Aggregation Phenomena in Langmuir-Blodgett Films of Polar Stilbene Amphiphiles

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The effect of incorporating polar-substituted stilbene groups into two-dimensional molecular assemblies was studied. A homologous series of stilbene-containing hexadecanoic acids was found to exhibit H-aggregation in supported Langmuir-Blodgett (LB) monolayers. The spectral properties of these aggregates are insensitive to the particular homologue used, either alone or in 1:1 mixtures. This result, particularly when considered in the context of its extreme similarity to that obtained from the LB films formed by alkyl-substituted stilbene fatty acids, suggests that H-aggregation is a minimum free energy packing assembly for stilbene units in LB films. β-Stilbene methylation prevents the molecules from tight packing and produces a pronounced perturbation on the H-aggregate absorbance spectrum.

Introduction

Dye aggregation is characterized by close packing of the chromophores in the two-dimensional assembly, which results in a strong coupling of the π-systems, and distinct changes in spectral and photophysical behavior.[1-3] Two typical examples for such aggregation are the J- and H-aggregates of cyanine dyes.[4] In the J-aggregates,[5,6] a relatively large red shift in the lowest absorption transition relative to the nonaggregated dye is observed, while in the H-aggregates a blue shift is observed.

Langmuir-Blodgett (LB) monolayers[7] are especially suited for studies of dye aggregates, since they provide a highly ordered environment for the molecules, similar to that of a solid matrix, where aggregation of aromatic molecules is observed frequently.[8] In such molecular assemblies, aggregation is enhanced, and can be avoided only by dilution with inert molecules that serve to separate the chromophores. Kuhn and co-workers studied dye aggregation in monolayers,[9-11] and proposed a coherent exciton model for the excited state.[12] However, while the details at the molecular level of the transitions involved in the excitonic couplings are not fully understood,[13,14] the excitonic nature of the excited state is recognized.[15,16]

A number of stilbene-derivatized fatty acids have been shown to have a strong tendency to form aggregates in supported monolayers.[17-20] Stilbene is a particularly well-suited probe of microheterogeneous media, as both its photophysical and photochemical properties have been shown to be extremely medium sensitive.[21] In addition, depending on the geometric arrangement of the chromophores, different types of aggregates can, in principle, be produced, ranging from those whose transition moments are aligned at an angle nearly 90° to their line of center (H-aggregates) to those having an angle of <30° (J-aggregates).[22] Thus far, the H-aggregate has been the predominant aggregate form observed for stilbene fatty acids in LB films.[17-20] However, the factors that lead to the formation of the different types of assemblies in these systems are not well understood. The attainment of systematic control over stilbene aggregation promises to lend unique optical and photochemical properties to the resulting assemblies, as a result of cooperative effects.[19,23]

In this study, the structures of the monolayers formed by the homologous series of 4,4'-donor-acceptor-substituted stilbene fatty acids, C_nC_m ($n + m = 16$, Scheme 1), are investigated as a function of the position of the stilbene chromophore in the alkyl chain, thereby varying the distance of the chromophore from the COOH head group. The geometric arrangement of the stilbenes in an LB film

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(1) Kuhn, H. In *Light-Induced Charge Separation in Biology and Chemistry*; Gerischer, H., Katz, J. J., Eds.; Dahlem Konferenzen: West Berlin, 1979; pp 151-169.
(2) Gilman, P. B. In *Photographic Sensitivity*; Cox, R. J., Ed.; Academic Press: London, 1973; p 187.
(3) Sturmer, D. M. In *Special Topics in Heterocyclic Chemistry*; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, 1977; p 540.
(4) Herz, A. H. *Photogr. Sci. Eng.* **1974**, *18*, 323.
(5) Jelley, E. E. *Nature* **1936**, *138*, 1009.
(6) Scheibe, G. *Angew. Chem.* **1936**, *49*, 563.
(7) Ulman, A. *An Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-Assembly*; Academic Press: Boston, 1991.
(8) *Organic Molecular Aggregates: Electronic Excitation and Interaction Processes*; Reineker, P., Haken, H., Wold, H. C., Eds.; Springer: Berlin, 1983.
(9) Kuhn, H.; Möbius, D.; Bucher, H. In *Techniques of Chemistry*; Weissberger, A., Rositer, B. W., Eds.; Wiley: New York, 1973; Part 3B, Vol. 1.
(10) Kuhn, H.; Möbius, D. *Angew. Chem.* **1971**, *83*, 672.
(11) Kuhn, H.; Möbius, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *10*, 620.
(12) Möbius, D.; Kuhn, H. *Isr. J. Chem.* **1979**, *18*, 375.
(13) Tanaka, J.; Tanaka, M.; Hayakawa, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3109.
(14) Delany, J.; Morrow, M.; Eckhardt, C. J. *Chem. Phys. Lett.* **1985**, *122*, 347.
(15) McRae, E. G.; Kasha, M. J. *Chem. Phys.* **1958**, *28*, 721.
(16) Scherer, P. O. J.; Fischer, S. F. *Chem. Phys.* **1984**, *86*, 269.
(17) Mooney, W. F., III; Brown, P. E.; Russel, J. C.; Costa, S. B.; Pederson, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5659.
(18) Spooner, S. P.; Whitten, D. G. *Proc. Soc. Photo-Opt. Instrum. Eng.* **1991**, *436*, 82.
(19) Whitten, D. G.; Spooner, S. P.; Hsu, Y.; Penner, T. L. *React. Polym.* **1991**, *15*, 37.
(20) Heesemann, J. *J. Am. Chem. Soc.* **1980**, *102*, 2167.
(21) See, for instance: Saltiel, J.; D'Agostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445.
(22) Kasha, M. *Radiat. Res.* **1963**, *20*, 55.
(23) Spano, F. C.; Mukamel, S. *J. Chem. Phys.* **1991**, *95*, 7526.

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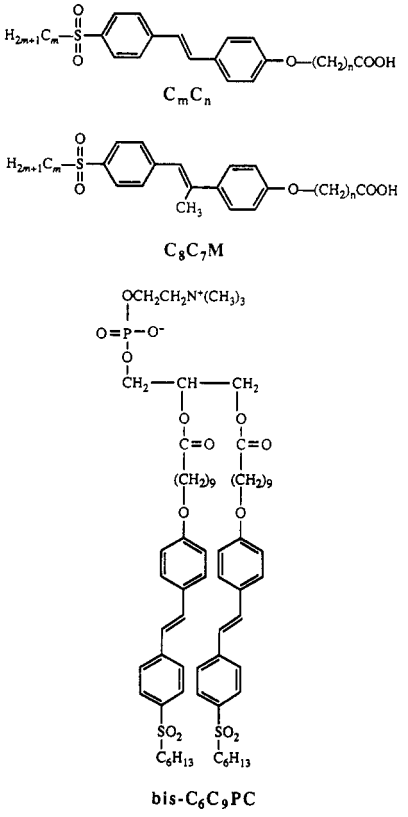
Scheme 1



can be further manipulated by using mixtures of two C_nC_m molecules that have varying positions of the chromophore along the C_{16} chain. The incorporation of the C_nC_m functionalities into derivatives of phosphatidylcholine allows for an extra factor of environmental control as the head group-controlled hydrocarbon chain packing should enforce a well-defined structure.[24]

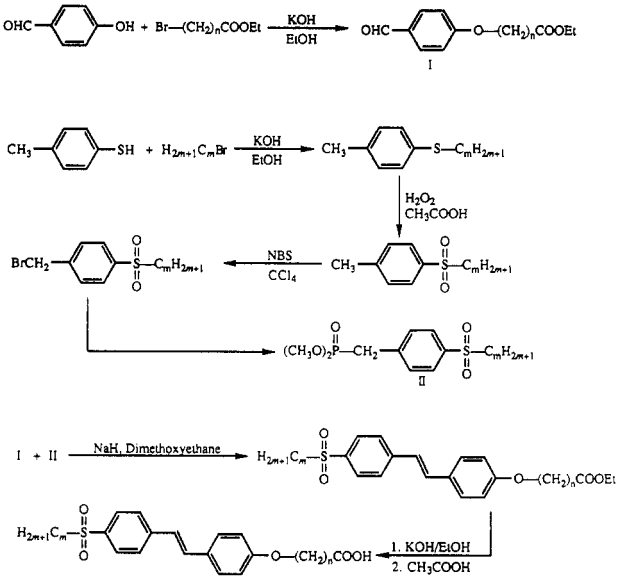
Recent studies have shown that incorporation of a sulfone functionality into alkanethiolate monolayers on gold has significant effects on the molecular packing in the resulting self-assembled monolayers.[25,26] Thus, the large in-plane dipole moment of the sulfone and its shape restrictions (O–S–O angle of 109°) also were anticipated to have important consequences on the monolayer structure formed by stilbene-substituted fatty acids, C_nC_m. Additionally, understanding the factors that control monolayer packing for 4,4′-donor–acceptor-substituted stilbenes in LB films is important, as resulting assemblies may be good candidates for second harmonic generation studies.[27,28]

Experimental Section

General. All glassware was dried overnight in the oven. All solvents are reagent grade and were dried previous to their use. Methylene chloride and benzene were distilled over calcium hydride and sodium with benzophenone, respectively. Triethylamine was allowed to stand over 3-Å molecular sieves and distilled from calcium oxide.

L-α-Glycerophosphorylcholine (GPC) as the cadmium chloride complex—used without further purification—and lipophilic

Scheme 2



sephadex LH-20 (25–100-mm beads) were purchased from Sigma Chemical Co. 4-(*N*,*N*-Dimethylamino)pyridine (DMAP)—recrystallized from chloroform/diethyl ether—and trimethylacetyl chloride were purchased from Aldrich Chemical Co. Rexyn I-300, mixed resin, is from Fisher Scientific.

The progress of the reactions and the purity of the final products were monitored by thin-layer chromatography (TLC) using silica gel adsorbent with a fluorescent indicator (Eastman Kodak Co.). Two solvent systems were used in the synthesis of bis(C_6C_9)PC as eluants for both TLC and column chromatography: (solvent A) methanol, chloroform, water (5:4:1, v/v/v); (solvent B) methanol, chloroform, water (25:65:4, v/v/v).

Ultraviolet (UV) spectra were obtained on a Hewlett-Packard 8452 diode-array spectrophotometer. NMR spectra were obtained on a GE QE-300 instrument at 300 MHz for proton and 75 MHz for ^{13}C in $CDCl_3$ (Aldrich) solution (unless otherwise specified), and shifts are referred to TMS internal standard. All chemical shifts (δ) are in parts per million (ppm), and coupling constants are in hertz (Hz). Melting points were determined on a Haake Buchler apparatus and are not corrected.

C_mC_n Fatty Acids. All C_mC_n fatty acids were prepared according to the routes described in Scheme 2. C_8C_7M was prepared using the same sequence of reactions, but using 4-hydroxyacetophenone as the starting material. The general synthesis of the sulfone-containing stilbene derivative was described before,[29] and will not be discussed here.

Data for C_6C_9: mp 139–140 °C; ^1H NMR δ 0.84 (t, J = 6.8, 3H), 1.24 (m, 4H), 1.31 (s, 12H), 1.41 (m, 2H), 1.70 (m, 6H), 2.34, (t, J = 7.69, 2H), 3.06 (t, broad middle peak, J = 7.94, 2H), 3.97 (t, J = 6.48, 2H), 7.08 (AB, $\Delta\nu$ = 65.72, J = 16.27, 2H), 7.18 (AB, $\Delta\nu$ = 169.38, J = 8.59, 4H), 8.23 (AB, $\Delta\nu$ = 65.77, J = 8.23, 4H).

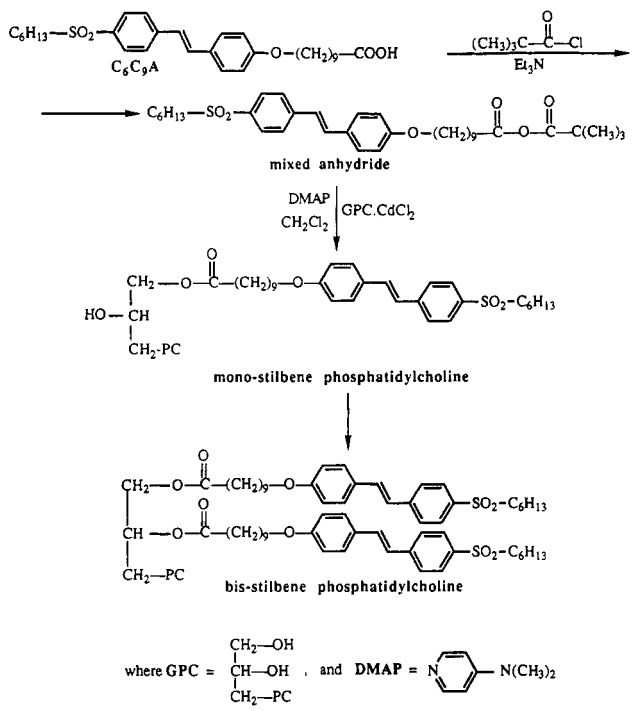
Data for C_8C_5: mp 163–164 °C; ^1H NMR δ 0.84 (t, J = 6.83, 3H), 1.21 (s, 8H), 1.33 (m, 2H), 1.55 (m, 2H), 1.73, (m, 4H), 1.82 (m, 2H), 2.40 (t, J = 7.15, 2H), 3.07 (t, broad middle peak, J = 7.90, 2H), 3.98 (t, J = 6.00, 2H), 7.09 (AB, $\Delta\nu$ = 64.77, J = 16.30, 2H), 7.17 (AB, $\Delta\nu$ = 170.95, J = 8.63, 4H), 7.73 (AB, $\Delta\nu$ = 66.29, J = 8.33, 4H).

Data for C_8C_7: mp 162–163 °C; ^1H NMR δ 0.84 (t, J = 6.86, 3H), 1.21 (s, 8H), 1.37 (s, 6H), 1.44 (m, 2H), 1.69 (m, 4H), 1.78 (m, 2H), 2.35 (t, J = 7.45, 2H), 3.06 (t, broad middle peak, J = 7.94, 2H), 3.96 (t, J = 6.43, 2H), 7.08 (AB, $\Delta\nu$ = 64.46, J = 16.26, 2H), 7.17 (AB, $\Delta\nu$ = 170.05, J = 8.66, 4H), 7.72 (AB, $\Delta\nu$ = 66.14, J = 8.26, 4H).

Data for C_8C_7M: mp 106–107 °C; ^1H NMR δ 0.84 (t, J = 6.76, 3H), 1.22 (s, 8H), 1.40 (s, 6H), 1.46 (m, 2H), 1.73 (m, 6H), 2.26 (s, 3H), 2.35 (t, J = 7.43, 2H), 3.11 (t, broad middle peak, J = 7.89, 2H), 3.97 (t, J = 6.40, 2H), 6.77 (s, 1H), 7.17 (AB, $\Delta\nu$ = 166.78, J = 8.68, 4H), 7.68 (AB, $\Delta\nu$ = 110.38, J = 8.24, 4H).

(24) For a review, see Gennis, R. B. *Biomembranes. Molecular Structure and Function*; Springer-Verlag: New York, 1982.
(25) Evans, S. D.; Urankar, E.; Ulman, A.; Ferris, N. *J. Am. Chem. Soc.* **1991**, *113*, 4121.
(26) Evans, S. D.; Goppert-Berarducci, K.; Urankar, E.; Gerenser, L. J.; Ulman, A.; Snyder, R. G. *Langmuir* **1991**, *7*, 2700.
(27) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.
(28) Lippitsh, M. E.; Draxler, S.; Koller, E. *Thin Solid Films* **1992**, *217*, 161.
(29) Ulman, A.; Willand, C. S.; Köhler, W.; Robello, D. R.; Williams, D. J.; Handley, J. *J. Am. Chem. Soc.* **1990**, *112*, 7084.

Scheme 3



Data for $C_{10}C_5$: mp 161–162 °C; ^{1}H NMR δ 0.85 (t, J = 6.93, 3H), 1.21 (s, 12H), 1.33 (m, 2H), 1.69 (m, 2H), 1.84 (s, broad, 4H), 2.45 (t, broad J not available, 2H), 3.06 (t, broad middle peak, J = 7.82, 2H), 4.00 (t, broad J not available, 2H), 7.08 (AB, $\Delta\nu$ = 62.26, J = 16.33, 2H), 7.17 (AB, $\Delta\nu$ = 171.75, J = 8.47, 4H), 7.72 (AB, $\Delta\nu$ = 65.89, J = 7.72, 4H).

Data for $C_{11}C_4$: mp 152–153 °C; ^{1}H NMR δ 0.85 (t, J = 6.82, 3H), 1.21 (s, 16H), 1.30 (m, 2H), 1.53 (m, 2H), 1.71 (m, 4H), 1.82 (m, 2H), 2.40 (t, J = 7.29, 2H), 3.07 (t, broad middle peak, J = 7.89, 2H), 3.98 (t, J = 6.30, 2H), 7.08 (AB, $\Delta\nu$ = 63.84, J = 16.32, 2H), 7.17 (AB, $\Delta\nu$ = 171.0, J = 8.62, 4H), 7.73 (AB, $\Delta\nu$ = 66.02, J = 7.73, 4H).

Data for $C_{12}C_3$: mp 174–175 °C; ^{1}H NMR δ 0.85 (t, J = 6.82, 3H), 1.20 (s, with a small m as a shoulder 18H), 1.30 (m, 2H), 1.69 (m, 2H), 2.13 (p, J = 6.51, 2H), 2.59 (t, J = 7.23, 2H), 3.07 (t, broad middle peak, J = 7.89, 2H), 4.05 (t, J = 6.02, 2H), 7.08 (AB, $\Delta\nu$ = 64.36, J = 16.25, 2H), 7.17 (AB, $\Delta\nu$ = 170.38, J = 8.65, 4H), 7.72 (AB, $\Delta\nu$ = 66.48, J = 8.34, 4H).

(C_6C_9)PC. The stilbene fatty acid phosphatidylcholine derivative was synthesized according to Scheme 3. The general synthetic approach is based on methods previously described in the literature.[30–33] Some modifications were required to adjust for differences in solubilities and the more hindered nature of our starting material.

Synthesis of Mixed Anhydride. The stilbene fatty acid derivative, C_6C_9A (0.47 mmol, 1.0 equiv), was dissolved in methylene chloride (20 mg/mL). Triethylamine (2.0 equiv) was added via syringe followed by trimethylacetyl chloride (6.0 equiv). The additions were carried out in a drybox. The reaction flask was sealed and stirred under a bed of nitrogen in the dark for approximately 5 h. The progress of the reaction was monitored by TLC (solvent B) (R_f(C_6C_9) = 0.68, R_f(anhydride) = 0.90). The solvent was removed with a stream of nitrogen, and the residue dried in a vacuum desiccator for 2 h to remove any unreacted chloride and triethylamine.

Synthesis of Bis(C_6C_9)PC. The crude mixed anhydride (3.0 equiv), dissolved in methylene chloride (20 mg/mL), was added via syringe to a suspension of L-α-glycerophosphorylcholine as the cadmium chloride complex (GPC·$CdCl_2$), 1.0 equiv, and 4-(*N*,*N*-dimethylamino)pyridine (DMAP), 2.0 equiv, in 1 or 2 mL of CH_2Cl_2. The reaction mixture was sealed and stirred in the dark under a bed of nitrogen for approximately 48 h. The reaction was monitored by TLC (solvent B). Completion of the reaction was achieved when no monosubstituted product was observed (R_f(bis(C_6C_9)PC) = 0.43). The solvent was removed by rotary evaporation and the residue dissolved in solvent A. The solution was filtered and passed through an ion exchange column, Rexyn (2.5 × 10 cm), to remove the $CdCl_2$ and DMAP. The solvent was removed by rotary evaporation. Benzene and ethanol were added to avoid foaming and complete azeotropic removal of water. The crude product was purified by passing it through a sephadex LH-20 column (2.5 × 15 cm) eluted with chloroform followed by recrystallization with chloroform/ether: yield of bis-(C_6C_9)PC 30%; ^{1}H NMR δ 0.86 (t, 6H, CH_3), 1.24–1.86 (m, 44H, CH_2), 2.33 (t, 4H, CH_2COOH), 3.10 (t, 4H, CH_2SO_2), 3.38 (br s, 9H, $N(CH_3)_3$), 3.84–4.7 (m and t, 12H, CH_2O and CH_2N), 5.22 (m, 1H, CHO), 6.87–7.9 (m, 20H, C_6H_4 and CH=CH).

Table 1. Summary of the Compression Behavior of the Monolayers Formed by C_mC_n, C_8C_7M, Some of Their 1:1 Mixtures, and Bis(C_6C_9)PC

		$\bar{A}$ (Å^2)		
m	*n*	first compression	second compression	collapse pressure (mN/m)
6	9	35	23–25	38
8	7	44	28–32	32
8	7[a]	43	34–35	29
10	5	42	33–34	23
11	4	38	25–26	39
12	3	52	32–34	28
8	5	36	27–28	36
1:1 C_8C_7/C_6C_9		44	35–36	27
1:1 $C_{12}C_3/C_6C_9$		46	31–32	30
1:1 $C_{10}C_5/C_6C_4$		50–52	33–35	30
1:1 $C_8C_7/C_{12}C_3$		42	30–32	28
1:1 C_8C_7/C_8C_7M		45	34–35	28
bis(C_6C_9)PC		90–94	69–74	45

[a] C_8C_7M.

Monolayers. A typical procedure for recording isotherms and deposition of monolayers was as follows. Stock solution concentrations of surfactants were typically 2.0 mg/mL in chloroform (Fisher, HPLC grade). The subphase used in all studies consisted of Milli-Q water (obtained by passing house-deionized water through a Milli-RO 10 Reverse Osmosis/Milli-Q UF Plus System, specific resistivity 18.2 MΩ) containing 3×10^{-4} M $CdCl_2$ and 5×10^{-5} M $NaHCO_3$ (pH 6.6–6.8). A stock solution of surfactant (50 μL) was spread on the subphase surface in a KSV 5000 trough and the chloroform removed by allowing an evaporation period of 10 min prior to compression. The monolayer was then compressed at ambient temperature at a typical barrier speed of 10 mm/min. Deposition was accomplished at a dipper speed of 5 mm/min and surface pressure of 15 mN/m onto quartz slides (9 mm wide × 1 mm thick). Arachidic acid was used as received from Analabs, Inc., and kept refrigerated.

Fluorescence Spectra. Steady-state fluorescence spectra were recorded on either a Spex Fluorolog or a Spex 1680 spectrofluorimeter equipped with a 150-W xenon lamp. Monolayer spectra were measured by orienting the slides at a 45° angle with respect to the excitation source, and the emission was detected at right angles. Solution-phase spectra were obtained in 1-cm-path-length quartz cuvettes with right angle detection. All slits were fixed at 1 mm. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

Results and Discussion

Table 1 summarizes the properties of the films formed by the individual C_nC_m, some of their 1:1 mixtures, the β-methylated stilbene compound, C_8C_7M, and the phospholipid modified to incorporate the esterified form of C_6C_9 (bis(C_6C_9)PC, Scheme 1). All the compounds form very stable monolayers. Upon initial compression of all the films, a larger mean molecular area ($\bar{A}$) and a broader

(30) Radhakrishnan, R.; Robson, R. J.; Takagaki, Y.; Khorana, H. G. *Methods Enzymol.* **1981**, *72*, 408.
(31) Morgan, C. G.; Thomas, W. E.; Moras, T. S.; Yianni, Y. P. *Biochim. Biophys. Acta* **1982**, *692*, 196.
(32) Khorana, H. G.; Chakrabarti, P. *Biochemistry* **1975**, *14*, 5021.
(33) Singh, A. *J. Lipid Res.* **1990**, *31*, 1522.

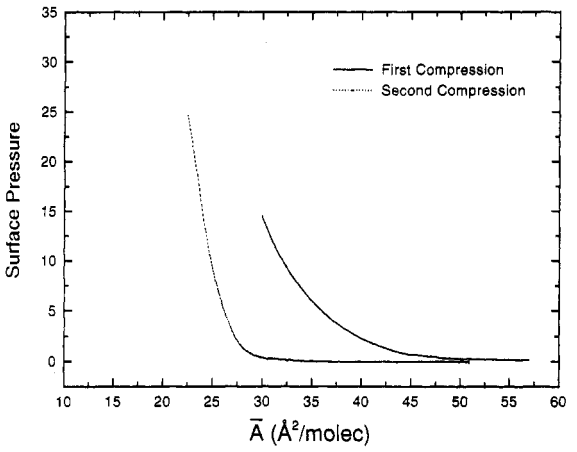


Figure 1. Representative isotherms for C_8C_7.

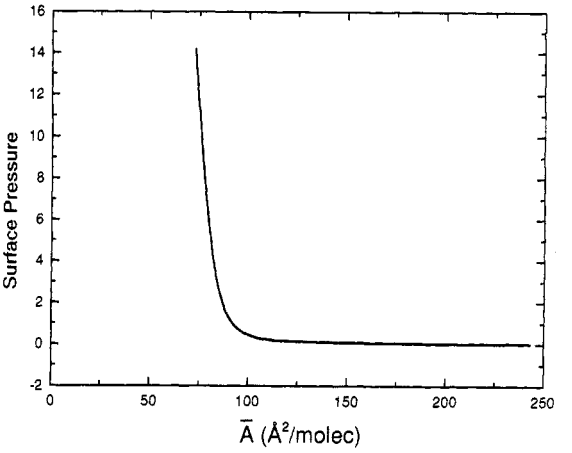


Figure 2. Representative isotherm for bis(C_6C_9)PC.

pressure–area isotherm are obtained than on the second and all subsequent compressions. Therefore, Table 1 summarizes $\bar{A}$ values for both first and second compressions of each film. Representative isotherms for C_8C_7 are shown in Figure 1.

The initial compression of the monolayers may impose a better packing arrangement that is retained upon the relaxation of the film and subsequent compressions. When the $\bar{A}$ values on the second compression are compared for the series of C_mC_n, it is apparent that their values differ significantly from one another, a result that is not anticipated for a simple homologous series. However, the stilbene-containing fatty acids are not simple molecules, and their two-dimensional order may result from competing packing requirements of the two alkyl chains and the planar π-system,[34] where the latter probably is the dominating one. We have seen, for example, differences both in adsorption kinetics and in packing and ordering in a homologous series of alkanethiolate monolayers on Au(111) surfaces, where a polar benzene unit was the π-system.[25] Molecular dynamics studies of this system showed that the sulfone groups form a plane of dipoles parallel to the substrate, and that a considerable stabilization of the assembly arises from electrostatic energy.[35] The $\bar{A}$ values for the 1:1 mixtures, however, stabilize at an average value of 34 Å² (Table 1).

Monolayers consisting of individual C_mC_n and of their 1:1 mixtures are readily transferable to solid supports (quartz slides). Multilayers, however, are not obtained. This result is unaffected by precoating the slides with arachidic acid, the use of prolonged drying times in between deposition of layers, or alternating the C_mC_n layers with arachidic acid. For the stilbene-modified phospholipid bis(C_6C_9)PC (Figure 2), however, up to three layers could be deposited in a Z-type fashion.[36] Contrary to the rigid C_mC_n monolayers, bis(C_6C_9)PC monolayers at the air–water interface should be more "liquidlike" due to the phospholipid structure. This combination makes them more manageable and allows the deposition of more than one layer. After the third layer the transfer ratios differ significantly from unity. This probably is due to structural changes during film transfer, as was observed in monolayers formed by related phospholipids (dipalmitoylphosphatidylcholine, DPPC).[37] In that case, these changes were

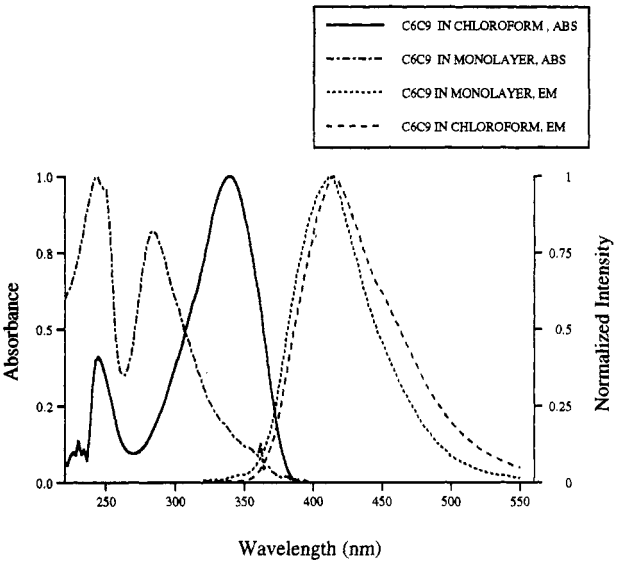


Figure 3. Absorbance and emission spectra of C_6C_9 in chloroform and in monolayers on quartz.

attributed to substrate–monolayer interactions. Some of the same forces may operate for the films formed by bis(C_6C_9)PC, preventing buildup of more than a few layers.

The absorbance and emission spectra of the monolayers obtained from the individual C_mC_n acids transferred to quartz supports, and their 1:1 mixtures, are virtually identical. Figure 3 presents the absorbance and emission spectra of C_6C_9 in chloroform and in monolayers. Figure 4 shows the absorbance and emission spectra of monolayers consisting of 1:1 mixtures (C_6C_9/C_8C_7 and $C_6C_9/C_{12}C_3$). In an organic solvent (chloroform), the absorbance spectra are dominated by a broad, intense band centered at 338 nm, whose shape and position are unaffected by dilution, indicating that it is due to intramolecular charge transfer. The monolayer absorbance spectrum is sharp and blue-shifted relative to that in chloroform, with the lowest energy maximum centered at 276 nm. This blue shift in the monolayer absorbance spectrum is consistent with the formation of an H-aggregate characterized by a parallel arrangement of the stilbene chromophores in a head-to-head-type arrangement.[18,19] Extracting coated slides with chloroform gives nearly quantitative recovery of the C_mC_n whose absorbance spectrum is, again, dominated by the charge-transfer band, illustrating that changes in the physical properties are not due to any chemical modification caused by film compression or transfer. Moving the stilbene moiety by two methylene units along the C_{16}

(34) Ulman, A.; Scaringe, R. P. *Langmuir* **1992**, *8*, 894.
(35) Shnidman, Y.; Ulman, A.; Eilers, J. E. *Langmuir* **1993**, *9*, 1071.
(36) Z-type deposition of phospholipids is not uncommon, See Lotta, T. I.; Laakkonen, L. J.; Virtanen, J. A.; Kinnunen, P. K. J. *Chem. Phys. Lipids* **1988**, *46*, 1.
(37) Riegler, H.; Spratte, K. *Thin Solid Films* **1992**, *210/211*, 9.

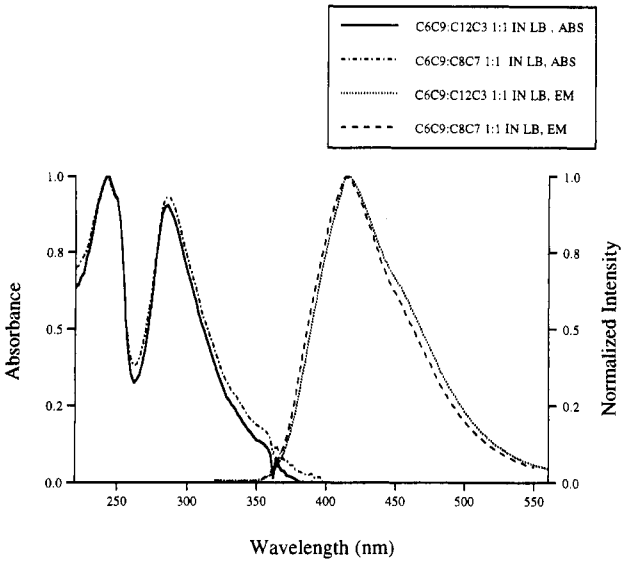


Figure 4. Absorbance and emission spectra of monolayers on quartz consisting of the 1:1 mixtures C_6C_9/C_8C_7 and $C_6C_9/C_{12}C_3$.

chain (C_8C_7) has no pronounced effect on the film properties (Table 1), or the absorbance and emission spectra of the resulting transferred monolayers.

The shape and position of the monolayer absorbance spectra are invariant to the particular C_mC_n used or to which C_mC_n is present in their two-component mixtures. For instance, 1:1 mixtures of $C_6C_9/C_{12}C_3$ or $C_{10}C_5/C_6C_9$, which are expected to have a large offset in the stilbene chromophores, still display monolayer absorbance spectra like those shown in Figure 4. The insensitivity of the monolayer absorbance spectra to the change in the particular materials under study illustrates that the aggregation is a result of preferential association of the stilbene units, rather than a formation of a forced assembly due to the compression of the monolayer. In the case of the two-component mixtures, however, phase separation cannot be ruled out. The individual components of the mixtures may phase separate into small pools when spread on a subphase surface, and thus aggregate with one another. A monolayer formed by a 1:18 molar mixture of C_6C_9 and arachidic acid also displays exclusively the H-aggregate absorbance spectrum, indicating that the C_6C_9 molecules still are capable of self-associating even at this high dilution.

The LB film absorbance spectra from C_mC_n and their mixtures are strikingly similar to the monolayer spectra displayed by stilbenes incorporated into alkyl chains of simple fatty acids (i.e., without 4,4′-donor–acceptor substitution). Thus, the molecular packing in the quartz-supported films must be essentially identical in these two systems, despite the presence of the 4,4′-substituents on the stilbene moieties of C_mC_n molecules whose substituents and dipole moments may have been expected to have a significant effect on the two-dimensional packing and ordering of the molecules. This result indicates that dispersive rather than electrostatic interactions are the dominant forces for aggregation of stilbene-incorporated amphiphiles in LB films. The H-aggregate is thus the preferred molecular arrangement for stilbene-substituted fatty acids in monolayer assemblies and must represent a minimum free energy conformation for the system.

The interpretation of a combination of blue-shifted absorption and red-shifted emission previously observed for stilbene LB films[17] was based on the Kasha model for dipole-induced splitting of excited-state energy levels. In this model, the fluorescence originating from the symmetry-forbidden lower excited state followed internal conversion from the higher energy-allowed state populated by absorption.[22] The apparent Stokes shift in these compounds, which measures this excitonic splitting between the excited-state energy levels, was about 10 000 cm^{-1}. In the case of C_mC_n, however, the positions of the emission spectra in chloroform and monolayer film do not differ appreciably (Figure 2). If the aggregated C_mC_n have a splitting similar to that measured for the stilbenes without 4,4′-donor–acceptor substitution, the fluorescence in the LB films of these compounds would be expected to occur around 400 nm. This would actually be slightly to the blue of the monomer emission in solution rather than to the red, as was seen previously. The reason is that the charge-transfer interaction has resulted in a substantial red shift of the solution monomer absorption and emission relative to the stilbenes without donor–acceptor substitution, while upon aggregation in the LB films the absorption occurs at similar wavelengths whether or not donor–acceptor substitution is present. Thus, especially in view of the uncertainty of the excitonic splitting to be expected in the C_mC_n compounds, it is quite possible that the solution monomer and LB aggregate fluorescences occur coincidentally at about the same wavelength. This could also account for the observation that the emission in the Langmuir–Blodgett films is broader than in solution and exhibits a shoulder on the long-wavelength side since the shapes of the monomer and aggregate fluorescences would not be expected to be identical. On the other hand, it is possible that the emission seen in the C_mC_n LB films is truly monomer emission. Possible mechanisms for such an effect can be suggested. One interpretation is that the excitation created in the aggregated form of the dye is trapped by a small residual population of monomer not evident in the absorption spectrum. (A slight shoulder in the absorption spectrum of C_6C_9 at about 350 nm may be due to monomer, but the very low absorption signal makes this difficult to determine.) Such a mechanism has recently been used to explain monomer-like emission from a hemicyanine dye aggregate. In that case the presence of the monomer was determined from the excitation spectrum that showed, in addition to the aggregate band, a peak at the known position of the monomer, although from the absorption cross sections it was estimated that the fraction of monomer was below 0.5%.[38] Also, Kuhn has shown that as little as 1 part in 10^4 of a monomeric excitation trap incorporated into a J-aggregated cyanine dye quenches half the excitation through energy transfer, leading to characteristic fluorescence from the trap.[39] However, to quench >90% of the aggregate emission, as must be the case in the present system, would, from ref 39, require a considerably higher trap concentration. Depending on the spectral overlap properties for resonance energy transfer, 0.1–1% monomer would be sufficient. No peak corresponding to the monomer is evident in the excitation spectra of any of the C_mC_n compounds examined so that, if present, it must have a low fluorescence quantum yield. Within the context of this mechanism, the deviation of the spectral shape from that of the solution monomer could be due to some residual aggregate fluorescence on the long-wavelength edge. A more speculative explanation for the observed fluorescence behavior is that the 4,4′-donor–acceptor-substituted stilbene aggregate largely loses its coupling in the excited state so that the excitation and therefore the emission become localized. The molecular origin of this effect presumably involves the donor–

(38) Evans, C. E.; Bohn, P. W. *J. Am. Chem. Soc.* **1993**, *115*, 3306.
(39) Kuhn, H. *J. Photochem.* **1979**, *10*, 111.

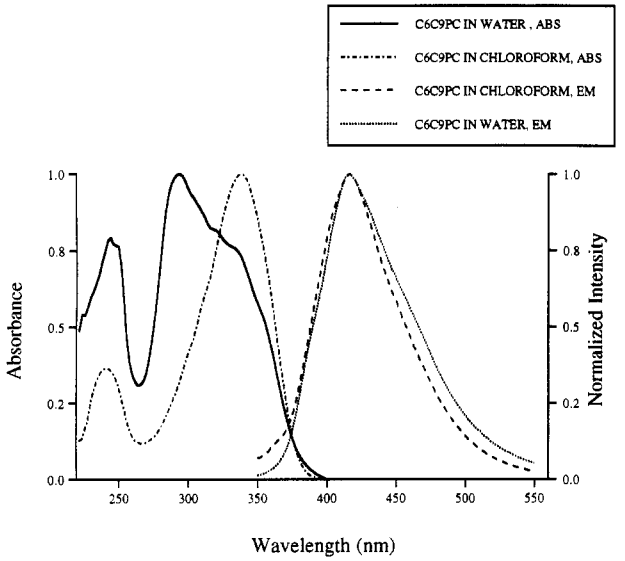


Figure 5. Absorbance and emission spectra of bis(C_6C_9)PC in water and in chloroform.

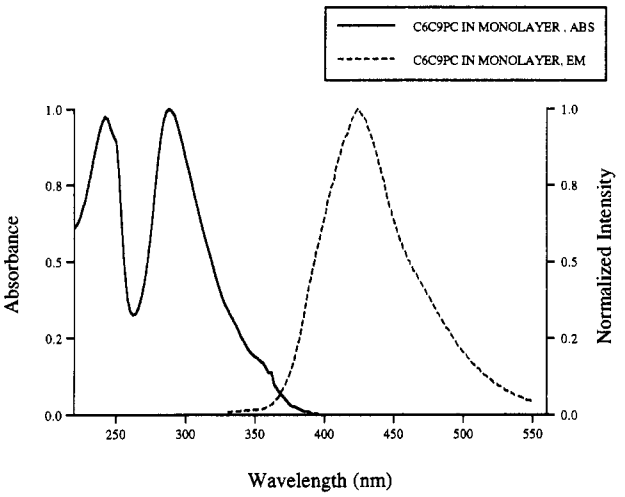


Figure 6. Absorbance and emission spectra of three bis(C_6C_9)-PS layers transferred to quartz.

acceptor substitution. Calculations predict an increase on the order of 15–20 D in the dipole moment of isolated molecules of the 4,4′-donor–acceptor-substituted stilbenes upon excitation.[40] This implies a strong, repulsive interaction between cofacially packed adjacent excited- and ground-state molecules. Although presumably moderated by the aggregation, such repulsion may still be present, weakening the coupling and resulting in monomer-like emission. More detailed photophysical characterization, including quantum yield and lifetime measurements, are needed to distinguish between these mechanisms.

The emission and absorbance spectra for the phospholipid bis(C_6C_9)PC in water and in chloroform, and of three layers transferred to quartz slides, are displayed in Figures 5 and 6, respectively. In chloroform, the emission and absorbance spectra are identical to those obtained for C_6C_9. The multilayer absorbance spectrum possesses the same shape as that from the C_6C_9 monolayer, but the maximum of the shortest energy band is slightly red-shifted (2 nm). This shift may reflect a difference in packing of the stilbene functionalities when they are incorporated into the phospholipid. The multilayer emission spectrum is 8 nm red-shifted relative to that found in chloroform. The crystal

(40) Willand, C. Private communication.

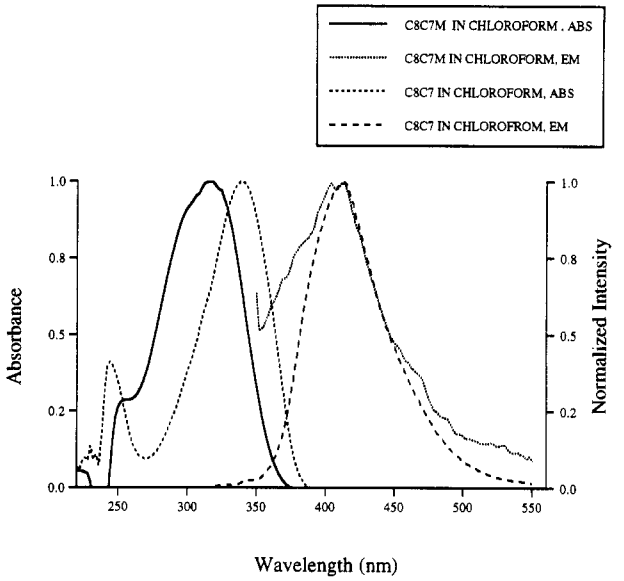


Figure 7. Absorbance and emission spectra of C_8C_7 and C_8C_7M in chloroform solutions.

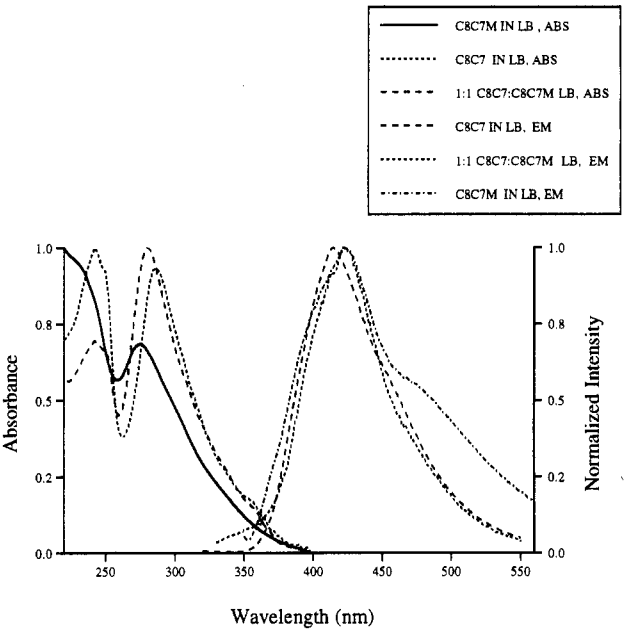


Figure 8. Absorbance and emission spectra of C_8C_7 and C_8C_7M in monolayers, in 1:1 mixed monolayers on quartz, and in solution.

structures of the parent phosphatidylcholines reveal the existence of an offset between the two fatty acid chains by two methylene groups.[24] This mismatch is expected to persist in the two chains of bis(C_6C_9)PC, resulting in a slight offset of the stilbene groups. Thus, the geometry for H-aggregation is not optimal. Yet, an absorbance spectrum virtually identical to that resulting from the monolayer of C_6C_9 is obtained from the phospholipid, indicating that a conformational change is induced that allows the stilbene groups to H-aggregate. This result further demonstrates that H-aggregation provides a minimum free energy conformation for the stilbenes in LB films regardless of whether the chromophore is incorporated into a phospholipid framework or not.

We have prepared C_8C_7M in the hope that H-aggregation would be more restricted, suppressed, or even eliminated. The C_8C_7M compression behavior is very similar to that of its unmethylated analogs (Table 1), and very stable films result from the compression of their monolayers.

The presence of the β-methyl group would be expected to significantly disturb the stacking of molecules in an H-aggregated-type assembly. In chloroform, the shapes of the absorbance and emission spectra are unchanged relative to those of C_8C_7, except that the absorbance maximum is shifted by 20 nm to a shorter wavelength. The emission and absorbance spectra of the C_8C_7 and C_8C_7M in solution, and in monolayers and 1:1 mixed monolayers on quartz, are shown in Figures 7 and 8, respectively. The monolayer absorbance spectrum of C_8C_7M is sharp and blue-shifted relative to that found in chloroform. But C_8C_7M possesses a monolayer absorbance spectrum whose shape and position are quite different from those obtained from the C_mC_n, illustrating that methylation does produce a significant effect on molecular packing. This difference in packing is reflected in a smaller blue shift between the monolayer and chloroform absorbance spectra for C_8C_7M (32 nm) than for C_8C_7 (52 nm). While an H-aggregated-type assembly still exists, its packing probably is "looser" than it is for C_8C_7, thus accounting for the spectral differences (Figure 4). The absorbance spectrum of the 1:1 mixture possesses a maximum whose position is in between those of its two individual components, indicating that molecular packing is intermediate to that found for the two individual components.

Conclusions

The homologous series of donor–acceptor-substituted stilbene fatty acids exhibit H-aggregation in supported monolayers whose spectral properties are insensitive to the particular homologue used either alone or in 1:1 mixtures. This result, taken together with the fact that the monolayer absorbance spectra of the C_mC_n are extremely similar to those obtained from the LB films formed by alkyl-substituted stilbene fatty acids, illustrates that H-aggregation is a minimum free energy packing assembly for stilbene units in LB films. The only effect of sulfone substitution in the C_mC_n appears to be manifested through the perturbation of the mean molecular area values of the homologues. β-Stilbene methylation prevents the molecules from tight packing, producing a pronounced effect on the H-aggregate absorbance spectrum.

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