

Aggregation in Hemicyanine Dye Langmuir-Blodgett Films: Ultraviolet-Visible Absorption and Second Harmonic Generation Studies

Michael A. Carpenter,[†] Craig S. Willand,^{*,‡} Thomas L. Penner,[‡] David J. Williams,[‡] and Shaul Mukamel[†]

Center for Photoinduced Charge Transfer, University of Rochester, Hutchison Hall, Rochester, New York 14627, Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2021, and Department of Chemistry, University of Rochester, Rochester, New York 14627 (Received: September 20, 1991)

Absorption spectroscopy and second harmonic generation have been used to examine the effect of systematic dilution on the aggregation of a hemicyanine dye in Langmuir-Blodgett films. As reported previously, the second-order nonlinear activity initially increases with decreasing dye concentration. Our present results show that the second-order nonlinear susceptibility correlates with the residual amount of the nonaggregated dye as a function of total dye concentration. This result, coupled with the observation that the frequency dispersion of the second harmonic generation shows only one nonlinearly active species, leads us to conclude that the dye aggregates evident in the absorption at high concentration do not exhibit a significant second-order nonlinearity.

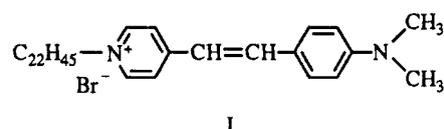
Introduction

For organic compounds, one of the most straightforward ways of forming the noncentrosymmetric structure required to exhibit second-order optical nonlinearity is to prepare a Langmuir (L) monolayer of a suitable derivative bearing a long hydrocarbon chain at the air-water interface and then to deposit it onto a substrate to form a Langmuir-Blodgett (LB) film. Because of their large molecular hyperpolarizability β , dyes of the type referred to as "hemicyanines" (actually styrylammonium salt dyes) are of considerable interest for nonlinear optical (NLO) applications.^{1,2} A number of investigators have examined such hemicyanines as L or LB films.²⁻⁸ One of the more remarkable nonlinear effects reported for such films is that, for a particular hemicyanine derivative, the second-order susceptibility $\chi^{(2)}$ as measured by second harmonic generation (SHG) increased when the dye was diluted with a NLO-inactive material such as a fatty acid.^{9,10} We subsequently showed that this was caused by the chromophores interacting at high concentration to form hypsochromically-shifted aggregates.¹¹ The loss in activity at high concentration could in part be caused by the use of an input laser frequency that resulted in a second harmonic frequency in resonance with the nonaggregated or molecular dye at low dye concentrations but not with the blue-shifted aggregated dye at high concentration. Beyond this simple dispersion consideration, our results also suggested that the aggregates had a lower effective β than molecular dye since the effect persisted even when the incident light was far from resonance for either species. At that time we examined only two concentrations and two laser input frequencies. We have now investigated the whole concentration range of hemicyanine dye and fatty acid spectrophotometrically and have made an extensive investigation of the frequency dispersion of $\chi^{(2)}$ spanning the absorption region of the different species. The results support and refine our earlier investigation. In fact, we demonstrate that the aggregates are essentially completely NLO-inactive and that the second-order nonlinear susceptibility correlates with the amount of monomeric dye in the film at all concentrations.

Experimental Section

The structure of the hemicyanine dye I is the same as used previously. The fatty acid used to make dilutions was eicosanoic or arachidic acid (AA).

LB films were prepared as previously described.¹¹ A KSV Instruments Model 2200 trough was used for film fabrication.



Since the nature of the species formed in these films is dependent on the preparation conditions, we repeat here the procedure used. The dye or dye-AA mixture was spread from chloroform solution onto a subphase consisting of 4 mM sodium tetraborate in water deionized and polished with a Millipore Corp. Milli-Q system. The pH of the subphase was 9.2. The solvent was allowed to evaporate for 10 min, and the film was then compressed to a surface pressure of 30 mN/m over 10 min and held for an additional 20 min. It was then deposited onto a fused-silica substrate that had been immersed in the subphase prior to spreading the film. The deposition rate was 2 mm min⁻¹. The substrates were cleaned by soaking in a 3:1 mixture of sulfuric: nitric acid for more than 24 h, rinsed copiously with Milli-Q water, dried in a jet of filtered nitrogen, and treated with an argon plasma for 5 min just prior to use. A series of mixtures of I and AA ranging from pure dye to a 1:10 molar mixture of I:AA was used to prepare LB films. Pressure-area isotherms were measured for each concentration and used to calculate the actual surface concentration of dye.

UV-vis absorption spectra were measured on a Cary 2290 spectrophotometer. This instrument was equipped with a rotation stage to permit oblique-incidence transmission measurements and a Glan-Taylor prism for polarization capability.¹² Data collection was computer-controlled using the Spectra Calc software of Galactic Industries Corp.

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* To whom correspondence should be addressed.

[†] Department of Chemistry, University of Rochester.

[‡] Eastman Kodak Company.

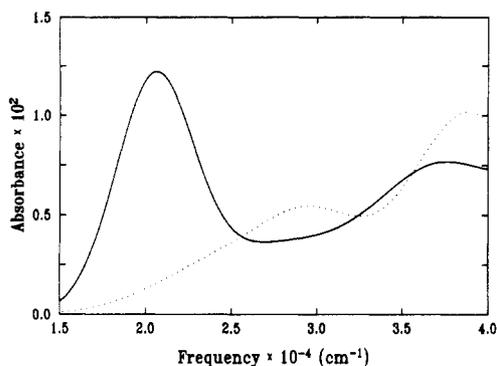


Figure 1. Absorption spectra of monolayers of dye I-AA on fused silica. The solid and dotted lines are for the 1:1 and pure dye, respectively.

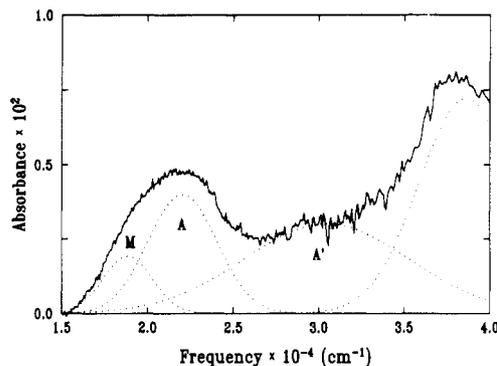


Figure 2. Fit of four Gaussian curves to absorption band of a LB monolayer of a 3:1 mixture of dye I-AA. The band labeled M is identified as the monomeric band. A and A' are different aggregate peaks. (See text.)

Second harmonic generation experiments were performed similarly to the procedure previously described.¹¹ Light from a 10-Hz, Nd:YAG-pumped dye laser was passed through polarization optics before being focused onto the sample using a 400-mm lens and a 45° angle of incidence. A 2 ω -absorbing filter was placed immediately before the sample to remove any spurious second harmonic light. The second harmonic light generated by the sample was separated from the fundamental using a ω -absorbing filter and a monochromator and subsequently detected by a photomultiplier tube. The resulting signal was processed using a boxcar averager and computer. In all cases, the SH was determined to be p-polarized for both p- and s-polarized input. This is consistent with an overall $C_{\infty v}$ symmetry for the molecular orientation with the symmetry axis lying along the surface normal.

Results and Discussion

UV-vis absorption spectra for mixed dye-AA and pure dye monolayer films using a normal-incidence geometry are depicted in Figures 1 and 2. It can be seen that the high (pure) and intermediate (3:1 dye I:AA) dye concentration films give clear evidence of blue-shifted absorption bands relative to the dilute dye concentration (1:1 dye I:AA) film whose absorption peak position is similar to that in chloroform solution. This is consistent with previous observations which suggested the existence of a H-aggregated dye species in highly concentrated hemicyanine dye films and identified the peak in diluted films with the monomeric dye.¹¹

Polarized absorption measurements carried out at an incidence angle of 45° yield a dichroic ratio for A_s/A_p of 1.05 for a diluted (1:1) dye mixture. For the aggregate band in the pure dye a similar value of 1.10 was measured. From these polarization results it can be concluded that monomeric and aggregated dye have similar tilt angle orientation. Since the relevant optical constants are not known, we cannot make an accurate assessment of the dichroic ratio in terms of an orientational order parameter. However, using a value of 1.1 for A_s/A_p and a reasonable estimation of the refractive index at the absorption yields a tilt angle

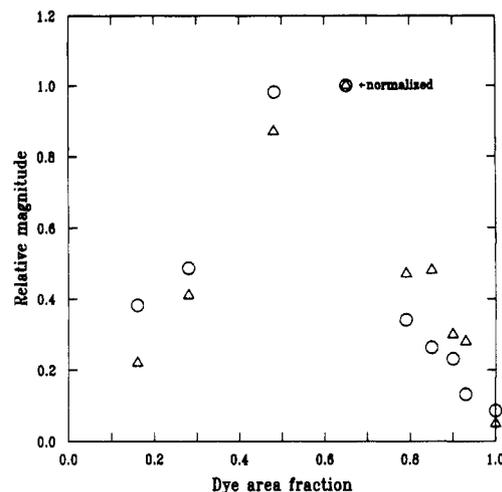


Figure 3. Plots of the monomer band absorption area (O) derived from the spectral curve fit and $\chi^{(2)}$ (Δ) measured as the square root of the second harmonic intensity vs the total dye concentration in the LB films.

of about 40°.¹² This agrees well with values of 37° and 40° previously reported for this chromophore by SHG polarization³ and electron diffraction,¹³ respectively.

The UV-vis spectra indicate that the degree of aggregation appears to be extremely dependent on the overall dye concentration. The most dilute (1:10) and pure dye films consist nearly entirely of monomeric and aggregated species, respectively, whereas the films at intermediate dye concentrations show evidence for the coexistence of both kinds of species. We performed a series of spectral deconvolutions of the absorption data using Spectra Calc software with the results for a typical film shown in Figure 2. Nonlinear least-squares analysis required four Gaussian bands to closely reproduce the observed spectra for all film concentrations over the whole spectral region. In all cases, the experimental and theoretical spectra were virtually indistinguishable. The Gaussian peak height, width, and position served as adjustable parameters for all deconvolutions. However, it was found that only that the peak heights were appreciably concentration-dependent; the peak width and positions showed little variation for all the films studied. The highest energy transition (38 700 cm^{-1}) showed reasonable Beer's law behavior with its area scaling linearly with overall dye content. This would seem to be an aggregation-independent transition of the hemicyanine dye.

The lowest energy transition (band M, 18 800 cm^{-1}), as reported earlier,¹¹ corresponds to the monomeric dye species. The area of this band derived from the curve fitting is shown in Figure 3 as a function of overall dye concentration. As with the high energy band, there is a linear dependence of area on overall dye concentration *but only for films where the mole fraction of dye is less than 0.5*. Above this level the monomer band monotonically decreases in intensity as more dye is added to the film. Finally, the pure dye film shows almost no evidence of the monomeric dye species.

The onset of the decrease in actual monomer dye concentration with increasing dye content occurs simultaneously with the appearance of two new bands A and A' (21 400 and 30 100 cm^{-1}). Whether these actually represent two specific aggregate sizes and/or packing geometries or alternatively a progressive change in these properties with concentration cannot be determined from our data. In any case their SHG properties appear to be identical (see below). For the pure dye film the band at 30 100 cm^{-1} predominates.

The major question is what effect the aggregation phenomenon has on the molecular hyperpolarizability β of the dye. The square root of the second harmonic intensity $I_{p-p}^{2\omega}$ is proportional to $\chi^{(2)}$.

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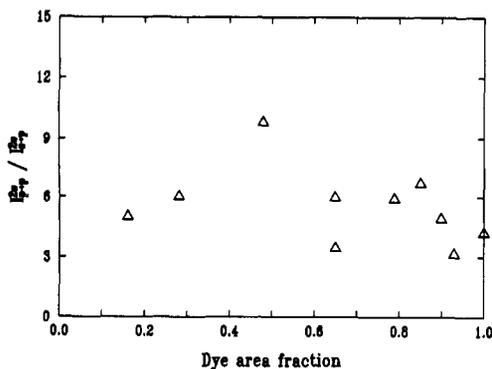


Figure 4. Second harmonic polarization ratios vs the total dye concentration in the LB films.

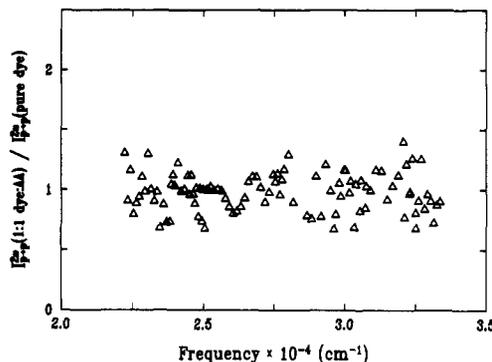


Figure 5. Relative second harmonic intensities of a 1:1 mixture of dye I:AA and pure dye films as a function of the frequency of the fundamental input beam.

This value, using 1064-nm input, is depicted in Figure 3 as a function of overall dye concentration along with the normalized monomer dye content derived from the absorption curve fitting. The similarity in the concentration dependence of these two properties strongly suggests that the monomer dominates in the SHG process. While it is true that this complex concentration profile of $\chi^{(2)}$ could be a result of differing orientations of the SH-active species, the second harmonic polarization ratios, a property strongly dependent on molecular orientation, indicate this not to be the case (see Figure 4). It must therefore be concluded that the monomer has a much larger hyperpolarizability than the aggregate species at this wavelength. Using a two-state model for the hyperpolarizability¹⁴

$$\beta(2\omega; \omega, \omega) = \frac{\beta_0 \omega^4}{(\omega_{eg}^2 - 4\omega^2)(\omega_{eg}^2 - \omega^2)} \quad (1)$$

where β_0 is the frequency-independent molecular hyperpolarizability and ω_{eg} is the transition energy. If $\beta_0(\text{monomer})$ and $\beta_0(\text{aggregate})$ are comparable in magnitude, then one would expect the dispersion of the second harmonic intensities for monomeric and aggregated dye films to be vastly different, especially in the near-resonant and resonant regimes. The dispersion of the ratio $I_{p-p}^{2\omega}(\text{mixed})/I_{p-p}^{2\omega}(\text{pure})$ is shown in Figure 5. As can clearly be seen, the aggregated (pure) and monomeric (mixed) dye films have identical frequency dependencies. Combining these results with the correlation of $\chi^{(2)}$ and monomer amount as a function of dye concentration leads us to conclude that the aggregate does not contribute to the second harmonic signal.

There are a number of possible explanations for this lack of nonlinear response in the aggregate. First, the aggregates may be oriented with the chromophores lying in the plane of the film. However, the aggregate nonlinear response is about 2 orders of magnitude less than that of the monomer, requiring nearly perfect alignment in the plane of the film for this to be the cause. Also, the results of our linear dichroism measurement indicate that the

orientation of the chromophores is very similar for the monomeric and aggregated forms. Second, intermolecular interactions may produce a reduction in $\beta_0(\text{aggregate})$ relative to the monomer. Such effects could result from either dipole-dipole interactions of neighboring molecules in the aggregate¹⁵ or simple geometrical canceling of the overall nonlinearity due to a center of inversion symmetry in the aggregate. With a tilt angle of ca. 40° it is difficult to visualize how the dye molecules could be arranged in a totally antiparallel orientation in the LB film. However, the aggregates appear to be completely inactive, suggesting that the observed phenomena are not entirely due to dipole-dipole effects. Regardless of the explanation, it seems most plausible to conclude that the aggregate has a much lower intrinsic nonlinearity than the monomer

$$\beta_0(\text{aggregate}) \ll \beta_0(\text{monomer}) \quad (2)$$

Although our results strongly support the idea that the formation of an NLO-inactive aggregate is the source of the apparent increase of $\chi^{(2)}$ on dilution of hemicyanine dye I, there are reports in the literature by Morowsky and co-workers indicating that aggregates of this same compound are, in fact, more active than the monomeric dye.^{16,17} Comparison of the position of the aggregate absorption peak we have measured ($\lambda_{\text{max}} = 332 \text{ nm}$) with that in their publications ($\lambda_{\text{max}} = 410 \text{ nm}$) leads us to conclude that the aggregates formed in the respective sets of experiments are spectroscopically different and quite probably have a different structure, orientation, and therefore $\chi^{(2)}$. The formation of different aggregates results from the different conditions under which the films have been prepared. We have been able to duplicate the 410-nm aggregate reported by Morowsky et al. We find that, as briefly mentioned by these authors,¹⁷ it is necessary to compress the film rapidly and immediately after spreading the dye solution and to deposit it within a short time after compression to form a substantial amount of the 410-nm aggregate. In fact, we find that allowing the film to equilibrate at each stage as we have done in the present experiments yields only the aggregate that we report peaking at 332 nm in this and our previous report.¹¹ Although the equilibration time is critical, the composition of the subphase does not appear to be a major factor as long as it is not acidic (pH > 4) since we have also obtained the shorter wavelength-absorbing aggregate on deposition from pure water. However, the peak is slightly shifted to 355 nm probably due to the different counterion.⁵ Spectra we have monitored at the air-water interface confirm that the 410-nm aggregate is a labile species and disappears on standing at the air-water interface over a period of 20–30 min. Deposition onto fused silica appears to stabilize it.

We will report more fully on the formation and properties of these different aggregate species in a subsequent paper. We wish to emphasize that the LB films of I prepared and characterized in the present paper show the same anomalous dilution effect on SHG behavior as the original reports of Girling et al.^{9,10} and that our proposal of a lack of NLO activity of these aggregates satisfactorily explains the anomalous increase in the effective $\chi^{(2)}$ on dilution of the dye with fatty acid in the films.

Intermolecular interactions may in principle lead to a cooperative enhancement of optical nonlinearities.¹⁸ Molecules located within a coherence size should interact cooperatively with the radiation field, resulting in a possible enhancement. Such cooperativity has been observed in spontaneous emission (superradiance)^{19,20} and has also been proposed to explain the nonlinear optical response of the 410-nm hemicyanine aggregates.¹⁷ Such enhancements may be important in the design of optical materials. We believe that the cancellation of nonlinearities observed here is by no means universal. Other dyes can show cooperativity

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provided the geometrical arrangement and the intermolecular interaction strength are appropriate. A search for such systems is currently underway.

Conclusions

We have prepared a series of Langmuir–Blodgett films of a hemicyanine dye diluted with varying amounts of fatty acid and deposited onto fused silica. Linear spectroscopy shows that, under the preparation conditions, extensive aggregation of the dye occurs at mole fractions of dye greater than 0.5 as indicated by the formation of a new hypsochromically-shifted absorption peak. The absorption spectrum can be resolved into four bands, of which the highest energy one is unperturbed as a function of concentration, a long-wavelength peak identified with the monomeric dye species, and two aggregate bands. Linear dichroism indicates that the chromophore is equally tilted from the surface normal in the monomeric and aggregated states. Both the relative $\chi^{(2)}$ obtained from SHG measurements and the amount of monomeric dye in the films show the same behavior as a function of the dilution by arachidic acid; both initially increase with a decrease

in overall dye concentration and then below a mole fraction of 0.5 decrease in an approximately linear fashion. The wavelength dispersion of the second harmonic generation from LB films of pure dye and a 1:1 mixture with arachidic acid are identical despite having drastically different absorption spectra. These results lead us to conclude that the aggregates formed in the films at a mole fraction of dye above 0.5 are completely NLO-inactive. This inactivity is a consequence of intermolecular interactions within the aggregate that is either geometrical (caused by near centrosymmetric aggregate structure) or electronic (dipole–dipole coupling) in nature or some combination of the two.

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Registry No. 1, 103998-45-4; AA, 506-30-9; eicosanoic acid, 506-30-9.

Structurally Defined Redox Assemblies. Molecular Level View of Phospholipid Quinone Monolayers at the Air–Water and Gold–Water Interfaces

Min D. Liu, Charles R. Leidner,*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

and John S. Facci*

*Xerox Webster Research Center, 800 Phillips Road, Webster, New York 14580, and Center for Photoinduced Charge Transfer, Department of Chemistry, University of Rochester, Rochester, New York 14627
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Langmuir–Blodgett techniques have been employed to prepare well-defined, redox-active monolayers of an anthraquinone-functionalized dipalmitoylphosphatidylcholine, DPPC-AQ, and mixed monolayers of DPPC-AQ and DPPC at the air–water and gold–water interfaces. The π - A isotherms of the mixed monolayers indicate the formation of a eutectic composition near 25 mol % DPPC-AQ. A comparison of the Langmuir film behavior of DPPC, DPPC-AQ, and the anthracene analogue DPPC-AN indicates that the bulky anthraquinone group reorients from the hydrophobic region of the monolayer in expanded (LE) films to the aqueous subphase in condensed (LC) films. The extended molecular conformation is also evident in supported monolayers (“heads-down” DPPC-AQ on gold) from ellipsometric measurements. The thickness of a condensed Au/DPPC-AQ film is ca. 9 Å greater (36 Å vs 27 Å) than the corresponding DPPC monolayer. Analysis of the ellipsometric data suggests that DPPC-AQ transfers to the Au surface in an extended conformation at all accessible transfer pressures. The cyclic voltammetric response of the supported monolayers immersed in aqueous perchlorate electrolyte is well-defined and nearly ideal. Subtle voltammetric features of the various monolayers in perchlorate electrolyte are enhanced in aqueous chloride and *p*-toluenesulfonate electrolytes, especially in condensed films. Such behavior is further exaggerated in trilayers. These voltammetric features are explained in terms of the supramolecular architecture of the monolayer.

Introduction

Redox reactions of molecules within structurally well-defined assemblies are ubiquitous in biological processes. Respiration and photosynthesis are prime examples where a structurally defined “reaction center” composed of spatially segregated redox partners leads to specific and efficient energy transduction.¹ The recent heightened interest in structurally defined redox assemblies within

the electrochemical community has arisen largely because of the need for molecularly defined electrode surfaces, as exemplified by the body of work on the adsorption of functionalized alkanethiols on gold,² sequentially assembled bilayers³ and pillared films⁴

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