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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, dyes of the type referred to as "hemicyanines" (actually styrlylammonium salt dyes) are of considerable interest for nonlinear optical (NLO) applications. A number of investigators have examined such hemicyanines as L or LB films. 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. We subsequently showed that this was caused by the chromophores interacting at high concentration to form hypochromically-shifted aggregates. The loss in activity at high concentration could in part be caused by the use of an input laser spanning the absorption region of the different species. The results support and refine our earlier investigation. 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 deionized and polished Milli-Q water. 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. Data collection was computer-controlled using the Spectra Calc software of Galactic Industries Corp.

Experimental Section

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

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Second harmonic generation experiments were performed similarly to the procedure previously described. Light from a 10-Hz, Nd:YAG-pumped dye laser was passed through a polarization optics before being focused onto the sample using a 400-mm lens and a 45° angle of incidence. A 2ω-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 second harmonic intensity immediately before the sample to remove any spurious second harmonic light was determined to be p-polarized for both p- and s-polarized input. This is consistent with an overall C2v 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. 

Polarized absorption measurements carried out at an incidence angle of 45° yield a dichroic ratio of $A_p/A_s$ 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 $A_p/A_s$ and a reasonable estimation of the refractive index at the absorption yields a tilt angle.

The solid and dotted lines are for the 1:1 and pure dye, respectively.

![Figure 1.](image)

**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.](image)

**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.)

Whether these actually represent two specific aggregate sizes with increasing dye content occurs simultaneously with the appearance of about 40°. This agrees well with values of 37° and 40° previously reported for this chromophore by SHG polarization and electron diffraction, 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 frequency dependence 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, 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 $\chi^{(2)}$ of the dye. The square root of the second harmonic intensity $I_{2\omega}$ is proportional to $\chi^{(2)}$.

Aggregation with Heminicyanine Dye


orientation of the chromophores is very similar for the monomeric and aggregated forms. Second, intermolecular interactions may produce a reduction in \( \beta_2(\text{aggregate}) \) relative to the monomer. Such effects could result from either dipole–dipole interactions of neighboring molecules in the aggregate\(^{15,16,17} \) 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 an 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

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\beta_2(\text{aggregate}) \ll \beta_2(\text{monomer})
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Although our results strongly support the idea that the formation of an NLO-inactive aggregate is the source of the apparent increase in \( \chi^{(2)} \) 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.\(^3 \) 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 the course 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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Structurally Defined Redox Assemblies. Molecular Level View of Phospholipid Quinone Monolayers at the Air-Water and Gold-Water Interfaces

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Langmuir–Blodgett techniques have been employed to prepare well-defined, redox-active monolayers of an anthraquinone-functionalized dipalmitylphosphatidylcholine, DPPC-AQ, and mixed monolayers of DPPC-AQ and DPPC at the air–water and gold–water interfaces. The x–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 multilayers. 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 alkane-thiols on gold,2 sequentially assembled bilayers3 and pillared films4

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