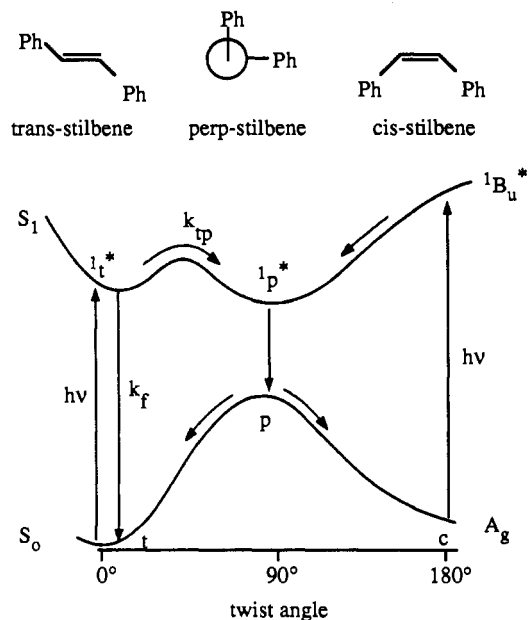
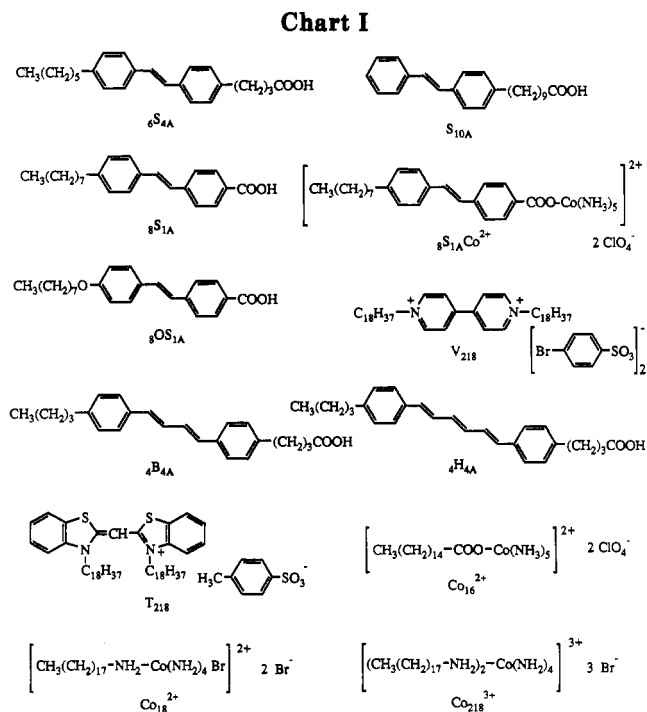


Figure 1. Schematic representation of ground- and excited-singlet-state energies of stilbene as function of angle of rotation for *trans*-*cis* interconversion.

One of the features of *trans*-stilbene that has rendered it attractive for photochemical investigation is its prominent fluorescence, which, though relatively inefficient in nonviscous fluid solution ($\phi_f = 0.05$ in benzene, $\tau_f = 60$ ps) due to competition with decay to the p state (Figure 1), permits facile mechanistic investigations of photoreactivity in many cases.^{39,40} Since the lowest energy transition of *trans*-stilbene is strongly allowed (the strongly forbidden upper $^1A_g^*$ excited state, which is lowest lying in higher α,ω -diphenylpolyenes, is well above the fluorescent singlet in *trans*-stilbene and plays little role in determining its oscillator strength⁴¹⁻⁴³), fluorescence would be the main, if not exclusive, deactivation channel in the absence of twisting to p. Consequently, the forced rigid *trans*-



stilbene "analogue" indeno[2,1-*a*]indene has a quantum yield for fluorescence of near 1 and a fluorescence lifetime of 1.7 ns.⁴⁴ For *trans*-stilbene itself, an increase in viscosity in dilute solution leads to an increase in fluorescence efficiency and lifetime with a concurrent decrease in the efficiency of *trans*-to-*cis* photoisomerization.⁴⁵

Stilbene and Related Compounds in Micelles and Vesicles

Many studies of stilbene photoreactivity in different media have employed substituted or modified *trans*-stilbene chromophores which are expected to show similar photoreactivity but, in some cases, possess molecular structures either rendering them more compatible with the medium or better defining the type of site within the medium or microenvironment the stilbene chromophore should occupy. The effects anticipated and observed with different structures differentially incorporating the stilbene chromophore should depend strongly upon the degree of organization of the host medium and its dynamic nature. A rather striking example of the differences that can occur between different media can be shown by comparing reactivities of a series of different stilbene derivatives in detergent micelles and aqueous solutions of phospholipids or synthetic double-chain bilayer-forming surfactants.

trans-Stilbene and the several stilbene fatty acid derivatives (SFAs) of structure nS_{mA} or S_{nA} shown in Chart I can all be solubilized in both detergent micelles and in the bilayer-forming phospholipids.⁴⁶⁻⁴⁹ For

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Table I. Quantum Yields (ϕ) and Lifetimes (τ) for Stilbene Fatty Acid Excited Singlets in Various Media

SFA	medium	ϕ_f	ϕ_c	τ_f (ps)
S_{4A}	MCH ^a	0.08	0.48	210
	SDS ^b	0.12	0.44	260
	DPPC ^c	0.51	0.15	1400
S_{16A}	MCH	0.08	0.50	
	SDS	0.12	0.40	
	DPPC	0.44	0.15	
${}_4S_{6A}$	MCH	0.21	0.37	500
	SDS	0.39		740
	DPPC	0.92	0.01	1780

^a Methylcyclohexane. ^b Sodium dodecyl sulfate micelles. ^c Dipalmitoylphosphatidylcholine small unilamellar vesicles.

simple detergent micelles such as sodium dodecyl sulfate (SDS), incorporation of *trans*-stilbene or the SFAs leads to relatively little change in the stilbene photophysics; in general, there is a small increase in fluorescence lifetime and efficiency with a slight decrease in the *trans*-to-*cis* isomerization quantum yield.^{49,50} The difference between *trans*-stilbene and the SFAs (which one might expect to be incorporated in a more organized fashion) is nearly negligible, and the overall photo-physical behavior in aqueous SDS is quite similar to that in homogeneous solution (e.g., methylcyclohexane or other organic solvents), (Table I). In contrast, incorporation of the stilbenes into aqueous phospholipid solutions results in sharp increases of fluorescence and decreased isomerization, which is highly sensitive to both the temperature/phase of the bilayer and the overall structure of the stilbene-containing molecule.⁴⁹⁻⁵¹ For those stilbene fatty acid derivatives such as ${}_4S_{6A}$ and ${}_6S_{4A}$ in which the stilbene is "embedded" in the middle of a fatty acid backbone, isomerization is virtually eliminated in the low-temperature or gel phase of the bilayer.⁴⁹

The versatile reactivity of the stilbene chromophore in nonphotochemical processes also shows a sensitivity both to medium and to the site of the stilbene chromophore in functionalized amphiphiles. For example, the formation of weak "Mulliken-type" charge-transfer (CT) complexes with electron-deficient organic cations such as methyl viologen (MV^{2+}) is readily detectable in SDS micelles for *trans*-stilbene and all of the SFAs shown in Chart I; the dramatic enhancement of CT complex formation compared to that in homogeneous solution (for example, methanol or acetonitrile, Table II) is readily attributable to concentrating both reagents in the relatively small fraction of the micellar pseudophase.^{47,52-54} When the measured equilibrium constants are corrected for the local reagent concentration, there is remarkably little difference from those from reaction in homogeneous solution.⁵³ Similar results were obtained by Martens and Verhoeven in a study of complex formation between pyrene and MV^{2+} in SDS.⁵⁵ While simple micelles seem to exhibit little partitioning of the hydrophobic stilbene chromophore

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Table II. Observed and Corrected^a Equilibrium Constants (K_c , M^{-1})^b for Formation of Charge-Transfer Complexes between Stilbene Derivatives and Methyl Viologen in Solution and in Microheterogeneous Media

compound	solvent			
	SDS _{aq}		DCP _{aq}	
	CH ₃ CN	CH ₃ OH	measd	corr ^a
<i>trans</i> -stilbene	15.5		2450	13.9
S_{4A}			2150	12.2
S_{6A}	15		2440	13.8
S_{10A}			2250	12.8
${}_6S_{4A}$			1840	10.4
1,4-diphenylbutadiene		13.3		116.7
1-(4-methoxyphenyl)-1-phenyl-1,3-butadiene	20.4	112.2	3180	17.8

^a Corrected for volume of micelle or vesicle pseudophase. ^b Data from refs 47, 57, and 59.

Table III. Suppression of Amphiphilic Stilbene (S_{6A})-Methyl Viologen Charge-Transfer Complex Formation by Addition of 1-Hexanol to Aqueous SDS Micelles at 20 °C

[1-hexanol], M	K_c , M^{-1} ^a		
	0.03 M SDS		0.05 M ^b SDS measd
	measd ^b	corr ^c	
0	2520	22	1270
0.008	2080	16	1150
0.040	920	12	750
0.120	190	5	165

^a Data from ref 57. ^b Measured from fluorescence quenching. ^c Corrected for volume of the microheterogeneous pseudophase consisting of surfactant (SDS) plus alcohol.

and dicationic viologen, conversion of the micelles to microemulsion droplets or "alcohol-swollen" micelles by the addition of alcohols results in a sharp suppression of the fluorescence quenching which can be associated with a much lower equilibrium constant (Table III) for CT complex formation.^{53,56-59} Here again, the complex formed between stilbene and viologen also undergoes a blue shift in absorption maximum, suggesting that its average solubilization site is considerably less polar.

The reactivity of stilbene and the various stilbene amphiphiles with methyl viologen in detergent or phospholipid bilayers is somewhat more complex.⁵⁰ Since neutral (zwitterionic) phospholipids bind the viologen dication only relatively weakly,⁶² we used vesicles (liposomes) of dihexadecyl phosphate (DHP) or 1:1 DHP:dipalmitoylphosphatidylcholine (DPPC).^{50,53} Although it is necessary to use anionic surfactants to ensure nearly complete binding of the

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Table IV. Rates of Bromination of *trans*-Stilbene and SFAs (k_r , $M^{-1} s^{-1}$) in Homogeneous Solution and Microheterogeneous Media

compound	medium		
	ethanol:water 1:1 (v/v)	SDS ^b	DPPC ^c
<i>trans</i> -stilbene	210	5400	470
S _{4A}	490	8900	2600
S _{10A}		7300	30
4S _{6A}		4900	5
6S _{4A}	1100		11

^a Data from refs 50 and 64. ^b 0.28 M SDS in water at 25 °C. ^c DPPC vesicles prepared by probe sonication.

dicationic viologen to liposomes, a study of the binding of MV²⁺ to aqueous DHP indicates that the driving force is largely entropic, consistent with a hydrophobic effect where solvent release is more important than the more evident ion-ion attraction or ion exchange. Other studies⁶² suggest that various viologens may penetrate extensively into the hydrocarbon portion of various bilayer assemblies. In any case, the simple stilbenes, diphenylpolyenes, and stilbene fatty acids in DHP or DHP/DPPC exhibit "static" fluorescence quenching with methyl viologen and new long-wavelength transitions consistent with CT complex formation.⁵⁷ The complex equilibrium constants for nonamphiphilic stilbenes and diphenylpolyenes in the bilayer systems are only slightly lower than those for detergent micelles when corrected for the "concentrating" effect of the liposomes. However, only about one-half of the stilbene fluorescence is quenchable, consistent with the inability of the viologen to initially reach the stilbenes contained in the inner leaflet of the bilayer.⁵³ Complex formation for the SFAs with MV²⁺ in DHP or DHP/DPPC does show significantly more variation than that in SDS (Table II) but persists to an extent, perhaps surprisingly, in view of the fluorescence behavior cited above and the reactivity toward bromination discussed below. Studies with *p*-donor (hydroxy or alkoxy) or *p*-donor-*p*-acceptor stilbene or diphenylbutadiene derivatives in phospholipids or mixed DHP-phospholipid liposomes give evidence for at least two solubilization sites for these molecules, which we have suggested are most reasonably interpreted as a relatively nonpolar bilayer-incorporated (intercalated) site and a more polar interfacial or nonintercalated site.^{50,59,63}

In a companion study to the investigation of stilbene-viologen CT complex formation, we have examined the bimolecular bromination of *trans*-stilbene and the SFAs in detergent micelles and liposomes.^{60,64} While bromine is very soluble in both aqueous and organic solutions, the electrophilic addition of bromine to alkenes requires considerable charge separation in the rate-determining transition state, and thus bromination rates should be highly sensitive to medium polarity. Bromination of the stilbene series in aqueous SDS is very rapid (Table IV) and most sensitive to the degree of alkyl substitution on the stilbene chromophore; no differences in rate can be observed that could be attributed to rate retardation on this reaction time scale by reaction occurring in a nonpolar site. In contrast, for the liposome-incorporated stilbenes there is a wide variation of reactivity observed for both DHP and DPPC that runs quite

counter to that observed in homogeneous solution or detergent micelles and that gives a clear indication of lowered reactivity for the stilbenes the "deeper" or more tightly it is incorporated into the hydrocarbon interior of the bilayer leaflet of the liposome.^{50,64} The lowest reactivity is exhibited by those stilbene fatty acids (S_{10A}, 6S_{4A}, and 4S_{6A}) which are indicated by the fluorescence studies to be embedded deep in the hydrophobic interior of the vesicle wall.

In summary, our studies with *trans*-stilbene derivatives in detergent micelles indicate a relatively polar, disordered solvent environment for all of the compounds examined regardless of whether they are amphiphilic, apolar, or substituted with polar substituents. In contrast, incorporation of the stilbene into different types of molecules results in solubilization in quite different sites for more organized structures such as phospholipid and detergent bilayers or liposomes.⁶⁵⁻⁶⁷ For the amphiphilic SFAs, in particular, the stilbene chromophore can occupy a site which is simultaneously quite rigid and reasonably nonpolar. Organization similar to that "enforced" by the bilayer host at a polar-apolar interface has also been observed by substituted stilbene amphiphiles such as stilbazolium salts and related compounds in other microheterogeneous media such as Aerosol OT reversed micelles;⁶⁸⁻⁷¹ in this case, the combination of high effective local concentration combined with enforced orientation leads to stereochemical control of cyclodimerization very similar to that observed in the crystal⁷² and in other functionalized layered systems.²²

Stilbene Fatty Acids in Langmuir-Blodgett Films and Supported Multilayers

The initial goal in preparing the SFAs was to obtain a functionalized molecule relatively similar in length, shape, and surfactant properties to a saturated fatty acid that could easily be incorporated into Langmuir-Blodgett (LB) films and supported multilayers both pure and in mixtures with a saturated fatty acid such as archidate (C₂₀, AA) host.⁴⁶ In fact, the water-insoluble *trans* isomers of the various SFAs give excellent pressure-area isotherms (Figure 2) either pure or in SFA-AA mixtures that resemble quite closely those for simple fatty acids of comparable length both in compression behavior and in the limiting area per molecule for the maximally compressed films.^{73,74} Ellipsometry and other physical measurements of the transferred layers indicate similar quality and thickness of supported multilayers made by sequential transfer

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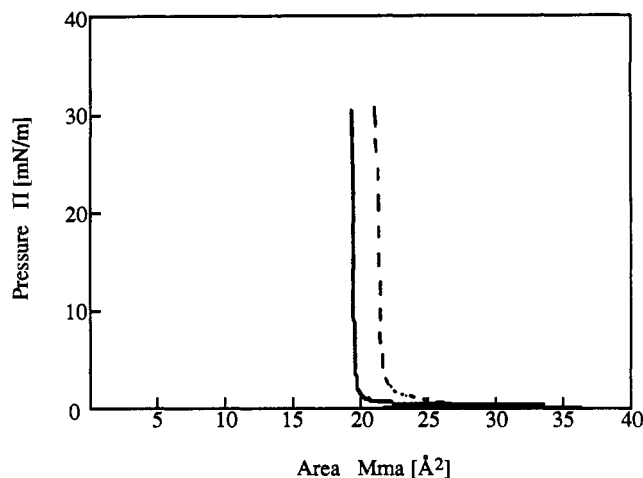


Figure 2. Compression isotherms of films of AA (—) and $6S_{4A}$ (---) at the air-water interface.

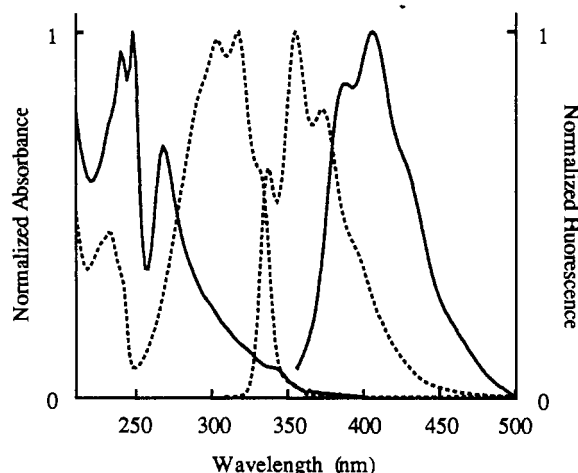


Figure 3. Comparison of absorption and fluorescence spectra for cyclohexane solution (---) and multilayers of the SFA $4S_{8A}$ (—).

of the films to rigid quartz or glass supports.⁷⁵ Thus, the SFAs can be readily incorporated into supported multilayers; in contrast, the *cis* isomers of the SFAs give much expanded isotherms and do not form sufficiently stable compressed films to permit their transfer to rigid supports.^{46,74}

While the pressure–area isotherms of the SFAs are “normal”, the absorption and fluorescence of the SFAs in spread compressed films and supported multilayers are quite different from the monomer absorption and fluorescence observed in organic solution or in the detergent micelles or liposomes described above (Figure 3).⁷⁴ That the altered spectra result from a physical rather than a chemical change is made clear by the finding that quantitative recovery of the SFA occurs simply by extracting it from the supported multilayer by an organic solvent.⁷³ The spectroscopic behavior observed (blue shift in the intense absorption, red shift in fluorescence, and long fluorescent lifetime) can be attributed to an “H” aggregation, which is reasonable to expect from an anticipated “card-pack” orientation of the stilbene chromophores in the compressed monolayer film or supported multilayer.^{76,77} Aspects of the type of aggregate expected for different possible relative

(75) Hsu, Y.; Penner, T. L.; Whitten, D. G. *J. Phys. Chem.* **1992**, *96*, 2790.

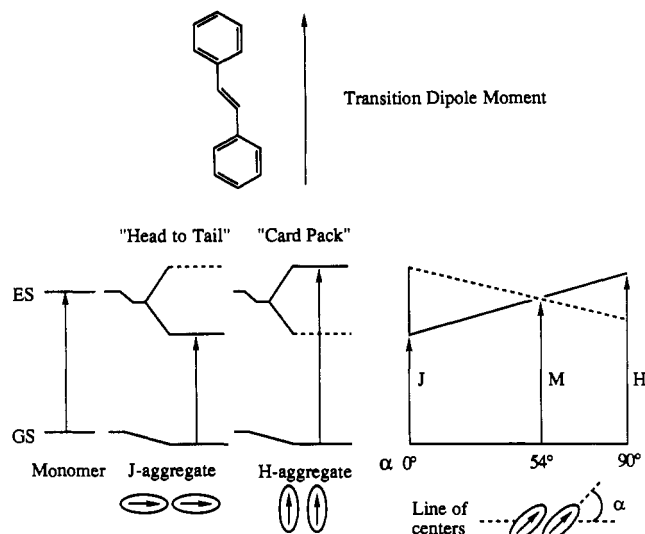


Figure 4. Schematic representations of possible aggregates formed by self-association of *trans*-stilbene or SFAs.

orientations of SFAs are outlined in Figure 4. The H aggregate excitonic splitting gives a high-energy allowed transition and a low-energy forbidden band. Absorption is dominated by the high-energy band, but the long-lived fluorescence occurs from the low-energy band and is thus strongly red-shifted. Typical calculations suggest that limiting aggregation of this sort occurs with a relatively low number (6–20) of monomers preaggregate.^{74,79} The H aggregate (as followed by absorption and fluorescence) is the only detectable species in supported monolayers or multilayers of pure SFA or mixtures of a single SFA diluted with a saturated fatty acid such as AA to as low as 1:10. At the lowest practical dilutions (1:20) for spectroscopic and photophysical studies (1:20), small changes are observed (*vide infra*) but the spectra are still dominated by the H aggregate and little or no monomer intermediate can be detected.^{74,80}

Similar aggregation behavior as indicated by absorption and fluorescence is observed for supported mono- and multilayers of several other surfactant α,ω -diphenylpolyenes and modified stilbenes (Figures 5 and 6). However, for the butadiene ($4B_{4A}$) and hexatriene ($4H_{4A}$) surfactants, the aggregate spectrum is replaced by spectra similar to that for the monomer in solution as the functionalized surfactant is diluted 1:20 with AA.^{79,80} Evidently, here, the tendency to form aggregate is somewhat lower than for the corresponding SFAs. It is also noteworthy that the various substituted surfactant stilbenes show remarkably similar aggregate absorption spectra to those of the SFAs. This is true even for amphiphilic stilbenes substituted with strong donor and acceptor groups (for example, $8OS_{1A}$), which have solution monomer spectra quite different from those of the SFAs.⁸⁰ Moreover, the aggregate fluorescence spectra for different stilbene amphiphiles show considerable variation in both the degree of structure and emission maximum.

(76) Studies on the compressed films of SFAs at the air–water interface show absorption⁷⁷ and fluorescence⁷⁸ essentially identical to that observed in the supported multilayer.

(77) Möbius, D., unpublished result.

(78) Patterson, L., unpublished result.

(79) Spooner, S. P.; Whitten, D. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **1991**, 1436, 82.

(80) Spooner, S. P., unpublished results.

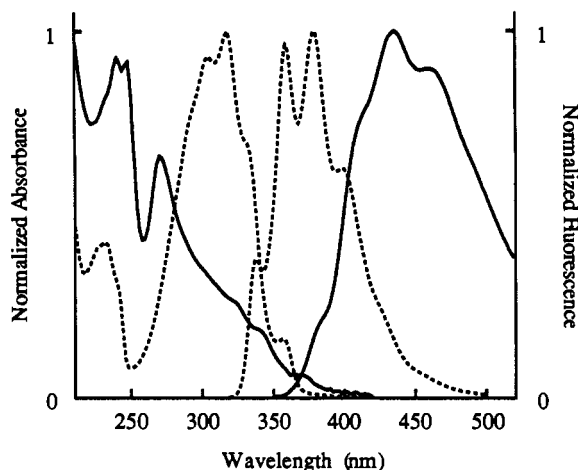


Figure 5. Normalized absorbance and fluorescence spectra of $4B_{AA}$ in cyclohexane (---) and supported multilayers (—) of composition 1:1 $4B_{AA}$:AA.

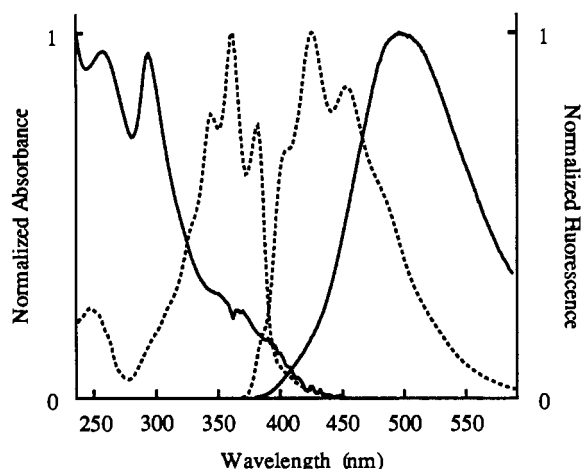


Figure 6. Normalized absorbance and fluorescence spectra of $4H_{AA}$ in cyclohexane (---) and supported multilayers (—) of composition 1:1 $4H_{AA}$:AA.

Irradiation of the SFAs or diphenylpolyene aggregates in multilayers either pure or in mixtures with AA leads to very little photochemical reaction other than a very slow bleaching on prolonged irradiation to produce unidentified products.^{73,74} The aggregate fluorescence can be readily quenched, however, by the incorporation of energy or electron acceptors to the assemblies. Quenching of the stilbene aggregate fluorescence by the thiocyanine dye (T_{218}) was found to occur over relatively long distances (over several layers), as would be anticipated by the excellent overlap between donor (stilbene aggregate) fluorescence and acceptor (cyanine) absorption; a critical or one-half quenching distance of 80–90 Å was observed, in good agreement with that calculated by a Förster-resonance model and with critical distances observed for other donor-acceptor pairs with similar photophysical matches.^{81,82} However, while appreciate quenching of SFA aggregate fluorescence is observed over relatively long donor-acceptor separation distances, there is little or no “antenna effect”, which could arise from interlayer transfer of

(81) Mooney, W. F.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5712.

(82) Kuhn, H.; Bücher, H.; Mann, B.; Möbius, D.; Szentpaly, L. V.; Tillmann, P. *Photogr. Sci. Eng.* **1967**, *11*, 233. Kuhn, H. *J. Chem. Phys.* **1970**, *53*, 101. Kuhn, H.; Möbius, D.; Bücher, H. In *Physical Methods in Chemistry*; Weissburger, A., Rossiter, B., Eds.; Wiley: New York, 1972; Vol. 1, Part IIIb.

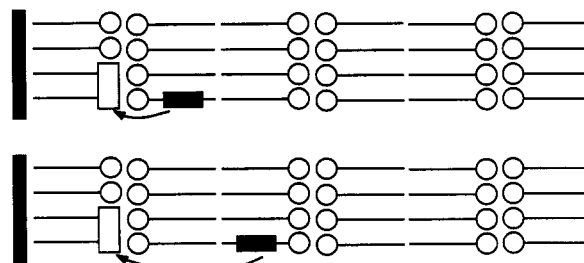


Figure 7. Schematic representation of quenching of SFA fluorescence by V_{218} or Co_{218} in SFA multilayer assemblies. Top, 5–80% quenching of stilbene fluorescence by viologen or cobalt complex, depending upon the quencher and stilbene position. Bottom, no quenching of stilbene fluorescence by viologen or cobalt.

excitation when multiple layers of SFA aggregate are contacted with a single monolayer of the energy-accepting cyanine.⁸¹ The lack of an antenna effect is not surprising since the weak oscillator strength of H-aggregated SFA and poor fluorescence-absorption overlap are expected to result in inefficient transfer of energy between SFA aggregates, even when they are in adjacent monolayers.⁸³

The SFA aggregates can also be quenched by electron acceptors such as the surfactant viologen (V_{218}) or the four cobalt complexes ($8S_{1A}Co^{2+}$), (Co_{218}^{3+}), (Co_{18}^{2+}), and (Co_{16}^{2+}) when these quenchers are incorporated into the same or adjacent layers (hydrophilic-hydrophilic contact) layers,^{80,81} as diagrammed in Figure 7. There is considerable excited-state quenching when an electron acceptor is in assemblies with separation between the SFA and acceptor estimated to be on the order of 10–19 Å.⁸¹ The relatively long-range quenching of SFA fluorescence by electron acceptors is consistent with several other investigations of LB assemblies containing different substrate-quencher combinations but also leading to what is evidently long-range electron-transfer quenching with a very slow attenuation in quenching with increase in substrate-quencher separation.^{75,80,81,84–87} No quenching is observed when a fatty acid spacer separates the layer containing the SFA and that containing the acceptor. Moreover, when the quenching of a SFA aggregate bilayer is compared to that of a monolayer, the quenching can all be attributed to the interaction of excited SFAs in the leaflet adjacent to the quencher, again demonstrating the lack of a SFA-SFA aggregate antenna effect. One exception to this is the quenching of SFA aggregate fluorescence by $8S_{1A}Co^{2+}$, which evidently occurs over much longer distances and therefore probably results from energy-transfer quenching.⁸⁰ The lack of fluorescence from this compound both in solution and in supported multilayers is attributed to an intramolecular stilbene-cobalt³⁺ electron transfer which leads to rapid reaction in solution^{88,89} but to no detectable decomposition in the supported multilayers.⁷⁹

(83) Intralayer migration of energy via the exciton appears to be efficient.

(84) Kuhn, H. *J. Photochem.* **1979**, *10*, 111.

(85) Möbius, D. *Ber. Bunsen. Ges. Phys. Chem.* **1978**, *82*, 848.

(86) Miyashita, T.; Hasegawa, Y.; Matsuda, M. *J. Phys. Chem.* **1991**, *95*, 9403.

(87) Spooner, S. P.; Whitten, D. G. In *Photochemistry in Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 691.

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

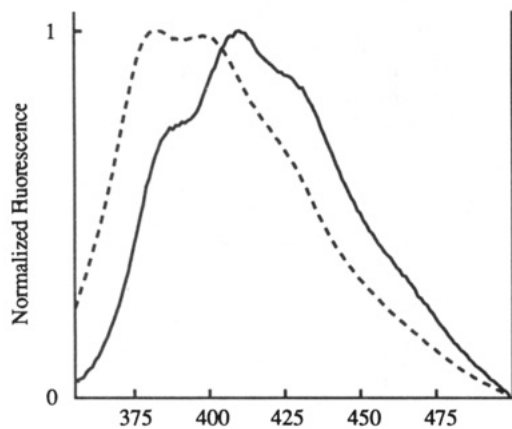


Figure 8. Comparison of fluorescence of a single SFA:AA multilayer (—) with that of the four-component mixture (---).

Photophysics of Mixed Stilbene Monolayers

The finding that Langmuir–Blodgett assemblies formed from a single SFA or surfactant α,ω -diphenylpolyene exhibit H aggregate behavior even though the same molecules show no tendency to aggregate in organic solvents suggested initially that the H aggregate formation occurring in the monolayers during their formation at the air–water interface was largely driven by a “packing phenomenon”.⁷⁴ As the diagram in Figure 4 suggests, varying the position of the stilbene chromophore in a SFA should lead to the possible formation of mixed aggregates which might, depending upon the relative orientations of the different monomers with respect to each other, lead to aggregates having properties ranging from J, through no net interaction, to H aggregation.^{74,80} We have investigated the photophysical properties of a number of mixtures of the SFAs and found that the mixtures show rather complex behavior at least to some extent inconsistent with a wide range of aggregate properties. First, it is observed that mixtures of different SFAs (for example, two different compositions which have been studied extensively are a six-component mixture consisting of S_{16A} , S_{12A} , S_{10A} , S_{6A} , S_{4A} , S_{2A} , and AA (1:1:1:1:5) and a four-component mixture consisting of S_{12A} , S_{6A} , S_{4A} , and AA (1:1:1:3)) show absorption and fluorescence remarkably similar (but with slight differences!) to those of the individual SFAs at the same “concentrations”.^{79–81} The isotherms are also quite similar for these mixtures and for single SFA–AA mixtures (although the initial increase in pressure or “lift-off” occurs at slightly larger areas per molecule for the mixture compared to a simple SFA–AA binary mixture). Although fluorescence decay is multiexponential (as it is for simple SFA multilayers) for these mixtures, it is dominated by a long-lived component with a lifetime similar to those measured for the single SFAs. The small differences in absorption (dominated by the H aggregate peak at 273 nm) and fluorescence (Figure 8) can be attributed (*vide infra*) to a reduction in size (perhaps to include a large population of H dimer) as the individual SFAs are “diluted”.

Although only small differences in the absorption and emission spectra of SFAs in mixtures are observed, the behaviors of assemblies containing the electron acceptors V_{218} , Co_{16}^{2+} , and $S_{1A}Co^{2+}$ are remarkably different from those of assemblies made from a single

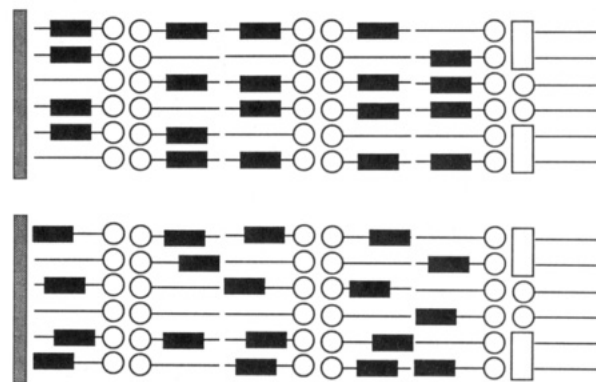


Figure 9. Schematic comparison of quenching of a five-layer assembly of a single SFA:AA ($6S_{4A}$) with that for a five-layer assembly of the four-component mixture. Top, as compared to a slide containing five layers of $6S_{4A}$, the addition of a layer of V_{218} results in a 5% reduction in the fluorescence intensity. Bottom, as compared to a slide containing five layers of the four-component mixture, the addition of a layer of V_{218} results in a 41% reduction in the fluorescence intensity.

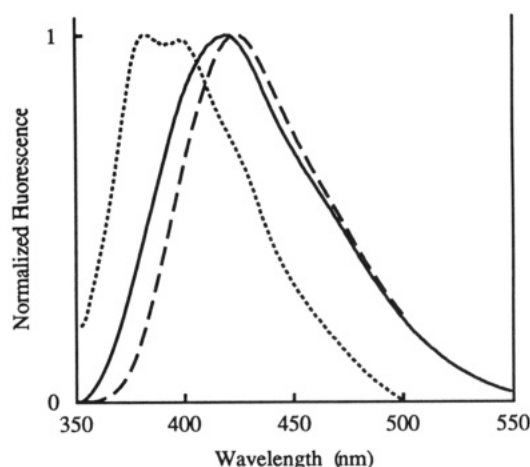


Figure 10. Fluorescence comparison of multilayers of four-component mixture (---), four-component mixture plus $8S_{1A}$ (···), and multilayers of $8S_{1A}$ alone (—).

SFA and the same quencher.⁸¹ As shown in Figure 9, there is considerable quenching of excitation delivered to multilayers of the mixed SFAs by a single layer of any of these quenchers. The observation of quenching of more than one-half of the fluorescence of assemblies containing five or more layers of the stilbenes demonstrates that the mixed layers provide a strong antenna effect or, in other words, that excitation energy can migrate effectively through the layers containing the SFA mixtures, in contrast to the behavior described above for layers of a single SFA.

In contrast to the behavior of mixtures of simple SFAs, the inclusion of surfactants such as $4H_{4A}$ or $8S_{1A}$, which have lower energy emitting aggregate states, into mixtures of SFAs leads to absorption spectra similar to those of the SFA mixtures but predominantly to emission characteristic of the aggregate observed for $4H_{4A}$ or $8S_{1A}$ alone (Figure 10).⁸⁰ This suggests both that “uninterrupted” H aggregates of these species are formed, even in the mixtures, and that intralayer migration to populate these aggregates occurs readily. Interestingly, for the SFA mixture– $8S_{1A}$ –AA system, we observe that quenching by an added layer of electron acceptor is considerably attenuated. Thus, for these assemblies, “trapping” or localization of excitation in

the H aggregate of ${}_8S_{1A}$ evidently hinders the flow of energy through the supramolecular multilayer.

Although several facets of the "architecture" and properties of the LB films at the air-water interface and supported multilayers constructed from these complex mixtures of functionalized surfactants are still under investigation, it is possible to make some key observations. The predominance of H aggregate absorption and fluorescence for a wide variety of SFA mixtures suggests that H aggregation is not simply controlled by packing and molecular shape but rather that the H aggregate (or at least an H dimer) is a relatively stable species whose formation is an example of apolar association which is, perhaps, closely analogous to formation of highly structured host-guest complexes between organic molecules in aqueous solutions.^{14,24-28} Although formation of the H aggregate is probably governed by solvation-desolvation processes and can thus be regarded as an example of the "hydrophobic effect",⁹ it seems quite clear that for the *trans*-stilbene chromophore the H aggregate represents an enthalpy minimum and hence dominates the isolation of "free" monomer or any other aggregate such as a J structure. The fact that ${}_4H_{4A}$ and ${}_4B_{4A}$ can be much more easily diluted to monomer suggests that the driving force for aggregate formation with these molecules may be considerably smaller. Returning finally to the layers of SFA mixtures, a major question remains as to whether the detected H aggregates consist mostly of patches of a single SFA aggregate or of mixed aggregates in which chromophore-chromophore attraction dominates packing based on overall amphiphile length and shape.¹⁴ In either case, it might be reasonable to expect the resulting assembly to provide much more close contact between adjacent layers in a multilayer assembly and thus enhance energy migration. A further reason for the enhanced migration of energy in the SFA mixture multilayers may well be the presence of trace monomer and smaller (likely dimer) aggregates resulting from an effective dilution. The fluorescence spectrum of the four-component mixture (1:1:1:7) shown in Figure 8 is

(90) Geiger, C.; Richard, W. G.; Furman, I.; Whitten, D. G., unpublished result.

very similar to that of a single SFA (${}_6S_{4A}$) diluted to the same extent (1:9) with only AA. However, the blue-shifted fluorescence shows virtually no emission where monomer fluorescence occurs, and subtraction of pure H aggregate fluorescence from the total emission reveals a structured fluorescence intermediate between monomer and pure H aggregate. Interestingly, this is very similar to the fluorescence observed for a bis-SFA phospholipid dispersed in DPPC vesicles which is expected to give predominantly, if not exclusively, an H dimer.⁹⁰ The intermediacy of this species in energy between monomer and the extended H aggregate may also play a role in providing an antenna effect, assisting energy migration in the mixed multilayers.

We are currently investigating examples and aspects of apolar association with surfactant stilbenes, other functionalized amphiphiles, and more complex "building blocks". The emerging evidence that apolar association can be an important organizational force in the formation and microstructure of organized assemblies suggests a rich array of possibilities for tailoring properties and reactivities within these media as well as in other materials. The more organized yet fluid assemblies such as bilayer vesicles offer particularly exciting prospects for obtaining new supramolecular structures; for example, bilayer vesicles of the pure bis-SFA phospholipid mentioned above can be constructed in which each liposome is effectively a single extended aggregate of relatively well-defined size and structure. Membranes, polymers, interfaces, and other materials with this type of well-defined nanostructure can be anticipated to offer novel reactivity and potential utility in a number of applications ranging from vectorial charge transfer to novel photophysical and thermal properties.

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