Protonation and monolayer aggregation studied by second-harmonic generation

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Various types of aggregates have been studied in Langmuir–Blodgett-type monolayers of selected pyridine and hemicyanine dyes. Environmental changes such as protonation or admixture of chromophores with opposite donor–acceptor characteristics result in dramatic changes of the measured surface susceptibility $\bar{\chi}_s^{(2)}$. Both enhanced $\bar{\chi}_s^{(2)}$ values in H aggregates following the shape of the linear absorption band and vanishing $\bar{\chi}_s^{(2)}$ values of antiparallel dimers or aggregates have been observed. The experimental results suggest that linear and nonlinear measurements need to be considered for a correct interpretation of the experimental results on monolayer aggregation.

1. INTRODUCTION

In recent years a growing interest in materials with large second-order nonlinear susceptibility has developed. Organic materials seem to be especially promising candidates for future optoelectronic applications. For an actual data compilation and recent review see Ref. 1. For the qualitative characterization of such materials with respect to nonlinear susceptibility $\bar{\chi}_s^{(2)}$ and nonlinear hyperpolarizability $\bar{\alpha}^{(2)}$, the method of second-harmonic generation (SHG) in monolayers deposited onto SHG-inactive surfaces, such as fused quartz, is now well established. However, it should be pointed out that the determination of microscopic molecular quantities such as the essential tensor component of $\bar{\alpha}^{(2)}$, $\alpha_{z'z'z'}^{(2)} = \beta$, is by no means straightforward. Actually, this relation is already a simplification because the β value derived from electric-field-induced SHG[1] contains, besides the component $\alpha_{z'z'z'}^{(2)}$, several spatially averaged contributions. In addition, all surface SHG measurements[2–5] start from the assumption that $\alpha_{z'z'z'}^{(2)}$ is the only nonvanishing component of the molecular hyperpolarizability tensor. Also, local-field corrections and molecular interactions are neglected; these two assumptions are generally not true for aggregates.[6,7] In particular, H-type aggregates, because of their narrow-band spectral concentration at the short-wavelength side of the linear monomer absorption band,[7,8] are attractive sources for large nonlinearities. Because both aggregates and monomers occur in the same monolayer with *a priori* unknown concentration ratios and unknown absorption cross section of molecules in the aggregate phase, the derivation of molecular nonlinear properties from such a two-component system is complicated. Consequently we would like to demonstrate that a combined study of linear absorption measurements and SHG of monolayers leads to a better understanding of such systems.

2. EXPERIMENT

All monolayer samples were first prepared on aqueous subphases by standard Langmuir–Blodgett (LB) techniques and were subsequently transferred onto solid substrates from fused quartz. Linear absorption measurements for various angles of incidence and under s- and p-polarized excitation were performed with a monolayer absorption spectrometer.[9] Measurements under normal incidence served to check for the absence of rotational anisotropies. The dichroic absorption spectra of Figs. 1–3 were taken under an angle of incidence of 45°. This procedure was also used for the calibration of the surface density N_s of the samples of the protonation series (see Subsection 3.A); samples were prepared by spreading acidified dye solution in isopropanol on purified quartz plates, using cotton wads. For the sake of simplicity, all susceptibility data refer to a coverage density $N_s = 2.5 \times 10^{14}$ cm^{-2}.

The nonlinear-optical measurements were carried out with a tunable dye laser pumped by an excimer laser and a Nd:YAG laser operating at its fundamental wavelength (1064 nm). The dye laser provided pulses of 15 nsec, with a pulse energy of 3–20 mJ, depending on the wavelength of operation (700–940 nm). The Nd:YAG laser pulses lasted 4 nsec with 12-mJ energy. As reference samples for the nonlinear measurements we used the two hemicyanine derivatives, compounds 1 and 2, with the following chemical structure formulas and β and $\chi_{yzy}^{(2)}$ values measured at 1064 nm (Ref. 10):
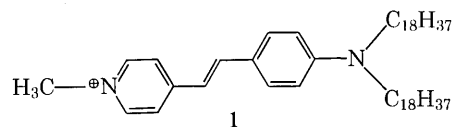
$\beta(1) = 2.5 \times 10^{-27}$ esu, $\chi_{yzy}^{(2)}(1) = 4.3 \times 10^{-14}$ esu;
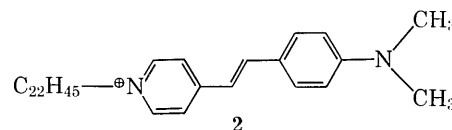
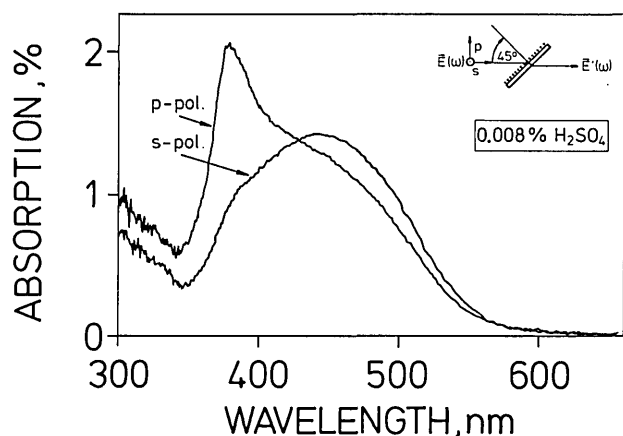$\beta(2) = 2.3 \times 10^{-28}$ esu, $\chi_{yzy}^{(2)}(2) = 9.8 \times 10^{-14}$ esu. Both susceptibilities were derived from the expression

Fig. 1. Dichroic linear absorption spectrum of HAPP-covered LB samples with vanishing nonlinearity after 0.008% H_2SO_4 addition. Inset shows the definition of s- and p-polarized excitation geometry.
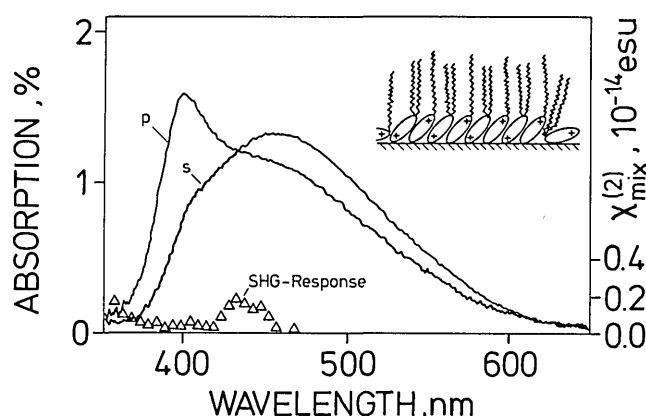

Fig. 2. Dichroic absorption spectra of hemicyanine monolayer mixture together with the SHG response. The inset shows the schematically assumed arrangement of both dyes.
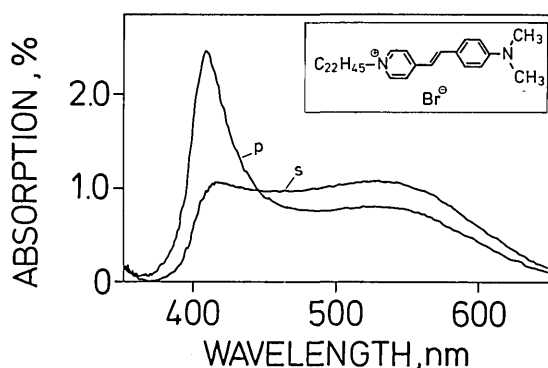

Fig. 3. Dichroic absorption spectra of hemicyanine monolayers forming H aggregates with peak absorption at 405 nm. Inset shows chemical structure formula.

$$\chi^{(2)}_{yzy} = \chi^{(2)}_{xzx} = \chi^{(2)}_{zxx} = \chi^{(2)}_{zyy} = \tfrac{1}{2}N_s \sin^2 \vartheta \cos \vartheta \beta, \qquad (1)$$

with ϑ denoting an average tilt angle between the molecular z' axis and the surface normal.[4,5,11,12]

Hemicyanine monolayers showed, under linear and non-linear tilt angle analysis, rather large values for ϑ for monomer orientation and a strong tendency for the upright posi-

tion for molecules in H aggregates. The occurrence of measurable aggregation critically depended on the preparation. All LB layers were transferred from the surface of pure Milli-Q-water with a transfer speed of typically 1 cm/min and a surface pressure of 30–40 mN/m. The formation of H aggregates could be enhanced by compression of the dye film immediately after spreading the dye solution. Also, the composition of the subphase was found to play a critical role for H-aggregate formation. Obvious differences in nonlinear properties[7,12-14] of hemicyanines may be explained with different conditions of monolayer preparation.

3. RESULTS

We now present three selected experimental examples, in which aggregation plays a major role for monolayer characterization.

A. Protonation Studies

In Ref. 7 it was demonstrated that the nonlinearity of hemicyanine monolayers prepared from compound 1 could not be increased by protonation. A systematic investigation of other substances previously characterized with respect to their nonlinear behavior[11] revealed that the pyridine derivative hexylaminophenylethenylpyridine (HAPP), with the chemical structure
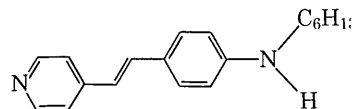
shows, in linear absorption, both an increase and a decrease of the absorption band near 500 nm when protonated by HCl addition in liquid solution (Fig. 4). Hence we expected a concomitant increase and decrease of its nonlinearity because of changes in the resonant enhancement of the second-harmonic radiation on excitation with the dye laser at 870 nm. In fact, the second-order susceptibility $\bar{\chi}^{(2)}_s$ should follow the shape of the linear absorption $\alpha^{(1)}$ at frequency 2ω.[2]

Figure 5 shows the dependence of $\sqrt{I_{45°,s}}^{SH}$ versus the protonation-induced absorption at 435 nm of the (solid) dye film. Addition of H_2SO_4 rather than HCl resulted in more-reproducible monolayer absorption data because the presence of water in HCl caused inhomogeneous dye layers.

$I_{45°,s}^{SH}$ denotes the measured SHG signal under excitation with a fundamental wave polarized at 45° with respect to the plane of incidence, an angle of incidence of 45°, and s-polarized SHG detection. Because $I_{45°,s}^{SH}$ is proportional to $|\chi^{(2)}_{yzy}|^2$ and this susceptibility component follows $\alpha^{(1)}(2\omega)$, we expect a linear dependence of the square root of the second-harmonic intensity versus protonation-induced absorption. This is in fact the case, as shown in Fig. 5. Also given in this figure are experimental data for $\chi^{(2)}_{yzy}$, taking into account a constant tilt angle of 66 ± 5° and an approximate coverage density $N_s = 2.5 \times 10^{14}$ cm^{-2}. Addition of 0.003% H_2SO_4 to the solution of HAPP before the solvent is evaporated on the quartz substrate apparently raised the susceptibility $\bar{\chi}^{(2)}_s$ by a factor of 4.7. Note that the addition of 0.003% H_2SO_4 to a 5×10^{-4} M solution of HAPP in propanol corresponds to a HAPP:H_2SO_4 ratio of 1:1. The value for $\bar{\chi}^{(2)}_s$ remained constant to as great as 0.006% addition of H_2SO_4. Further
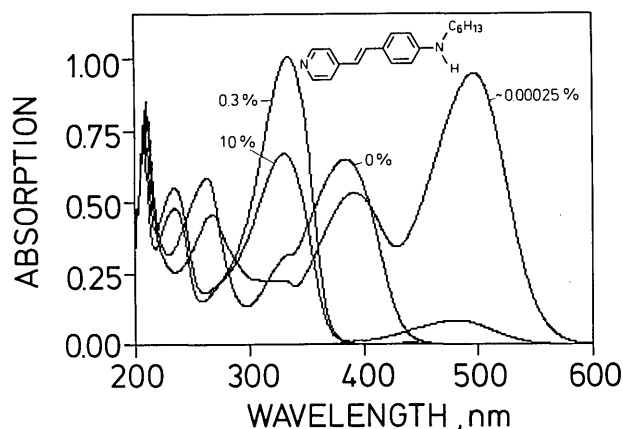
Fig. 4. Linear absorption spectra of HAPP in a propanol solution with the addition of various percentages of HCl.
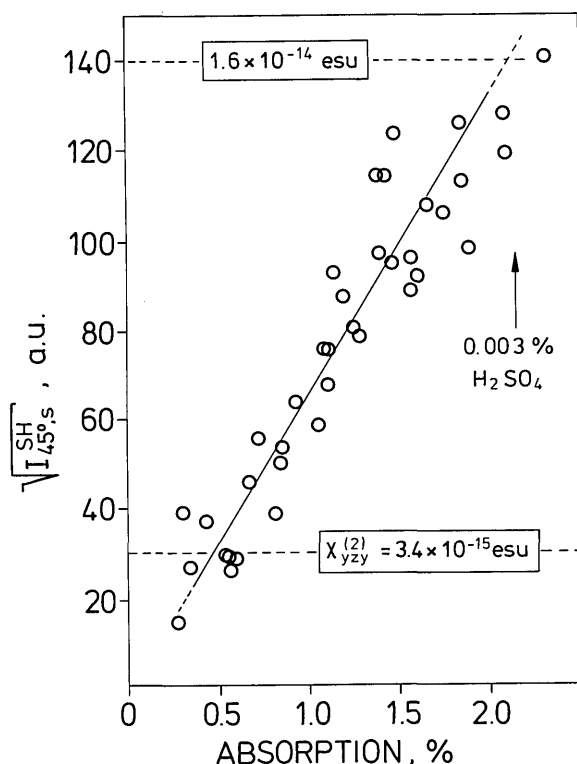

Fig. 5. Square root of selected SHG signals versus protonation-induced absorption of a LB film at 500 nm. Susceptibility data for unprotonated dye monolayer and for protonation by 0.003% H_2SO_4 addition are also given.

protonation led to a surprising effect. In approximately 30% of the experiments with H_2SO_4 addition the nonlinearity $\bar{\chi}_s^{(2)}$ dropped by nearly 2 orders of magnitude to 2.3×10^{-16} esu. In the other cases it remained approximately constant. A comparison of the linear absorption spectra revealed that the drop of the second-harmonic signal was in coincidence with the occurrence of a strong H-type aggregate band at approximately 430 nm. As an example, Fig. 1 shows the dichroic linear absorption spectrum of a sample with almost vanishing nonlinearity after 0.008% H_2SO_4 addition. We conclude that the HAPP molecules in the proton-

ated form tend to spontaneous aggregation, leading to inversion-symmetric oligomers.

B. Mixed Monolayers

The second-harmonic-efficient hemicyanine chromophore 1 has the disadvantage for practical applications of forming monolayers with rather large tilt angles ($\vartheta = 82°$ according to Ref. 10), whereas hemicyanine 2 showed ϑ values between 42° (Ref. 12) and 55°,[7] depending on the actual procedure of LB monolayer preparation. To improve the orientation and to study the influence on the aggregation behavior we tried LB mixtures of both dyes, resulting in dichroic absorption spectra, as shown in Fig. 2, taken for a mixture of 1.4:1.0 of compound 1 to compound 2 and again normalized to a total coverage density $N_s = 2.5 \times 10^{14}$ cm^{-2}. The nature of the absorption band centered at 405 nm, which is presumably due to H-type aggregates formed from both constituents of the mixture, has been studied by SHG on excitation at 810 nm. In comparison with the susceptibility of compound 1 at this wavelength and concentration (5.3×10^{-14} esu), the nonlinearity of the mixture dropped by a factor of 50 to $\chi_{mix}^{(2)} = 0.1 \times 10^{-14}$ esu, indicating an antiparallel orientation of both chromophores in the aggregate phase, as depicted in the inset of Fig. 2. A systematic variation of the excitation wavelength between 720 and 940 nm revealed that the resulting susceptibility at the spectral position of the antiparallel aggregates is even lower than the $\bar{\chi}_s^{(2)}$ contribution of the remaining monomers that show up near 440 nm (triangles in Fig. 2).

C. H Aggregates

Experimental results concerning the formation of H-type aggregates are presented in Figs. 3 and 6. Figure 3 shows dichroic absorption spectra of monolayers prepared from pure hemicyanine 2. Figure 6 depicts details of nonlinear measurements, indicating that the second-harmonic intensity $I_{p,p}^{SH}$ (p-polarized excitation between 720 and 940 nm, p-
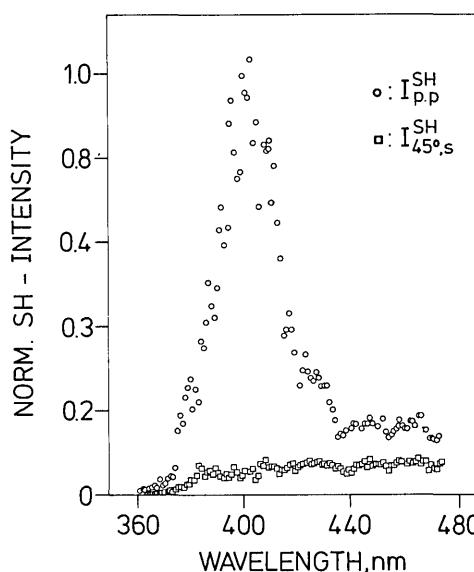

Fig. 6. Nonlinear response of H aggregates between 360 and 470 nm for two different second-harmonic intensities, $I_{p,p}^{SH}$ and $I_{45°,s}^{SH}$. For details, see the text.

polarized second-harmonic detection) follows approximately the square of the p-polarized linear absorption band centered at 405 nm, as shown in Fig. 3.

The second-harmonic intensity $I_{45°,s}^{SH}$, however, does not follow the shape of the linear absorption at all. Hence the computation of a wavelength-independent tilt angle by the ratio of respective second-harmonic intensities according to Refs. 3, 15, and 16 is impossible. Apparently the two-component system must be characterized by wavelength-dependent fractions $\partial N_s(\lambda)/\partial\lambda$ (for monomers) and $\partial N_s{}^*(\lambda)/\partial\lambda$ (for aggregates), with

$$\int_{\Delta\lambda} [N_s(\lambda)/\partial\lambda]d\lambda = N_s,$$

$$\int_{\Delta\lambda} [N_s{}^*(\lambda)/\partial\lambda]d\lambda = N_s{}^*. \tag{2}$$

The quantities N_s and $N_s{}^*$ denote the total coverage densities for molecules in monomers and aggregates, respectively, and $\Delta\lambda$ describes the width of the linear absorption band. A wavelength-dependent tilt angle $\vartheta(\lambda)$ could be described by the expression

$$\vartheta(\lambda) = \frac{N_s(\lambda)\vartheta_0 + N_s{}^*(\lambda)\vartheta^*}{N_s + N_s{}^*}, \tag{3}$$

where ϑ_0 and ϑ^* denote average tilt angles of narrow distribution functions for both subspecies. Because the wavelength-dependent fractions $N_s(\lambda)$ and $N_s{}^*(\lambda)$ are difficult to identify from both linear and nonlinear experimental data, we propose a different approach. This approach makes use of the dominant contribution of those components in the susceptibility tensor that are related to the near vertical alignment of molecules in H aggregates. For this purpose the relation between microscopic polarizability and surface susceptibility can be split into contributions that are due to aggregates ($\bar\chi_s{}^*$) and monomers [$\bar\chi_s^{(2)}$]:

$$\bar\chi_{mix}^{(2)} = \bar\chi_s{}^* + \bar\chi_s^{(2)}$$

$$= N_s{}^*\langle T_{xyz}^{x'y'z'}\rangle^*\bar\alpha^* + N_s\langle T_{xyz}^{x'y'z'}\rangle\bar\alpha^{(2)}. \tag{4}$$

The quantity $\langle T_{xyz}^{x'y'z'}\rangle$ describes the spatially averaged transformation from the molecular coordinate system x', y', z' to the laboratory coordinates x, y, z. For molecules of rodlike structure and a dominant component $\alpha_{z'z'z'}^{(2)}$, the nonvanishing components of $\bar\chi^{(2)}$ are the components of Eq. (1) together with the following expression for $\chi_{zzz}^{(2)}$:

$$\chi_{zzz}^{(2)} = N_s\alpha_{z'z'z'}^{(2)}\cos^3\vartheta^*. \tag{5}$$

Experimentally it has been established that near 405 nm the contributions from $\chi_s{}^*$ prevail and should primarily be due to $\chi_{zzz}{}^* = N_s{}^* = N_s{}^*\,\alpha_{z'z'z'}^*\cos^3\vartheta^*$. The angle ϑ^* is the tilt angle of molecules in the aggregate $\alpha_{z'z'z'}^* = \beta^*(\lambda)$, which is their respective, wavelength-dependent dominant polarizability component with $\beta^*(\lambda) \sim \alpha^{(1)}(2\omega)$.

Linear-optical measurements and the results from Ref. 7 suggest that $N_s{}^* = 0.5(2.5 \times 10^{14}\,\mathrm{cm}^{-2}) = 1.25 \times 10^{14}\,\mathrm{cm}^{-2}$. The β value for hemicyanine monomers has been determined to be 7.7×10^{-29} esu, and the susceptibility $\chi_{zzz}{}^*$ has been determined to be 5.3×10^{-14} esu; both data were taken for 405 nm. Hence we can evaluate the ratio β^*/β for various

Table 1. Ratio of β Values for Aggregates and Monomers

ϑ^* (deg)	β^*/β
0	5.5
10	5.8
20	6.6
30	8.4
40	12.3

assumptions of the tilt angle ϑ^* (see Table 1). Note that the tensor component $N_s{}^*\,\beta^*\cos^3\vartheta^*$ is predominant for assumed tilt angles ϑ^* as great as 40°, where, with the inclusion of linear Fresnel factors (Refs. 16 and 17), this contribution is still larger than all other tensor components by a factor of 5. Table 1 also shows that the ratio β^*/β always exceeds 5.5 and that a realistic consideration of ϑ^* fluctuations may lead to a ratio as high as 10. In fact, enhancement of the molecular hyperpolarizability ratio $\beta^*/\beta = 6$ was obtained in Ref. 7 from intensity considerations.

4. SUMMARY AND CONCLUSION

Three selected examples of aggregation phenomena occurring in LB-type monolayers were studied in detail. It was demonstrated that the application of both linear- and nonlinear-optical techniques is necessary to reveal subtle details of aggregation, such as opposite arrangement of charge-transfer complexes in inversion-symmetric H aggregates.

Protonation of a selected pyridine derivative leads to a considerable increase in its molecular second-order nonlinearity. The buildup and decrease of protonation-induced absorption bands could be monitored by the concomitant changes in the nonlinear surface susceptibility $\bar\chi_s^{(2)}$. The most dramatic event was the protonation-induced change from an optimized susceptibility $\chi_{opt}^{(2)} = 1.6 \times 10^{-14}$ esu (due to H_2SO_4 addition by nearly 2 orders of magnitude) to $\bar\chi_s^{(2)} = 2.3 \times 10^{-16}$ esu (due to spontaneous aggregation into inversion-symmetric oligomers).

The formation of H aggregates in pure hemicyanine monolayers was studied. The assumptions usually used in surface SHG, such as nonexisting molecule–molecule interactions or the concept of a wavelength-independent dominant tensor component $\alpha_{z'z'z'}^{(2)}$ of the molecular hyperpolarizability tensor, no longer hold in such a two-component system of molecules in monomers and aggregates. In agreement with a previous investigation, we established that the hyperpolarizability per molecule in an aggregate, β^*, exceeds (despite the reduced linear absorption) the β value of the monomer at the same wavelength by a factor of at least 6. Alternatively, we might interpret this result as an indication that under the given experimental conditions six molecules of monomer hyperpolarizability β form an aggregate and radiate coherently.

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