

Energy- and Electron-Transfer Quenching of Surfactant *trans*-Stilbenes in Supported Multilayers: The Use of Hydrophobic Substrate Chromophores To Determine Short-Range Distance Dependence in Assemblies¹

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Abstract: A study of energy and electron transfer of H-aggregated surfactant *trans*-stilbenes in supported multilayer assemblies is reported. The fluorescent state of the stilbenes is quenched over moderately long (80–90 Å) distances by a surfactant thiocyanine dye concurrent with sensitization of the thiocyanine fluorescence. Although relatively long-range donor → acceptor excitation energy transfer occurs, the stilbene aggregates do not transfer excitation efficiently among themselves; consequently, there is little evidence for an antenna effect in assemblies containing multiple layers of the stilbene. For assemblies containing the stilbenes together with a surfactant cobalt(III) complex or viologen, quenching of the stilbene fluorescence is also observed. In these cases the quenching occurs over much shorter distances, and no new emission or net photochemical changes can be detected. For the viologen it appears electron-transfer quenching is dominant; for the cobalt complexes the quenching observed could be ascribed either to electron transfer or to energy transfer. Electron-transfer distances and rates estimated from these studies appear consistent with results from recent investigations with quite different systems.

The study of photochemical and photophysical phenomena in organized assemblies is an area of considerable activity. On one hand, the use of a truly organized medium offers the possibility for examining a molecular process in a controlled environment; thus in principle a phenomenon such as electron transfer or energy can be studied under conditions where such key parameters as distance, orientation, and medium properties are known and/or can be regulated. On the other hand, the possibility for building a macrostructure from regulatable microscopic units suggests a capability for molecular engineering in which processes such as photosynthesis can be mimicked by using reasonably simple components. Many approaches have been used to construct and study "photoreactive" organized assemblies; indeed the assemblies used have been themselves of a wide variety ranging from surfactant assemblies such as micelles, vesicles, and polymerized surfactants, derivatized electrodes or colloidal particles, polymer beads and coated polymers to inclusion complexes, and various types of thin films on different supports.

Investigations of the distance dependence of electron transfer have recently focused on the mechanisms and rate of transfer occurring over distances greater than collisional.^{3–35} A number

of recent studies have presented evidence that tunneling can occur over edge–edge spacings as great as tens of angstroms in fairly short times. However, the wide variation of rate–distance values observed for different systems has prevented until now the development of a comprehensive and unified picture of this process. Thus while some studies suggest that moderately exothermic transfer through rigid glasses occurs over a distance of 15 Å in 10^{–8} s,²⁹ other investigations suggest that exothermic transfer over similar distances can be much slower ($k \sim \text{s}^{-1}$).³³

In contrast the requirements for efficient transfer of excitation from an excited donor to an acceptor have been fairly well-defined both theoretically and experimentally. The theory of Förster³⁶ has been tested by numerous experiments, and long-range energy transfer can be regarded as a reasonably well-understood phenomenon. Some of the most elegant demonstrations of long-range energy transfer and tests of the theory have come from studies of Kuhn and co-workers using surfactant dyes in supported multilayers.^{37–39} The construction of these assemblies using

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surfactants in which a cyanine dye constitutes the hydrophilic head group as substrates and energy acceptors is easily carried out by successive transfer of spread films from the air-water interface to a rigid support. The incremental spacing provided by the length of an extended fatty acid (25–28 Å) provides a convenient ruler for determining distance-dependence in the 50–150 Å range. Although some studies have suggested that electron transfer can occur across a monolayer or bilayer with reasonable rates,^{6,7,15–20,40} other investigations suggest that rates over such distances may be extremely slow such that alternate mechanisms to direct electron transfer may account for observed phenomena in some cases.⁴¹

The use of multilayer assemblies to investigate electron transfer as well as energy transfer offers a number of potential advantages. However, for this it would be desirable to have surfactant substrates in which the distance between donor and acceptor could be varied over a range shorter than the span of an extended fatty acid. One way of accomplishing this would be to construct surfactants in which a reactive chromophore is contained in the hydrophobic portion of a surfactant as a substitute for a polymethylene portion of the hydrocarbon chain. Although several attempts have been made to prepare such functionalized surfactants, only a few cases have been demonstrated where the surfactants are oriented in the hydrocarbon portion of monolayer films and multilayer assemblies and away from the interface region.^{21,42}

We have recently described the synthesis and monolayer-forming properties of a series of *trans*-stilbene carboxylic acid derivatives, MSNA, which include the *trans*-stilbene chromophore at the end of a fatty acid chain (S10A, S12A) or as an intrachain unit (4S6A).⁴³ These surfactant stilbenes exhibit solution photochemistry much like their nonsurfactant counterparts;⁴⁴ they also exhibit behavior in monolayer films at the air-water interface very similar to that of fatty acids having a comparable chain length.⁴³ Studies of films and supported multilayers prepared from mixtures of surfactant stilbenes and fatty acids such as arachidate (C20) indicate that the stilbene residues in the hydrophobic portion of the films and assemblies. Interestingly, it is found that the stilbenes incorporated into these assemblies do not exhibit the photophysical behavior anticipated for a monomeric chromophore but rather show an excitonic excited state which can best be described as an "H" aggregate.⁴³ Calculations suggest that the "H" aggregate consists of several monomers associated in a regular "card-pack" array; characteristics of the aggregate include a long wavelength structure fluorescence with a relatively long (ca. 4–5 ns) fluorescent lifetime.⁴³

In the present paper we report a study of electron-transfer and energy-transfer quenching in multilayer assemblies using excited singlet states of the stilbene aggregates as donors in each case. The studies have employed three different surfactant stilbenes (4S6A, S10A, and S12A) which should have the hydrophobic stilbene chromophore at different depths in the monolayer. These have been studied in conjunction with several potential quenchers incorporated in the hydrophilic portion of a surfactant. By constructing assemblies containing the stilbene in one layer and the hydrophilic quencher in adjacent or separated layers it is possible to study the two processes over a wide range of distances not easily accessible with previously used substrate-quencher combinations. The studies presented have yielded several interesting results. Investigations of energy transfer show that despite aggregation and "unusual" orientation the stilbenes are efficient donors of singlet excitation over reasonably long (80–90 Å) distances.

Electron-transfer quenching of the stilbene aggregate excited states can also be demonstrated; while much shorter distances are observed in this case, the rate and range for the transfer appears closely consistent with recent studies employing rigid hydrocarbon spacers. Most importantly, the dependence of both energy transfer and electron transfer with location of the stilbene chromophore in the amphiphile structure supports the assignment of orientation of the chromophore within a single monolayer as predicted on the basis of the extended molecular configuration.

Experimental Section

Materials. The surfactant stilbenes were prepared and purified by methods previously described.⁴³ Arachidic and palmitic acids were used as received from Analabs, Inc. and kept under refrigeration. Chloroform (Fisher Certified) for the spreading of monolayers was used as received. Water for monolayer work was triply distilled (once from alkaline permanganate and once from sulfuric acid) as previously described.^{39,43} The surfactant thiocyanine dye (T218) was a gift of Dr. D. Möbius and used as received.

Synthesis of Surfactant Cobalt Complexes. *trans*-Dibromobis(ethylenediamine)cobalt(III) bromide was prepared according to published methods⁴⁵ with the following modifications: the starting material was (carbonato)bis(ethylenediamine)cobalt(III) bromide; concentrated (9 M) hydrobromic acid and hydrogen bromide gas were used in place of the corresponding hydrogen chloride reagents; after isolating the dull green colored product from the mother liquor the first time, the solid was redissolved in 9 M HBr, and the solution was resaturated with HBr gas, closed, and left standing for 3–4 days at room temperature in the dark; after suction filtration of this second reaction mixture, the bright green solid was washed with aqueous HBr and absolute ethanol, then taken up in 95% methanol (giving a mostly clear, bright green solution), filtered again, and recovered from the methanol by rotary evaporation: yield 80%. Anal. Calcd for $\text{CoC}_4\text{H}_{16}\text{N}_4\text{Br}_3$: C, 11.47; H, 3.83; N, 13.38; Br, 57.24. Found: C, 11.36; H, 3.82; N, 12.90; Br, 54.86.

***cis*-Bromo(1-octadecylamine)bis(ethylenediamine)cobalt(III) Bromide (Co18).** Into a 200-mL, round-bottom flask with stir bar was weighed 2.10 g (5.0 mmol) of *trans*-dibromobis(ethylenediamine)cobalt(III) bromide. About 80 mL of dimethylsulfoxide was added, and the clear green mixture was heated to 60 °C with stirring over 20–30 min. (During this time the solvation of one bromide ligand per complex can be discerned by the solution color change from green to purple via brown.)^{46,47} Then 1.35 g (5.0 mmol) of 1-octadecylamine was added all at once, the flask was capped with a septum, and heating and stirring were continued in reduced light for 48 h.

The clear, deep purple-red reaction mixture was cooled to room temperature and filtered by suction to remove any undissolved, uncomplexed amine or dioctadecylamine complex (see below). A 160-mL volume of triply distilled water was then added with stirring, causing an opaque, pink-purple suspension to form. After 10 min of stirring, the mixture was filtered by suction. The purple, noncrystalline solid was washed twice with 10-mL portions of water.

The crude product was transferred to a 100-mL beaker, about 50 mL of reagent acetone was added, and the mixture was stirred briskly for 10 min, after which the acetone was decanted and discarded. The process was repeated. The same procedure was then performed by using chloroform. This sequence removes virtually all bulk water and unreacted starting materials. The red-violet product was then filtered by suction, air dried, and dried in a desiccator: yield 57%. The complex is soluble in dry Me_2SO and DMF, slightly soluble in methanol, and insoluble in water and nonpolar organic solvents. Two bands (instead of one) in the 870–900- cm^{-1} region of the infrared spectrum identified this as the *cis* isomer.⁴⁸ The proton NMR spectrum corroborated the presence of the alkyl tail and the *cis* stereochemistry.^{49–51} The UV-vis spectrum strongly resembles that of bromopentaminecobalt(III) bromide: ¹H NMR ($\text{Me}_2\text{SO}-d_6$) 5.5 ppm (m, 4 H), 4.5 ppm (m, 4 H), 2.6 ppm (m, 12 H), 1.6 ppm (s, 2 H), 1.25 ppm (s, 30 H), 0.9 ppm (m, 3 H). Anal. Calcd for $\text{CoC}_{22}\text{H}_{55}\text{N}_5\text{Br}_3$: C, 38.38; H, 8.07; N, 10.17; Br, 34.82. Found: C, 38.29; H, 7.81; N, 9.37; Br, 32.35.

***cis*-Bis(1-octadecylamine)bis(ethylenediamine)cobalt(III) Bromide (Co218).** This complex is synthesized analogously to Co18 with the following modifications: (1) 3 equiv of 1-octadecylamine are added

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Table I. Spreading Solvents and Conditions for Surfactants Used in This Study

surfactant	spreading solvent	conditions ^a
stilbenes (MSNA)	CHCl ₃	forms good film pure for ($m + n$) ≥ 10 ; all can be layered with 1:1 arachidate:stilbene or greater
Co18	dimethyl sulfoxide:CHCl ₃ 1:1 (v/v)	forms poor films pure; requires a 2-3 mol excess of cosurfactant
Co218	dimethylsulfoxide:CHCl ₃ 1:11 (v/v)	can be spread pure; anionic cosurfactant added in excess improves film and transfer
V218	CH ₃ OH:CHCl ₃ 1:150 (v/v)	gives broad isotherms with 1:5 V218:arachidate but coats well
T218	CHCl ₃	always coated with large excess of arachidate

^a Subphase 3 $\times 10^{-4}$ M Cd²⁺ and 5 $\times 10^{-5}$ M HCO₃⁻ in triply distilled water.

instead of 1, (2) the volume of solvent is increased by about 50%, (3) the reaction time can be decreased to 24 h, and (4) the orange, noncrystalline product may be purified by a Soxhlet extraction with methanol for 4-6 h if contamination by the pinkish purple C18 is suspected: yield about 60%. The complex has solubility properties analogous to those of C18, except that its solutions tend to be more gelatinous. Anal. Calcd for CoC₄₀H₉₄N₆Br₃: C, 50.15; H, 9.89; N, 8.77; Br, 25.03. Found: C, 50.96; H, 10.55; N, 8.72; Br, 22.70.

N,N'-Dioctadecyl-4,4'-bipyridinium *p*-Bromobenzenesulfonate Monohydrate (V218) (Dioctadecyl Viologen). 4,4'-Bipyridine (0.25 g, 1.3 mmol), (1-octadecyl)-4-bromobenzenesulfonate (2.00 g, 4.0 mmol), and 30 mL of acetonitrile were combined in a 50-mL, round-bottom flask equipped with a reflux condenser, stirring bar, and drying tube. The mixture was heated to reflux with stirring, and a gentle reflux was maintained for at least 10 h. During this time the initially clear and colorless solution became cloudy, and a white solid precipitated. The still warm reaction mixture was mixed with 100 mL of chloroform and filtered by suction. The solid was collected, stirred with 50 mL of fresh chloroform for 30 min, and recollected. The product was recrystallized from 2-propanol to give large, shiny white plates: yield about 35%; mp 220-222 °C dec. The product was slightly soluble in 2-propanol (and to a lesser extent in ethanol and methanol), very slightly soluble (ca. 10⁻⁴ M) in CHCl₃, and insoluble in water and most other organic solvents. The analysis is best for a monohydrate. Anal. Calcd for C₅₈H₉₂N₂O₇S₂Br₂: C, 60.39; H, 8.04; N, 2.43; Br, 13.86. Found: C, 60.46; H, 8.36; N, 2.45; Br, 14.21.

Monolayer Film and Multilayer Deposition Studies. The details of the techniques and facilities used in preparing films and assemblies have been described elsewhere.⁴³ All assemblies used in the present study of fluorescence and fluorescence quenching were supported on 12 mm \times 35 mm \times 1 mm slides of Suprasil quartz obtained from Heraeus-Amersil Inc. These slides have virtually no absorbance in the 200-700-nm region, and they give very little "background" fluorescence in the 300-500-nm region. All slides were precoated with five layers of cadmium arachidate. Table I gives the spreading solvents and conditions used for layering the various surfactants used in this study.

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 "ozone-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") radiometric procedure⁵² involving the reference channel B. A 9.5 $\times 10^{-5}$ M Rhodamine B solution in ethylene glycol was used as a quantum counter.^{52,53} 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 it afforded a satisfactory intensity along with good, convenient reproducibility of intensity. All MSNA monolayers for spectroscopic measurements contained 30 mol % of the SNA 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, by providing enough sample so that monolayer fluorescence could be easily observed, and for convenience. Spectra were very reproducible in terms of maxima and minima and good to $\pm 10\%$ 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. For studies of fluorescence quenching with the dye T218, the layers containing the dye were diluted with arachidate so that the film contains a ratio T218:cadmium arachidate = 1:20; this ratio gives nearly monomeric T218 and films having excellent transfer properties from the air-water interface to quartz supports. The studies with Co18, Co218, and V21, as quenchers employed mol fractions of the quencher ranging from 0.03 to 0.22 in mixtures with arachidate. Ultraviolet spectra were recorded on a Perkin-Elmer Model 576ST double-beam spectrophotometer. Photolyses were carried out with a Schoeffel Model LPS-255 1000-W 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.⁵⁴

Results

The structures of the substrates (MSNA) and quenchers (T218, Co18, Co218 and V218) used in this study are shown in Chart I. As described previously, the surfactant stilbenes used in this study all show a strong, structured and relatively long-lived fluorescence in multilayer assemblies that has been attributed to an exciton of an "H" aggregate.⁴³ This fluorescence in multilayers (λ_{\max} 390-400 nm) overlaps well with the absorption spectrum of the surfactant thiocyanine dye T218 (λ_{\max} 430 nm) which has been shown in previous studies by Kuhn and co-workers to be an excellent acceptor of singlet excitation in studies of long range energy transfer in multilayer assemblies.³⁷⁻³⁹ Although the excited states of the stilbene exciton should be quenched by T218 in an energy transfer step, it is clear on the basis of excited state energetics and redox potentials⁵⁵⁻⁶² that quenching of stilbene excited states by T218 by electron transfer is energetically unfavorable.

When the surfactant stilbenes are incorporated into multilayer assemblies containing low-to-moderate concentrations of the dye T218 in adjacent or nearby layers, there is a strong attenuation of the stilbene fluorescence in the range 350-420 nm concurrent with the appearance of T218 fluorescence at 450-500 nm upon activation at 330 nm (Figure 1). The intensity of stilbene fluorescence decreases and that of T218 increases monotonically as the "distance" between the chromophores is reduced (Table II). That the observed increase in thiocyanine fluorescence at 485 nm is due to energy transfer from the stilbenes and not to direct activation of T218 is indicated by the finding that irradiation of assemblies containing only T218 and arachidate with 330-nm

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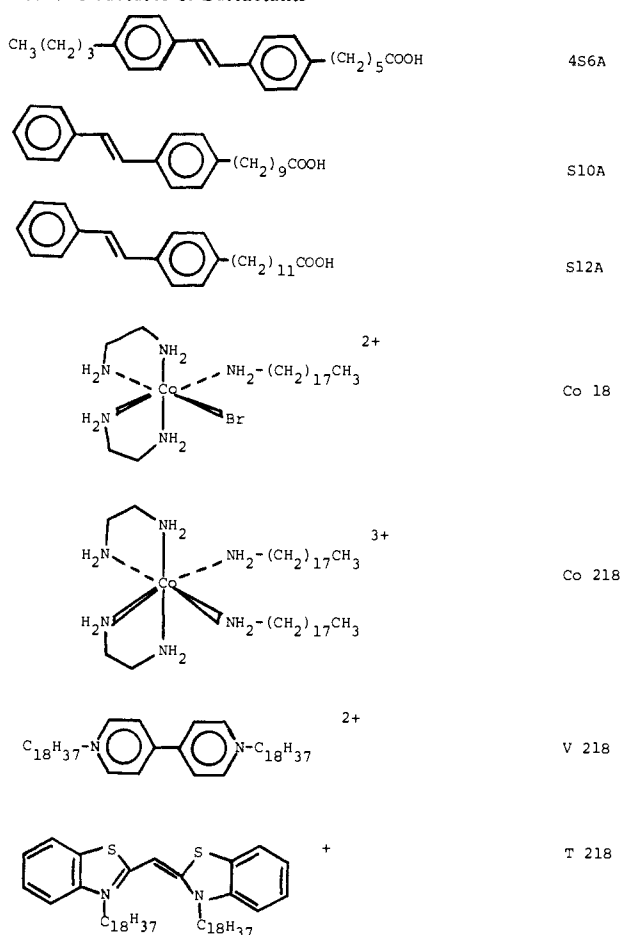
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Table II. Fluorescence of Stilbene Aggregates and Thiocyanine as a Function of Assembly Structure

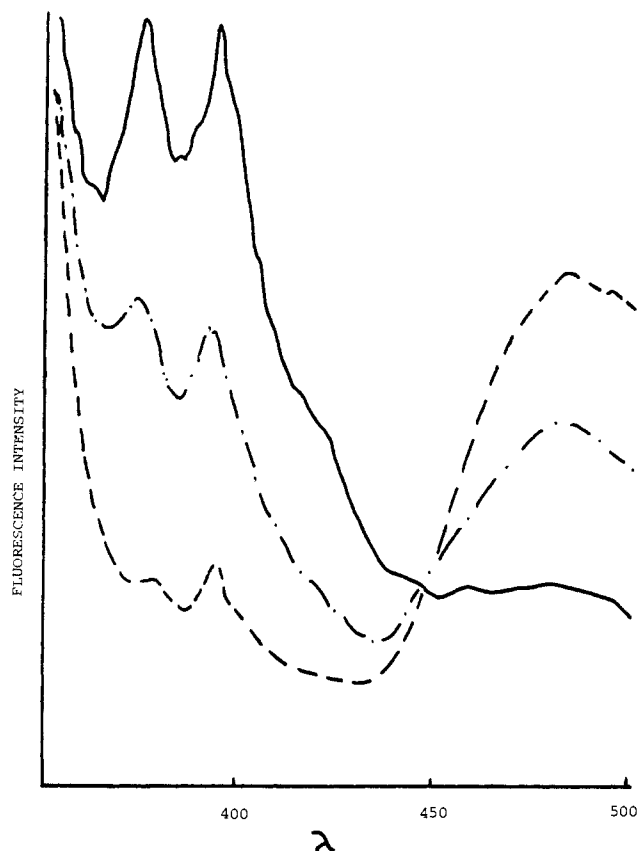
assembly ^a	stilbene	no. det	I_{395}^b	I_{395}^{rel}	I_{485}^b	I_{485}^{rel}
=T O—S ^c	456A	5	0.3 ± 0.3	0.02	12.7 ± 2.0	1.0
=T O—S—O O—	456A	5	0.8 ± 0.7	0.06	12.3 ± 3.5	0.96
=T O—O O—S	456A	3	6.1 ± 0.6	0.48	11.5 ± 1.0	0.89
=T O—O O—S—O O—	456A	2	6.7 ± 1.1	0.52	6.5 ± 0.9	0.45
=T O—O O—O O—S	456A	3	12.5 ± 5.0	0.98	3.8 ± 1.2	0.29
=T O—O O—O O—S—O O—	456A	3	15.7 ± 8.5	1.23	3.3 ± 0.8	0.16
—O O—S	456A	3	12.8 ± 0.5	1.00	1.5 ± 0.3	0.0
=T O—S	S10A	3	0.9 ± 0.6	0.06	8.7 ± 0.6	1.0
=T O—S—O O—	S10A	6	2.0 ± 0.8	0.13	8.3 ± 1.2	0.95
=T O—O O—S	S10A	12	7.2 ± 1.3	0.46	9.9 ± 1.1	1.16
=T O—O O—S—O O—	S10A	4	9.1 ± 1.0	0.58	6.2 ± 0.5	0.68
=T O—O O—O O—S	S10A	3	15.4 ± 1.4	0.99	4.2 ± 0.5	0.42
=T O—O O—O O—S—O O—	S10A	2	14.0 ± 0.6	0.90	3.2 ± 0.05	0.29
=T O—O O—O O—O O—S	S10A	1	15.8	1.01	2.0	0.13
S—O O—	S10A	15.6 ± 0.1	1.00	1.0	0.0	

^aAll assemblies over 5 layers of cadmium arachidate on quartz. ^bArbitrary units. ^c=T = layer of T218:arachidate, mole fraction T218 = 0.05; O—S = layer of surfactant stilbene:arachidate, mole fraction MSNA = 0.30.

Chart I. Structures of Surfactants

excitation leads to negligible fluorescence at 485 nm (λ_{act} for T218 alone is 410 nm). Table III compares the fluorescence of assemblies containing T218 and the stilbenes as a function of the assembly architecture and the number of stilbene layers.

Fluorescence lifetimes at 395 nm (S10A) and 490 nm (T218) were measured for assemblies containing only the stilbene, only T218, and an assembly containing the two compounds in adjacent layers with hydrophobic-hydrophobic contact.⁵⁴ The intensities relative to unquenched and fully quenched at 395 and 490 nm are 0.32 and 0.39, respectively. For all three of these samples (including both wavelengths for the assembly containing the two dyes) the fluorescence was observed to be biexponential; Table IV lists the lifetimes and the percentages for each of these samples. For the assembly containing only S10A and arachidate the predominant component is the long-lived fluorescence previously ascribed to an excitonic state.⁴³ The significance of the short-lived

**Figure 1.** Fluorescence quenching-sensitization with MSNA and T218: (—) unquenched surfactant stilbene fluorescence, (---) stilbene-T218 separation ~ 85 Å, and (-·-) stilbene-T218 separation < 40 Å.**Table III.** Fluorescence of Stilbene Aggregates and Thiocyanine as a Function of Number of Stilbene Layers

assembly ^{a,b}	I_{395}	I_{485}	I_{395} (no=T)
=T O—S—O O—	2.2	8.3	17.0
=T O—S—O O—S	6.5	10.3	24.4
=T O—S—O O—S—O O—S	17.8	17.1	54.4
=T O—S—O O—S—O O—S—O O—S	46.4	15.7	78.2
S—O O—S			
=T O—S—O O—S—O O—S	74.8	17.9	
S—O O—S—O O—S			

^aAll assemblies over quartz precoated with 5 layers of cadmium arachidate (outer surface hydrophobic). ^b=T refers to T218/arachidate layers, mole fraction T218 = 0.05; O—S = S10A.

component is uncertain in this case; although it could be attributed to some monomeric stilbene (similar lifetimes have been observed for S10A in phospholipid vesicles above Tc),⁶³ it is also possible

Table IV. Fluorescence Lifetimes of S10A and T218 in "Pure" and Mixed Assemblies

assembly ^{a,b}	λ_{act} (nm)	τ_{395} (ns)	τ_{490} (ns)
=T O—	430		0.5, 51% 2.4, 49%
S—O O—S	330	0.9, 27% 5.2, 73%	
=T O— S—O O—	330	0.3, 63% 5.3, 37%	1.7, 52% 4.0, 48%

^a Assemblies over quartz precoated with five layers of cadmium arachidate. ^b Mole fraction of T218 = 0.05 (remainder arachidate); mole fraction of S10A = 0.30 (remainder arachidate).

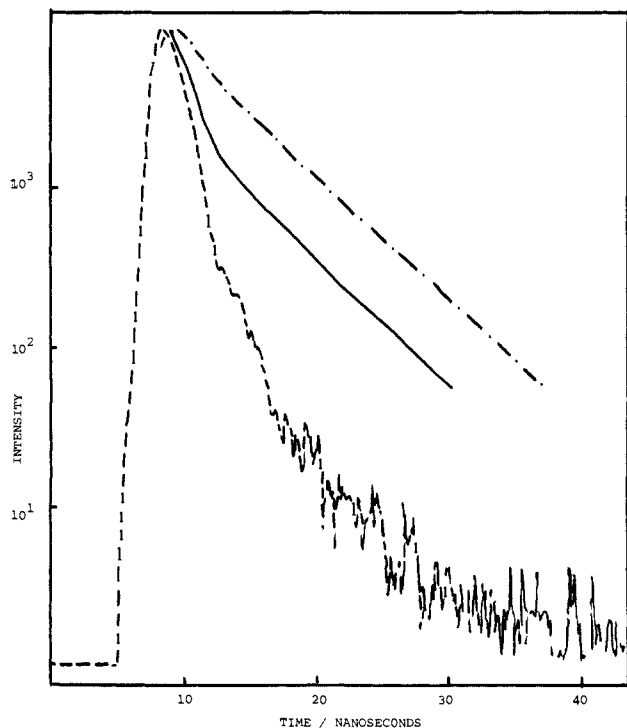


Figure 2. Fluorescence decay from multilayer assemblies containing S10A and T218: (---) lamp profile, (-.-) assembly containing S10A and arachidate only, and (—) fluorescence decay from assembly containing S10A and T218 in multilayers as shown in Table IV.

that the short-lived component is in part an artifact which can be attributed to scattering problems particular to the assemblies. Interestingly, the quenched samples show a prominent component at 395 nm which has essentially the same lifetime as the long-lived component of the unquenched S10A assemblies (5.4 ns) while the T218 fluorescence in mixed assemblies has both fast and slow decays slower than the corresponding ones for directly excited T218.⁶⁴ Figure 2 compares the decay of S10A fluorescence from quenched and unquenched assemblies.

(63) Suddaby, B. R.; Brown, P. E.; Russell, J. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 5609.

(64) In order to understand why the presence of MSNA lengthens the biexponential lifetimes of T218, one must first consider the origin of the dye's excitation. In the pure T218 film with no stilbene, the dye was excited directly and essentially instantaneously by 490-nm light and fluoresced without delay. In the mixed films, the excitation of the dye was not direct. T218 was excited solely by energy transfer from the MSNA exciton. A built-in delay of the excitation thus existed—note that both components of the T218 fluorescence decay were about 1.4 ns longer and the ratio of fast to slow components remained unchanged. As can be seen from looking at the associated MSNA data, the energy transfer appeared to originate almost exclusively in the slow (i.e., 5 ns) component. Since the rate of energy transfer is proportional to the rate of fluorescence in the unquenched case, one would expect that the energy transfer would be slower than if the fast component were involved. Although a shifting of the origin should not normally affect the rate constant and lifetime that one extracts from a curve, in this case it is reasonable that the 1.4 ns shift was lost in the lamp pulse initially, and the convolution program, unable to distinguish the difference, fit the mixed-film decay as if it started at time zero. Thus, because of a lack of resolution at short times, the observed lifetime of the T218 is longer.

Table V. Fluorescence of Stilbene Aggregates in Multilayer Assemblies in the Presence of Surfactant Electron Acceptors (Representative Data)

assembly ^{a,b}	stilbene	X_Q^c	I_{395}^d
=V V==		0.21	0
S—O O—S	S10A		17.7
S—O V==	S10A	0.21	3.0
S—O O—	S12A		7.8
S—O V==	S12A	0.21	3.4
S—O V==	4S6A	0.21	1.0
S—O O—S	4S6A		14.8
S—O O— —O O— =V O—	S10A	0.21	9.1
S—O O— =V O—	S10A	0.21	9.1
S—O O— —O V==	S10A	0.21	9.7
S—O Co—	S10A	0.05	8.4
S—O Co—	S10A	0.10	6.8
S—O Co—	S10A	0.05	5.7
S—O Co==	4S6A	0.05	7.3
S—O Co==	S10A	0.05	9.4
S—O Co==	S12A	0.05	10.3
S—O Co—	S12A	0.05	10.0

^a Quartz slides precoated with 5 layers of arachidate; V== = V218:arachidate; S—O = surfactant stilbene:arachidate $X_{\text{stil}} = 0.30$; Co— = Co18:arachidate; Co== = Co218 arachidate; O— = arachidate. ^b || denotes layering pattern repeated. ^c Mole fraction of quencher. ^d 25 °C, arbitrary units.

Table VI. Fluorescence of Stilbene Assemblies: Quenching of Multiple Layers of S10A and 4S6A by Dioctadecyl Viologen (or V218)

assembly ^a	stilbene	I_{394}^b
=V O—S S—O O—S S—O O—S	S10A	49.6
S—O O—S S—O O—S	S10A	74.4
=V O—S S—O O—S S—O O—S	4S6A	13.7
S—O O—S S—O O—S	4S6A	47.1
=V O—S S—O O—S S—O O—S	1:1 S10A:4S6A	19.1
S—O O—S S—O O—S	1:1 S10A:4S6A	32.1

^a Quartz slides precoated with 5 layers of arachidate; symbols as in Table V. ^b Arbitrary units.

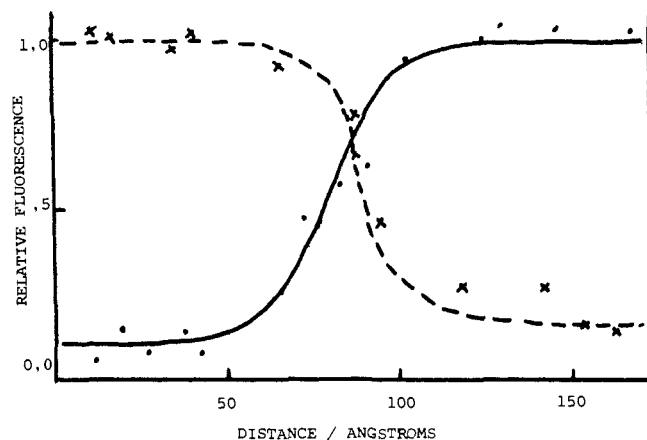
The fluorescence of the various stilbenes in supported multilayers is also quenched by the incorporation of the cobalt(III) complexes Co18 and Co218 or surfactant viologen V218 in the same or adjacent layers. In this case there is no change in the envelope of the stilbene fluorescence upon addition of the quencher nor is there any appearance of new emission. Table V lists intensity quenching data for several assemblies containing different substrate-quencher combinations. Short-term irradiation of these assemblies results in no detectable spectral change in the case of all three quenchers, indicating that no prominent permanent photoreaction accompanies the quenching. Attempts to determine the presence of any transient photoproducts by laser flash photolysis were unsuccessful in each case. Although the absence of a detectable signal may be regarded as an inconclusive result, it is probable that a long-lived, intensely absorbing transient such as a reduced viologen radical in the case of V218 as a quencher could have been detected in these experiments. As in the case of quenching of S10A fluorescence by T218 described above, studies of the quenching of the stilbene fluorescence by the cobalt complexes or V218 using single photon counting techniques showed a prominent component with a fluorescence lifetime within experimental error of that in unquenched assemblies together with an ill-defined faster decay. The observation of a prominent, "unquenched" fluorescent lifetime in all cases of quenching of the stilbene exciton fluorescence, even where intensity quenching is substantial, points to a nondiffusional quenching in which some of the aggregates are "out-of-range" of the quenchers as will be discussed later.^{9,10} The effect of a single layer of V218 upon the fluorescence of assemblies containing multilayers of S10A or 1:1 S10A/4S6A was investigated; Table VI compares fluorescence intensities obtained for several of these assemblies.

Discussion

Quenching of Stilbene Aggregate Fluorescence by Energy Transfer. As pointed out above, the fluorescence from the various

Table VII. Interchromophore Distances between Surfactant Stilbenes and Quenchers in Supported Multilayers

assembly	stilbene	distance, Å	
		edge-edge	center-edge
=Q O—S—	4S6A	10.15	14.81
	S10A	15.15	19.81
	S12A	17.65	21.31
=Q O—S—O	4S6A	39.94	44.60
	S10A	32.13	37.79

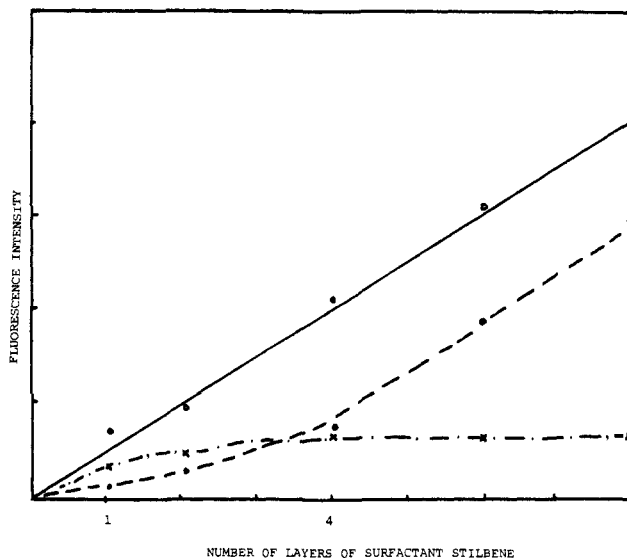
**Figure 3.** Fluorescence intensity in multilayers containing S10A or 4S6A and T218 as a function of chromophore separation: (—) stilbene aggregate fluorescence and (---) T218 fluorescence.

surfactant stilbenes overlaps well with the absorption spectrum of T218 such that a Förster-type, singlet-singlet energy transfer from stilbene to the thiocyanine would be expected to occur over moderate distances.^{37,38} This expectation is borne out as evidenced by the sensitization of T218 fluorescence concurrent with the quenching of the stilbene fluorescence as shown in Table II. The distance dependence of the energy transfer may be evaluated if we compare the fluorescence intensity for the two chromophores as a function of assembly structure in the multilayers. The length of an extended chain of arachidic acid is 28.3 Å, and thus the "spacing" added by each monolayer of cadmium arachidate should correspond to this. The stilbene chromophore is calculated to have a length of 9.32 Å; for the surfactant stilbenes we tabulate distances from the hydrophilic head to edge and center as indicated in Table VII. If these distances are now used in conjunction with the data from Table II, a plot of relative fluorescence intensity vs. donor-acceptor distance (Figure 3) is obtained. The points for the two different surfactant stilbenes S10A and 4S6A fall on the same curve, and the general shape of the curves is very similar to those obtained in other investigations of singlet-singlet energy transfer in multilayer assemblies. From the plots shown in Figure 3 we can obtain d_0 , the distance for half-quenching of donor fluorescence; the plot for fluorescence at 395 nm gives $d_0 = 80$ Å while that for T218 fluorescence at 490 nm gives $d_0 = 90$ Å; the crossing point for the two curves and the average of the aforementioned values both give $d_0 = 85$ Å.

These experimental results can be compared with a theoretical treatment for long-range energy transfer developed by Förster and modified for multilayer assemblies by Kuhn and co-workers.^{37,38} The excited donor molecule is portrayed as an electric oscillator producing a dipole field at a distance; the donor can lose energy by fluorescence, radiationless decay, or transfer of energy to a plane of acceptor molecules at a distance d . A relatively simple equation for the relationship between the fluorescence intensity of the donor and the interdistance between donor and acceptor planes can be derived (eq 1 and 2)

$$\frac{I_d}{I_0} = \left(1 + \left(\frac{d_0}{d} \right)^4 \right)^{-1} \quad (1)$$

$$d_0 = (\alpha)(1/n)(\lambda_D)q_D^{1/4}A^{1/4} \quad (2)$$

**Figure 4.** Fluorescence intensity as a function of total number of layers of S10A: (—) layers of S10A-arachidate only, (---) S10A fluorescence in assemblies containing variable numbers of layers of S10A over a single layer of T218-arachidate, and (-·-) T218 fluorescence in assemblies containing variable numbers of S10A layers added over initial T218 layer.

where I_d = emission intensity of the donor with the acceptor plane at a distance d , I_0 = the emission intensity of the donor in the absence of acceptor, α = a collection of constants determined by the orientation of the donor oscillator, n = the refractive index of the medium, taken to be 1.5, q_D = the fluorescence quantum yield of the donor in the fluorescent state in the absence of acceptor, and A = the absorbance of the acceptor layer at the fluorescence maximum, λ_D , of the donor.

The calculation of d_0 depends on the orientations of the transition moments of the donor and acceptor. For the MSNA, this dipole (on the basis of polarized emission studies)⁶⁵ is assumed to be *perpendicular* to the acceptor plane. (This dipole is parallel to the layer plane for T218.) Thus, it is calculated that $\alpha = (4\pi)^{-1}(9/2)^{1/4} = 0.116$. The fluorescence maximum of the MSNA band is 394 nm for S10A and 400 nm for 4S6A. Russell⁶⁶ has found $q_D = 0.38$ for S16A, which should be very similar to that for S10A or S12A; 4S6A should thus have $q_D = 0.27$ because of its shorter lifetime. The absorbance of a monolayer of T218 is estimated to be about 0.007 at 395–400 nm.³⁸ These values result in calculated $d_0 = 69$ Å for S10A and $d_0 = 64$ Å for 4S6A. These values are significantly smaller than the measured values reported above.

In summary the fluorescence quenching-sensitization experiments with the stilbene aggregates as excited donors and thiocyanine T218 as acceptor provide a consistent picture of an organized assembly in which energy transfer can occur over reasonably long distances. The agreement between measured and "calculated" values appears reasonable considering the fact that the stilbenes are clearly aggregated and not monomeric. The fact that some of the residual stilbene fluorescence has the same lifetime as that of unquenched assemblies indicates that there must be some isolation of different aggregates from one another despite the high mole fraction of stilbene (0.3) in single layers of the assemblies. This point raises the question of an "antenna effect" in multilayers containing the stilbenes or other chromophores similarly aggregated. In other words, the results presented thus far indicate that energy transfer from an excited stilbene aggregate to a well-matched acceptor can occur over distances in the range of 100 Å, but a second question is whether aggregate-aggregate energy transfer can provide an important channel for energy migration.

(65) McClure, D. S.; Dyck, R. H. *J. Chem. Phys.* **1962**, *36*, 2236.

(66) Russell, J. C., Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1982.

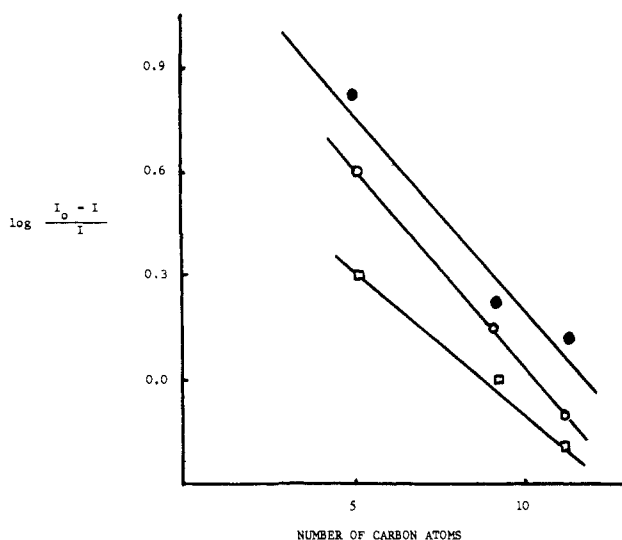


Figure 5. "Perrin" plots for fluorescence quenching of different surfactant stilbenes by electron acceptors: (□) C218, (○) Co18, and (●) V218.

The data presented in Table III suggest that any antenna effect from interaggregate transfer with the stilbenes used in this study is very small. This is most clearly seen by the presentation of these data in Figure 4. The stilbene fluorescence from multilayers with and without a single layer containing T218 is compared; simultaneously the fluorescence of the T218 as a function of added layers of stilbene is also presented. Two points emerge quite clearly: the stilbene fluorescence from multilayers is considerably attenuated for the first four layers (stilbene-T218 distance ≤ 90 Å) but almost unaffected at longer distances as evidenced by the nearly parallel lines for "quenched" and unquenched assemblies at n (number of stilbene layers) ≥ 4 . The "sensitized" fluorescence of T218 increases with number of added layers of stilbene up to $n = 4$ but remains essentially constant beyond. The lack of a prominent antenna effect for the aggregated stilbenes is probably not too surprising; the strongly forbidden nature of the low-energy transition in the H aggregates leads to a relatively unfavorable overlap between the "donor" emission and "acceptor" fluorescence. In this regard it can be noted that very strong antenna effects should be expected between J aggregates in multilayers.

Quenching of Stilbene Aggregate Fluorescence by Electron Transfer. As reported above the fluorescence of the stilbene aggregates is quenched by the presence of the potential oxidant acceptors Co18, Co218, or V218 in the same or adjacent assemblies. In these cases there is no appearance of new emission nor is there any evident chemical change on low-to-moderate steady-state irradiation. All three of these quenchers are relatively easily reduced, and on the basis of one-electron redox potentials estimated from nonsurfactant analogues ($E^{A/A^-} = 0.35$ and -0.45 V vs. SCE for Co18 and V218, respectively) it would be expected that the stilbenes ($E^{D^+/D} = 1.25$ – 1.35 V) should be oxidized from their lowest excited singlet or triplet states by these acceptors. In fact Adamson, Vogler, and Lantzke⁶⁷ have shown that the solution fluorescence of *trans*-stilbene-4-carboxylate (TSC) is strongly quenched by the addition of pentammine-cobalt(III) complexes, presumably by electron-transfer quenching. Subsequent studies in which the (TSC) pentammine-cobalt(III) complex was employed⁶⁸ showed that the singlet was quenched by intramolecular electron transfer and that stilbene oxidation products could be detected along with Co^{2+} on prolonged irradiation; in these studies it was shown that no redox chemistry occurred from triplet stilbene in the complex.⁶⁸ The cobalt complexes absorb weakly in the visible; thus there exists the possibility in these studies

that a Förster-type mechanism might account for fluorescence quenching with these quenchers. This possibility will be discussed in more detail below. For the viologen, V218, there is no absorption at wavelengths where the stilbene aggregates emit, and hence the probability of quenching by a mechanism other than electron transfer seems slight. In contrast to the quenching observed with T218, the fluorescence of the stilbene aggregates by the cobalt complexes and V218 is much less extensive such that there is relatively little quenching when "spacer layers" of cadmium arachidate are placed between layers of the stilbenes and quencher. Moreover, there is a significant difference when different stilbenes are compared with the same quencher. Thus for these quenchers a "distance profile" for quenching can be established by comparing the emission for the three different stilbenes 4S6A, S10A, and S12A whose distances from chromophore edge to the midpoint of the adjacent hydrophilic-hydrophilic interface are estimated to be 10.1, 15.1, and 17.6 Å, respectively.

Nondiffusional quenching is indicated since plots of quenching data (Table VI) show linearity between $\log((I_0 - I)/I)$ vs. distance (Figure 5). From these plots approximate $1/2$ quenching distances from the edge of the stilbene to the midpoint of the hydrophilic interface containing the quencher of 10, 16, and 19 Å can be established for the quenchers Co218, Co18, and V218, respectively, at a level of 3 mol % quencher.⁶⁹ These $1/2$ or "critical" quenching distances are much shorter than those observed above for T218 where energy transfer by a Förster mechanism should be operative; however, on first inspection they seem quite long for an excited-state electron-transfer quenching process. If it is assumed that the average separation between the energy-donating stilbene located in the hydrophobic region and the hydrophilic acceptor is approximately the value given above (10–19 Å) and that the quenching may be ascribed to a pseudo first-order electron-transfer process, we obtain rate constants at these distances, $k_{et} \sim 2 \times 10^8 \text{ s}^{-1}$. Since quenching increases as the mole fraction of the electron acceptor is increased, it is clear that the true pseudo-first-order rate constant should be somewhat higher.⁶⁹ In fact the values obtained in this study are actually quite close to the maximum values obtained recently in a study by Miller, Calcaterra, and Closs³⁰ in which a series of donors and acceptors separated by a ca. 1/-Å rigid steroid spacer were investigated. In this study it was found that maximum rates of electron transfer ($k \sim 10^9 \text{ s}^{-1}$) were obtained when the driving force for the process was ca. 1.1 eV.³⁰ In the present study we estimate the driving force for quenching of the stilbene aggregate excited state by electron transfer to be ca. 1.7 eV for V218 and ca. 2.4 eV for the cobalt quenchers. From the plot of k_{et} vs. ΔG° by Miller, Calcaterra, and Closs it appears that V218 should give close to a maximum rate while the cobalt complexes should be somewhat slower as is actually observed.³⁰ As we observed with the quenching of multiple layers of the stilbenes by T218, there is no evidence of a significant antenna effect in quenching of the stilbene aggregate fluorescence by Co18, Co218, or V218. Thus a vectorial quenching across several layers cannot be demonstrated with this study even when mixed layers of, for example, 4S6A and S12A are used.

That quenching of the stilbene aggregate fluorescence by V218 involves electron transfer appears reasonable since Förster type energy transfer is not possible. For the cobalt quenchers there is very weak absorption in the region where the stilbene aggregates fluoresce; however, a calculation⁷⁰ suggests that Förster energy transfer as observed above with T218 should play a negligible role at the distances we assume correct for both Co18 and Co218. On the other hand, since Co218 and Co18 have low-lying ligand-field excited states the possibility that quenching via a tunneling mechanism results in energy transfer as opposed to electron transfer⁷¹ cannot be excluded. However, since the quenching rates are similar to those observed for V218 where no energy transfer

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(68) Vogler, A.; Kern, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 270.

(69) As indicated by data in Table V, the extent of quenching increases as the mole fraction of quencher increases.

(70) Mooney, W. F., unpublished results.

(71) Zahir, K.; Böttcher, W.; Haim, A. *Inorg. Chem.* **1985**, *24*, 1966.

process is possible it seems reasonable that quenching in all three cases occurs by a similar mechanism. The consistent fall-off in quenching over the series 4S6A, S10A, and S12A with all three quenchers supports a picture in which the distance dependence indicated by the extended structure of the stilbene-poly-methylenecarboxylic acid is maintained in the supported multilayers. Whether the actual distances between stilbene edge and the hydrophilic acceptor is as great as indicated above could be questioned. Some possibilities for reducing this could include "roughness" of the hydrophilic interface which could be due to interdigitation or other phenomena. Though this could reduce the distance it would not alter the changes in distance as the different stilbenes are compared. The observation of rapid electron transfer over what appears to be relatively long distances in the assemblies is consistent with rate/distance relationships measured in other recent studies.^{29-32,34} This similarity suggests that tunneling mechanisms developed for frozen solutions or hydrocarbon "spacer" probably apply equally well for these Langmuir-Blodgett assemblies.¹⁰⁻¹⁴ The hydrophobic and interchain stilbenes have

thus been demonstrated as useful chromophores for incorporation in assemblies to investigate phenomena occurring at distances greater than contact/collisional but shorter than the span of two fatty acid chains. Their predilection for formation of H aggregates is an interesting but in some ways unfortunate characteristic which limits their use in an antenna or energy harvesting function; however, the features of these aggregates which make them ineffective as light harvesting pigments (low extinction coefficient, short wavelength absorption, and inefficient energy donation) could make them useful as energy receptors in future investigations.

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Registry No. 4S6A, 91202-35-6; S10A, 77824-98-7; S12A, 77814-49-4; Co18, 103439-09-4; Co218, 103439-10-7; V218, 64055-17-0; T218, 29523-00-0; *trans*-[Co(en)₂Br₂]Br, 15005-14-8; arachidic acid, 506-30-9; palmitic acid, 57-10-3.

Model for the Structure of the Liquid Water Network¹

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Abstract: The state of a water molecule in liquid water is defined by its time-average network environment. Two states are characterized. State A is the familiar four-coordinated state of the Bernal-Fowler model with tetrahedral hydrogen bonds. State B is five-coordinated. Reexamination of the static dielectric constant by the method of Oster and Kirkwood confirms the marked polar character of the four-coordinated state but shows that the five-coordinated state is only about half as polar. Explicit five-coordinated models are proposed which are consistent with polarity and satisfy constraints of symmetry and hydrogen-bond stoichiometry. The potential energy due to the dipole-dipole interaction of the central water molecule with its time-average solvent network is derived without additional parameters. This permits prediction of barriers to rotation, frequencies for hindered rotation and libration in the network, and $\Delta H_{A,B}$ and $\Delta S_{A,B}$. The results are in substantial agreement with relevant experiments. In particular, the barriers to rotation permit a consistent interpretation of the dielectric relaxation spectrum. The relative importance of the two states varies predictably with the property being examined, and this can account for some of the "schizophrenia" of aqueous properties. Since the two-state model is based on time-average network configurations, it does not apply when the time scale of observation is short compared to network frequencies, i.e., at infrared frequencies where continuum models may be successful.

In recent years there has been marked progress in computer simulations of liquid water and of aqueous solutions.²⁻⁵ These studies use the deductive scientific approach: They begin with a model and reason to the facts. The present paper tries to characterize the structure of the liquid water network by using

the alternative inductive approach, beginning with facts and reasoning to a model.

The resulting model will be consistent with the free energy and its temperature derivatives, the dielectric constant, the probable number of hydrogen-bonded nearest neighbors, intermolecular vibration frequencies, and dielectric relaxation dynamics. The model is explicit enough to be useful for prediction. In particular, it can explain the peculiar pattern of thermodynamic properties of nonpolar solutes in water which is commonly called "hydrophobic hydration".^{6,7} This application of the model will be reported separately.⁸

A key issue which any model of liquid water should face is the striking resemblance of the properties of water to those of a mixture consisting of two states in equilibrium.⁹⁻¹³ One state, call it state A, has a relatively low energy, low entropy, and large

(1) Work supported in part by a grant from the National Science Foundation.

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