

Optical Second-harmonic Generation in Langmuir–Blodgett Films of 2-Docosylamino-5-nitropyridine

G. Decher,^a B. Tieke,^{a*} C. Bosshard,^b and P. Günter^b

^a Ciba Geigy AG, Research Center Plastics and Additives, CH-1701 Fribourg, Switzerland

^b Institute for Quantum Electronics, Swiss Federal Institute of Technology, CH-8093 Zürich, Switzerland

The first preparation of non-centrosymmetric Langmuir–Blodgett multilayer films of 2-docosylamino-5-nitropyridine, and the first measurements of optical second-harmonic generation from these films are reported.

In recent years, interest in organic materials with nonlinear optical properties has increased considerably.^{1,2} Non-centrosymmetric, highly polarizable organic substances are likely to yield materials displaying large optical nonlinearities. Especially suited for device applications in high-speed image processing and optical communication are materials in the form of single crystals, fibres and thin films.¹ Thin films of exactly defined molecular arrangement and thickness can easily be obtained by the Langmuir–Blodgett (LB) deposition technique.³ Second-harmonic (SH) generation has previously been observed from monolayers at the air–water interface and from LB-films.^{5–8} Hitherto, investigations have been restricted to LB-films of two materials in alternating layer structure^{6,7} and to films of a single material in a head-to-tail arrangement of the molecules (Z-type structure).^{5,8}

We now report optical second-harmonic generation from a well ordered LB film of only one material, which does not exhibit a head-to-tail arrangement of the molecules. Docosylamino-5-nitropyridine (DCANP) can be described as a long-chain analogue of 2-cyclo-octylamino-5-nitropyridine (COANP), which exhibits large nonlinear susceptibilities in the crystalline state.⁹ DCANP (m.p. 82–85 °C) is easily synthesized by nucleophilic substitution of 2-chloro-5-nitropyridine with *n*-docosylamine in over 80% of the theoretical yield. It forms stable monolayers on pure water (Lauda filmbalance FW1; Milli-Q water; $\sigma \leq 10^{-18}$ S cm⁻¹). A pressure–area isotherm of DCANP is shown in Figure 1. From the molecular packing density at film collapse (0.31 nm² per molecule) a highly tilted arrangement of the alkyl chains can be deduced. A possible orientation of one molecule on the water surface is represented in Figure 1.

Monolayers of DCANP can easily be transferred onto various hydrophobic substrates [*e.g.* glass, quartz-glass, silicon hydrophobized with trichloro(octadecyl)silane, or zinc selenide] at a surface pressure of 18 mN m⁻¹ and a

temperature of 15 °C. For deposition the substrates were dipped perpendicularly through the monolayer, which was equally transferred on both down- and up-stroke. This way films of a thickness of 270 bilayers, showing no visible turbidity, could be prepared without any change in the transfer ratio. Fourier transform i.r. attenuated total reflectance (FTIR-ATR) spectra of LB-films on zinc selenide are essentially the same as those obtained from bulk material, indicating identical chemical species. Polarized u.v.–visible spectroscopy showed that the chromophores are homogeneously oriented parallel to the dipping direction over the whole film area [$\alpha_{\parallel}(374 \text{ nm}) = 24\,300 \text{ cm}^{-1}$; $\alpha_{\parallel}/\alpha_{\perp} = 1.6$].

Optical second-harmonic generation was studied on LB-films ranging from 5 to 270 bilayers in thickness. A Q-switched Nd-YAG laser (Quantronix 416, 2.3 kW at 1064 nm, repetition rate 500 Hz, pulse width 350 ns) was used. The laser was focused into the LB-film with a collimating lens (focal length 80 mm) down to a diameter of approximately 42 μm (estimated intensity $I^{\omega} = 220 \text{ MW cm}^{-2}$) and the second-harmonic signal ($\lambda = 532 \text{ nm}$) was detected as described previously.¹⁰ In all experiments the LB-films were irradiated with the laser beam perpendicular to the layer plane.

$$I^{2\omega} = \frac{2\omega^2 d_{\text{eff}}^2 l^2}{c^3 \epsilon_0 (n^{\omega})^2 (n^{2\omega})} (I^{\omega})^2 \text{sinc}^2 \left(\frac{\Delta k l}{2} \right) \quad (1)$$

The SH intensity is given by equation (1),¹¹ where $\text{sinc } x$ denotes $(\sin x)/x$, l is the sample thickness, d_{eff} is the effective nonlinear optical susceptibility, n is the refractive index, c is the speed of light, and $\Delta k = k_2 - 2k_1$ is the phase mismatch between the fundamental and the SH waves with wave vectors k_1 and k_2 , respectively. In agreement with theory [equation (1)] the measured SH intensity increases quadratically with

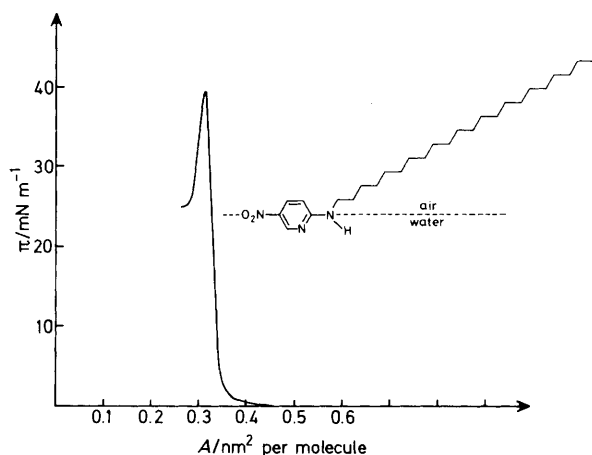


Figure 1. Pressure–area isotherm of a monolayer of DCANP at the air–water interface (Subphase Milli-Q water; T 15 °C); inset: suggested position of a DCANP molecule on the water surface.

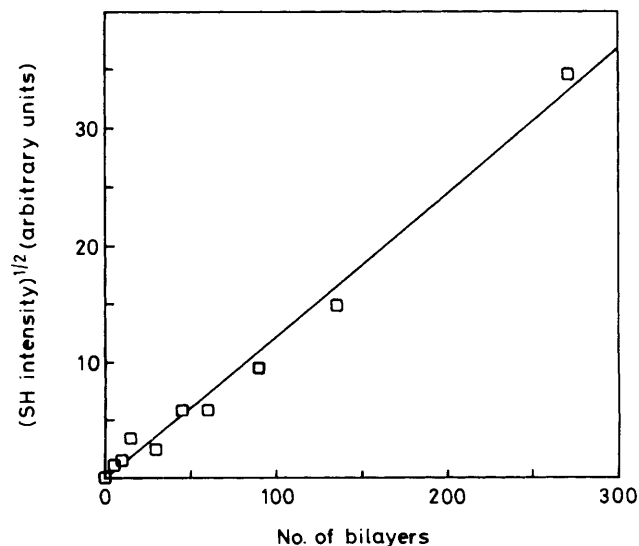


Figure 2. Square root of the second harmonic intensity as a function of the number of bilayers.

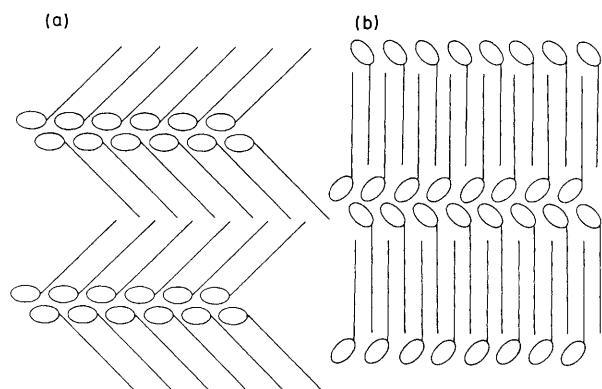


Figure 3. Two structural models for non-centrosymmetric LB-multi-layer films of DCANP: (a) a tilted Y-type bilayer and (b) an intercalated structure. In both cases the resulting macroscopic dipole moment is parallel to the layer plane (straight lines are alkyl chains; ovals represent chromophores).

the film thickness (Figure 2). A LB-film with a thickness of 270 bilayers had a peak conversion efficiency ($I^{2\omega}/I^\omega$) = 2×10^{-7} . Note that the data plotted in Figure 2 originate from different substrates (glass and quartz-glass) and different chemical batches of DCANP.

Independently of the polarization of the fundamental wave, the second-harmonic wave was polarized parallel to the dipping direction. Maximum SH intensities (Figure 2) were observed when the fundamental wave was also polarized parallel to the dipping direction. In the case of the 270 bilayer LB-film the maximum intensity was 110 (± 4) times stronger than the SH intensity resulting from a fundamental wave polarized perpendicular to the dipping direction, whereas for an 18 bilayer film this ratio was 20 (± 3).

Structural studies of the LB-films were carried out by small-angle X-ray scattering (SAXS). The diffractogram of a LB-film composed of 18 bilayers of DCANP showed 12 orders of the (001) reflection, which corresponds to a layer spacing $d_{001} = 4.42 \pm 0.03$ nm. Since the maximum length of DCANP in the fully extended conformation as calculated from a molecular model is only 3.65 nm, *i.e.* 17% shorter than the observed layer spacing, a head-to-tail arrangement of the molecules (X- or Z-type structure) can be ruled out.

Hence our results demonstrate for the first time optical second-harmonic generation from LB-films of a single material which do not exhibit an X- or a Z-type structure. Since the films are highly ordered and the intensity of the second-harmonic increases quadratically with the number of layers, the optical nonlinearity must be a property of the film and can be due neither to interfacial enhancement at the first layer nor to asymmetrical disorder induced by poor deposi-

tion. Two possible structures are shown in Figure 3. The molecules form either a head-to-head and tail-to-tail (Y-type) structure with a large tilt-angle of approximately 40° (± 10) with respect to the layer plane [Figure 3(a)] or an intercalated structure with the alkyl chains nearly perpendicular to the substrate [Figure 3(b)]. In both cases the non-centrosymmetry results from a unique alignment of the chromophores in a single direction. In the case of a Y-type structure this implies the formation of a 'herringbone' pattern as shown in Figure 3(a). The intercalated structure [Figure 3(b)] seems less likely since it can be formed only upon a phase transition of the alkyl chains during or after film transfer, making the formation of a well ordered structure rather unlikely. The formation of the 'herringbone' structure is probably induced by the dipping process and enhanced or stabilized by interlayer hydrogen bridging between the amino and nitro substituents of adjacent molecules. This type of hydrogen bridging is known to exist in single crystals of COANP.¹⁰ In addition, epitaxial deposition may also favour the formation of this unusual morphology.

Further studies concerning the nonlinear optical properties of the LB-films, the film morphology, and variations of the chemical structure are in progress.

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