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Langmuir-Blodgett films of amylose-esters and chiral azo-dyes

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CHAPTER 6

Structure and second harmonic generation of Langmuir-Blodgett films of two chiral amphiphilic azo-dyes.

SUMMARY

The properties and structure of Langmuir-Blodgett films of two new amphiphilic NLO-dyes containing stereogenic (chiral) centers were studied. The dye molecule, 4-[4'-(3R)-palmitoylpyrrolidine-1]-phenylazo]-3-nitro-benzoic acid (KZ16) forms homogeneous structures in the plane of the substrate when the monolayers are transferred into multilayers. Multilayers of 4-[4'-(3R,4R)-dipalmitoylpyrrolidine-1]-phenylazo]-3-nitro-benzoic acid (KDEZ16) which contain two alkyl chains on the pyrrolidine ring showed flow induced orientation in the plane of the film. The tilt angles of the molecules in the multilayer were determined by polarized FT-IR measurements combined with X-ray diffraction. A tilt angle of $\sim 55^\circ$ to the surface normal for the chromophore unit and $\sim 35^\circ$ for the alkyl chain of KZ16 was revealed. KDEZ16 molecules showed a tilt angle of $\sim 35^\circ$ for both the chromophore unit and the alkyl chain with the surface normal in the multilayer.

The SHG properties of mono- and multilayers of KZ16 with different architectures on glass were studied. When a non polar alignment (Y-type bilayer) was measured, a complete cancellation of the second order non linearity was observed. The stereogenic center did not contribute to a non centro symmetric structure at a measurable scale. Alternating layers of the KZ16 dye and arachidic acid behave almost ideal, giving a SHG depending quadratically on the number of bilayers.

INTRODUCTION

Second order non-linear optical effects in organic materials might lead to novel applications in optical communication^{1,2}. Maximum effects can be expected from specially designed

dye molecules situated in a non-centro-symmetric structure in the material. One way to obtain the necessary non-centro-symmetric structure might be the use of chiral dye molecules.

In Chapter 3 and 4 in this thesis ^{3,4,5,6} we reported about the behaviour of such a chiral dye; an ester of palmitic acid and 4-nitro-4'-[(3R)-hydroxypyrrolidine]-azobenzene.

The dye did not show the classical behaviour often found for amphiphilic molecules with the hydrophilic end is pointing to the water surface and the hydrophobic part pointing to the air. The dye appeared to form crystalline domains on the water surface which behaved like H*-aggregates ⁷. Stable transferable monolayers were formed upon mixing the dye with amylose-acetate. The chromophores appeared to be packed antiparallel in the dye domains, a less desired orientation regarding SHG (second harmonic generation). Langmuir Blodgett multilayers of the mixed system did not generate a significant SH signal. However, when the LB-films were heated above the melting point of the dye and cooled down slowly to room temperature, significant SHG was observed. Also cast films of this mixture showed second order non linearity. The second order non linear effects were much larger than those to be expected from an asymmetric interface. The morphology of the thin films after heating appeared to be changed compared to the non heated films, as detected by studying the heating and cooling process under crossed polarizers in a light microscope. The SHG-active films consisted out of large crystalline sheets.

In a first order approximation, the second harmonic generation is known to arise from non centro-symmetric structures ^{8,9}. We suggested that the nonlinear behaviour of the clear films arose from the large crystalline sheets in the film. The stereogenic centers might introduce the necessary non-centro-symmetry in the crystalline packing, however the resulting structure is not necessarily very much off a centro-symmetric one. To explain the large non linear effect, the H*-aggregates are supposed to enhance the effect. The role of H*-aggregates is not fully understood in relation with second order non linearities as is obvious from the literature ^{10,11,12,13,14}.

To get more insight in the influence of the stereogenic center and the H*-aggregates on the non-linear effects we studied the behaviour of a more classical LB-material closely related to the dye studied before.

Like most of the amphiphilic LB-materials, the dyes investigated here (KZ16 and KDEZ16) showed Y-type transfer. The layers were investigated by Fourier Transform Infrared spectroscopy (FT-IR), X-ray diffraction and UV-visible light spectroscopy. A model for the structure of the Y-type layers of the investigated dyes is presented.

In an other study the **SHG** of monolayers of these dyes has been studied in relation to local field effects¹⁵. Also **SHG** properties of mono-and multilayers of KZ16 with different architectures on glass were studied. The structural features of the thin films were studied and their SHG response will be explained in relation to the stereogenic centers of the dyes.

EXPERIMENTAL

Materials.

The synthesis of the chiral NLO-dyes will be reported separately¹⁶. The structural formulae of 4-[4'-[(3R)-palmitoylpyrrolidine-1]-phenylazo]-3-nitro-benzoic acid (KZ16) and 4-[4'-[(3R,4R)-dipalmitoylpyrrolidine-1]-phenylazo]-3-nitro-benzoic acid (KDEZ16) are shown in Figure 6.1.

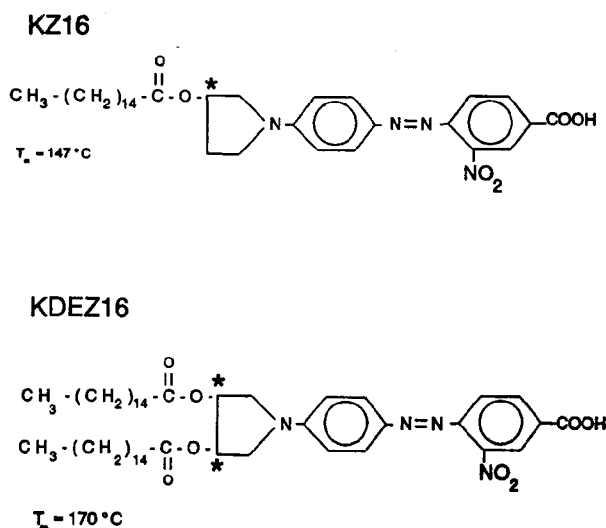


Figure 6.1 Structural formulas of the dye molecules, KZ16 and KDEZ16.

LB-measurements

Monolayer properties were studied by using a computer controlled **Lauda Filmbalance FW2**. The surface pressure was measured with an accuracy of 0.05 mN/m. The subphase was water, purified by double distillation or reversed osmosis and subsequent filtration through a **Milli-Q purification system**. Monolayers were spread from chloroform solutions (Uvasol quality) with a typical concentration of 1 mg of total solute/ml. Isotherms were measured

Structure and SHG of KZ16 and KDEZ16

with a standard compression speed of 10\AA^2 molecular unit⁻¹ min⁻¹.

Transfer experiments were carried out by a vertical dipping method at constant temperature and pressure. A dipping speed of 5 mmlmin was used for the up and down stroke transfer. Alternating layers were prepared using a **KSV 5000** double trough and double sided compression. The connected troughs were filled with pure Milli-Q water or with a **CdCl₂** solution (10^{-3} M) with a pH of 8.2. In the experiments described here, the deposition pressure was set at 28 mN/m for all the monolayers. The **subphase** temperature was 25°C and a dipping speed of 10 mmlmin was chosen.

The monolayers were deposited onto glass slides, cleaned ultrasonically with concentrated chromic acid, washed several times with Milli-Q water, washed ultrasonically with **acetone** and chloroform (all p.a. quality) dried and stored. Just before deposition, the substrate was rinsed with chloroform and partially hydrophobized by treatment with a hexamethyldisilazane-chloroform solution (3:1 v/v) at 50°C for 5 minutes.

Infrared Measurements

Infrared measurements were performed with a **Bruker IFS88** FTIR spectrophotometer equipped with a MCT-A D313 detector. Transmission spectra were recorded of samples on **ZnS** using 4 cycles of 250 scans each according to the method of **Arndt**¹⁷. All spectra were recorded at 4 cm⁻¹ and baseline corrected.

UV/visible light spectra.

A Pye-Unicam SP8-200 UV/Vis spectrophotometer was used to record the spectra of **mono-** and multilayers on one side of a glass slide as well as for the spectrum of the dye in chloroform solution.

X-ray diffraction.

X-ray measurements were performed with a PW 1830 generator and PW 1820 diffractometer with a monochromator in the diffracted beam. Chromium (λ 2.29 Å) was used as radiation source.

SHG measurements.

Linearly **polarized** light with a wavelength of 1064 nm from a Q-switched **Nd:YAG** laser was used. The laser beam irradiated the film at an angle of 45° and the reflected light was

monitored using a photo multiplier. Separation of the harmonic from the fundamental beam was accomplished by a Pellin-Brocca prism and suitable color filters. The fundamental beam was either p or s polarized. The SHG was detected after passing a sheet polarizer either in the p or s direction. Signal sampling and recording took place with a boxcar (Princeton Applied Research, model 162) and computer. The experimental set up is given in Chapter 5.

RESULTS AND DISCUSSION

The pressure-area isotherms of KZ16 and KDEZ16 at different temperatures are presented in fig 6.2A and 6.2B. The extrapolated cross sectional area of the KZ16 molecule in the condensed phase is 36 \AA^2 (Fig. 6.2A).

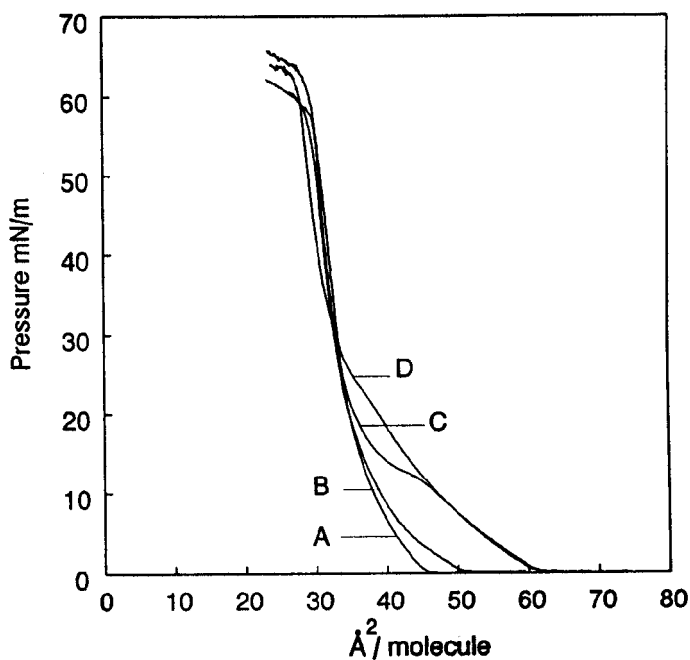


Figure 6.2A Surface pressure isotherms of KZ16 at different temperatures and subphases. A; H_2O , 15°C , B; H_2O , 24°C , C; $[\text{Cd}^{2+}] = 10^{-3} \text{ M}$ $\text{pH} = 8.2$, 13°C , D; $[\text{Cd}^{2+}] = 10^{-3} \text{ M}$ $\text{pH} = 8.2$, 27°C .

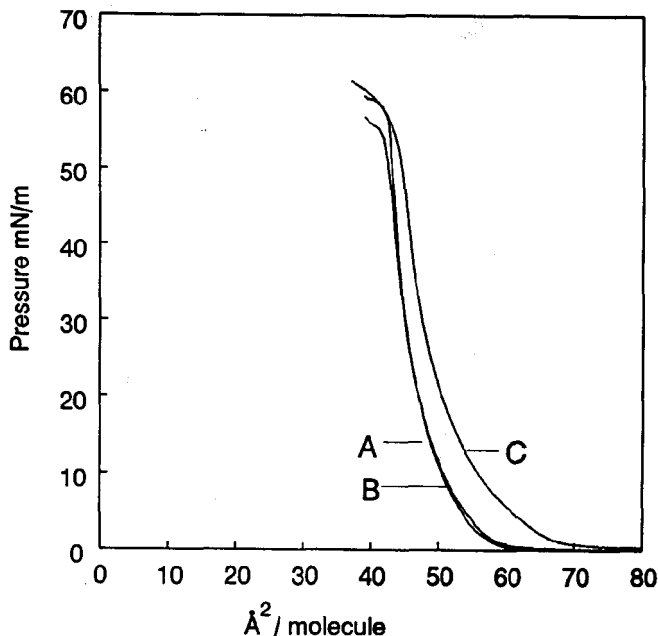


Figure 6.2B Surface pressure isotherms of KDEZ16 at different temperatures and subphases. A; H_2O , $13^\circ C$, B; H_2O , $23^\circ C$, C; $[Cd^{2+}] = 10^{-3} M$ $pH = 8.2$, $23^\circ C$.

The monolayer of the **KZ16-Cd** salt is more expanded in the lower pressure region as can be observed in Figure 6.2A. The isotherms of **KDEZ16** are shown in Figure 6.2B. For **KDEZ16** the cross sectional area of 52 \AA^2 is determined in the condensed state. When the subphase contains Cd^{2+} -ions the occupied area per molecule is 55 \AA^2 in the condensed state. The temperature has no influence on the behaviour of the monolayer of **KDEZ16** in the studied temperature range ($10\text{-}31^\circ C$).

According to the **Coring-Pauling-Koltun(CPK)** models of **KZ16** and **KDEZ16** molecules, the minimum cross sectional area of the molecules assuming that the orientation is perpendicular to the water surface, is 26 \AA^2 and 40 \AA^2 respectively. So from the cross sectional areas found in the isotherms in Figure 6.2A and B it can be deduced that the molecules on the water surface are tilted to a certain angle with the surface normal.

Figure 6.3 shows the stability of the monolayers of **KZ16** and **KDEZ16** at $23^\circ C$ and $\pi =$

28 mN/m. The monolayer of KZ16 on pure water is not completely stable. The stability is enhanced when CdCl_2 is added to the **subphase** and the pH is raised to 8.2.

The second hydrocarbon chain attached to the pyrrolidine ring of **KDEZ16** enhances the stability of the monolayer. Almost immediately a stable **monolayer** is formed on pure water as well as on Cd^{2+} (10^{-3}M).

The monolayers can be transferred onto solid substrates except the **KDEZ16** monolayer on Cd^{2+} (10^{-3}M). An incomplete transfer is obtained in that case, probably due to the formation of a very rigid monolayer. Increasing the temperature of the **subphase** to 31°C or slow down the dipping speed to 1 mm/min does not change the monolayer behaviour.

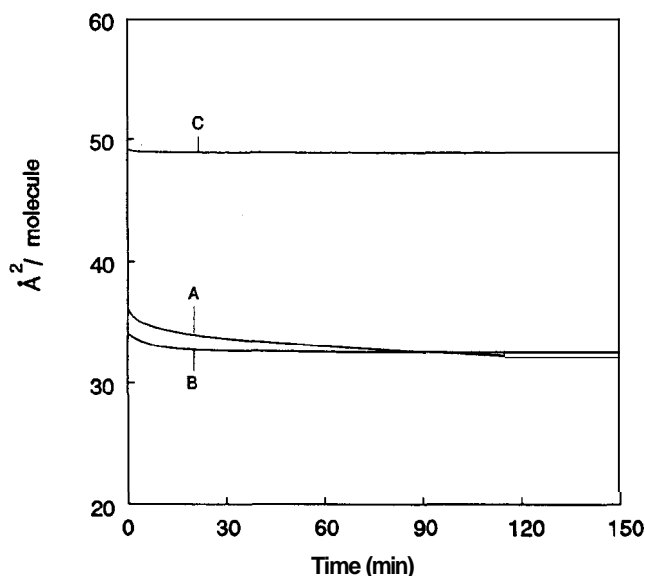


Figure 6.3 Stabilization of monolayers of KZ16 and KDEZ16 at 23°C and $\pi = 28 \text{ mN/m}$. A; KZ16 on H_2O , B; KZ16 on $[\text{Cd}^{2+}] = 10^{-3}\text{M}$, $\text{pH} = 8.2$, C; KDEZ16 on H_2O .

Multilayers were prepared from monolayers of KZ16 on **subphase** with Cd^{2+} (10^{-3}M) and a pH of 8.2. **KDEZ16** was spread on pure water. KZ16 shows a regular Y-type transfer with transfer ratios of 1.0 for the upstroke and 0.9 for the downstroke. **KDEZ16** shows a Z-type transfer for the first two dipping cycles and upon further dipping more Y-type transfer (upstroke 1.0, downstroke 0.7) took place.

X-ray diffraction revealed a layer structure for multilayers of KZ16 and KDEZ16. The results of the X-ray measurements are summarized in table 6.1.

Table 6.1 *X-ray diffraction measurements.*

LB layers (20)	Spacing (Å)
KZ16	45.8
KDEZ16	57.9

FT-IR spectroscopy was used in order to reveal the orientation of parts of the molecules in the multilayer. Since the optics of the reflection spectroscopy have been investigated extensively^{18,19}, many authors have applied these techniques to ultra thin layers^{20,21,22,23}. In this study polarized transmission spectroscopy was used to detect anisotropy parallel to the substrate surface due to flow induced orientation during the dipping process. ZnS was used as substrate. Studying the various vibrational band intensities reveals the orientation of the KZ16 and KDEZ16 molecules in the multilayer. In transmission only vibrations with a component of the transition dipole moment parallel to the substrate surface appear in the spectra. The multilayers were measured before and after heating the sample above the melting temperature and cooling down to room temperature which gives additional information about the orientation if the molecules rearrange in a random distribution after heating. An extra check can be obtained by measuring multilayers in the reflection mode. Reflection spectra are obtained from multilayers deposited on gold coated glass. Grazing angle reflection spectroscopy with p-polarized light detects only vibration modes which have a component of the transition moment perpendicular to the substrate surface.

Figure 6.4 shows the transmission spectra of 19 layers of the KZ16 salt. Spectrum A was obtained when the multilayer was measured "as deposited" and B was the result after heating the monolayer to 185°C for 10 minutes and cooling down to room temperature. Spectrum C shows the difference before and after heating.

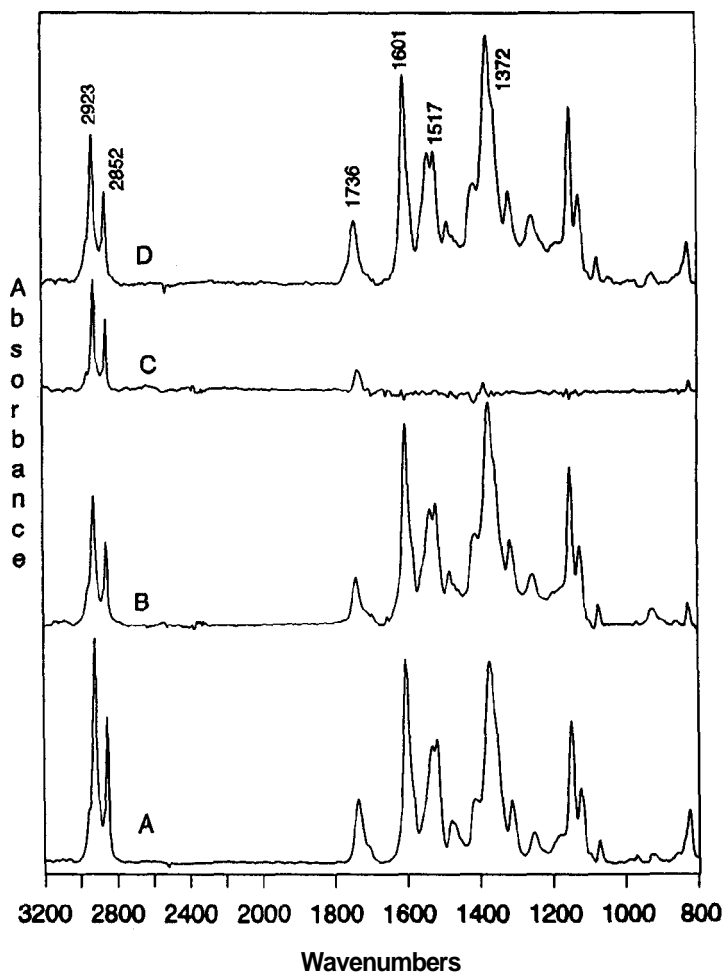


Figure 6.4 Transmission FT-IR spectra of KZ16-salt. A = 19 layers of KZ16-salt on ZnS as deposited, B = same layer after heating to 185°C for 10 minutes. C = difference spectrum before and after heating (A-B), D = bulk spectrum of KZ16-salt in a KBr pellet.

The bulk spectrum of the KZ16 salt was obtained by removing the collapsed monolayer of KZ16-salt on the LB-trough and mixing this material with KBr. A pellet was pressed and thoroughly dried. The bulk spectrum is given in Figure 6.4, spectrum D.

Table 6.11 presents the main mode assignments of the bulk spectra of the KZ16 salt and KDEZ16.

Table 6.II Band assignments of bulk spectra of KZ16 and KDEZ16

Mode	Transition moment M	KZ16 (cm^{-1})	KDEZ16 (cm^{-1})
$\nu_a \text{CH}_3$	\perp C-CH ₃	2953	2956
$\nu_a \text{CH}_2$	\perp C-C-C	2923	2921
$\nu_s \text{CH}_2$	\parallel C-C-C	2852	2852
$\nu \text{C}=\text{O}$ ester	\parallel C=O	1736	1743
$\nu \text{C}=\text{O}$ acid	\parallel C=O		1696
$\nu \text{C}=\text{C}$ (arom.)	\parallel longest molecular axis	1601	1603
$\nu \text{C}=\text{C}$ (arom.)		1532	1535
$\nu_a \text{NO}_2$	\parallel O-N-O, \perp C-N	1517	1517
δCH_2		1469	1468
$\nu \text{C}_{\text{ar}}-\text{N}$	\parallel C-N		1380
$\nu_s \text{COO}^-$		1372	
C-O-C		1144	1145
C-O-C		1120	1115

Two regions of interest can be distinguished in the spectra in Figure 6.4, the 3200 -2800 cm^{-1} area and the region between 1800-1000 cm^{-1} . The region of 3200-2800 cm^{-1} predominantly shows the vibrations associated with the aliphatic chain. The $\nu_a \text{CH}_2$ (2923 cm^{-1}) and $\nu_s \text{CH}_2$ (2852 cm^{-1}) are relatively strong in spectrum A compared to spectrum B. Assuming a random orientation of the alkyl chain after melting, the transition moments ν_a and ν_s in spectrum A have a preferred orientation with respect to the substrate surface. This reveals

a tilted orientation of the **alkyl** chain with respect to the surface normal, because the dipole transition moments are perpendicular to the plane of the **C-C-C** chain axis.

The region from 1800 to 1000 cm^{-1} gives information about the chromophore unit of the dye. The carbonyl mode of the ester group is clearly seen at 1736 cm^{-1} whereas the vibration mode of the carboxylic acid is almost completely absent. This indicates an almost complete conversion of **KZ16** to its cadmium salt. The symmetric carboxylate group at 1372 cm^{-1} is relatively intense, while the asymmetric carboxylate vibration (usually observed between 1610 - 1550 cm^{-1}) is not observed. After heating, the intensities of the vibrations associated with the chromophore unit do not change significantly.

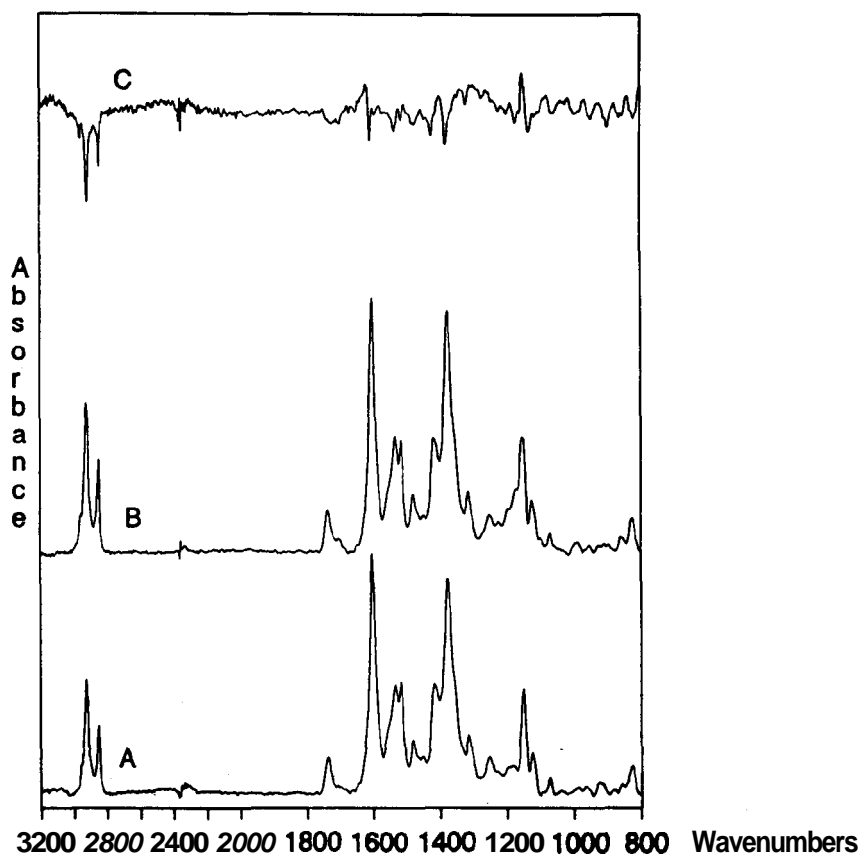


Figure 6.5 *GZR spectra of 9 layers of KZ16-salt on gold. A = as deposited, B = same film after heating to 185°C for 10 minutes, C = difference spectrum before and after heating (A-B).*

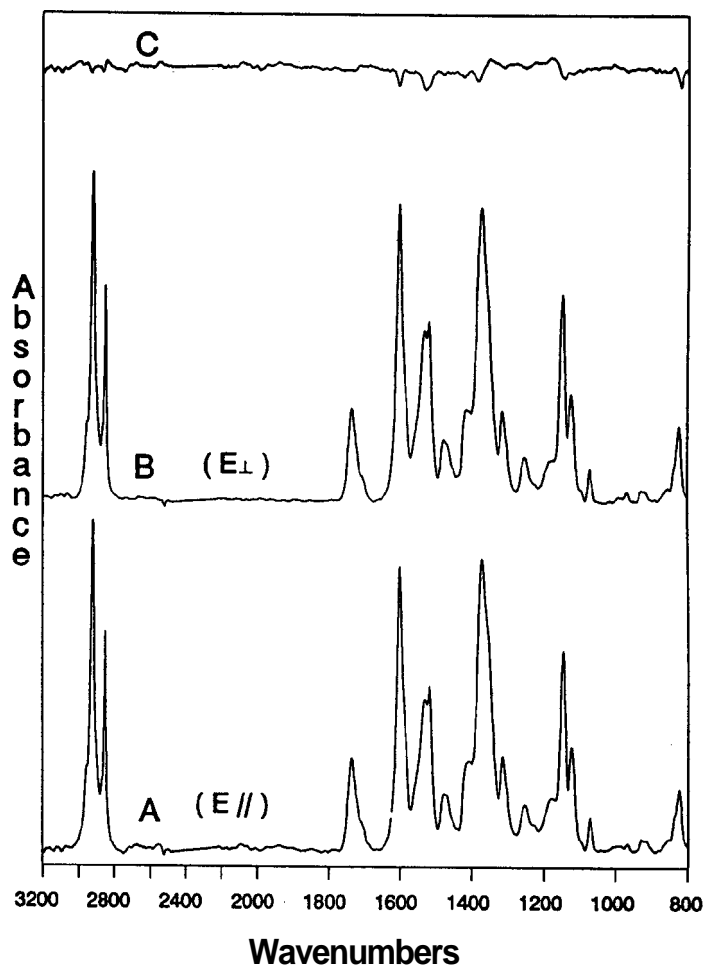


Figure 6.6 Polarized transmission spectra of a multilayer of the KZ16-salt (15 layers). A = polarized light parallel to the dipping direction, B = polarized light perpendicular to the dipping direction, C = difference spectrum (A-B).

This can be explained in several ways. One can assume that the chromophore does not have a preferred orientation. This seems not very likely because other parts of the molecule, the aliphatic chain and the carbonyl of the ester show preferred orientations. An other

explanation is a preferred tilt of the chromophore unit at an angle of 55° (the magic angle). A third possibility is a strong Cd-lattice that is not disturbed at 185°C and the preferred orientation of the chromophore unit is still present in spectrum B. According to the literature¹⁷ the regular Cd-lattice melts at 145°C . Comparison of the spectrum of the heated sample to the bulk spectrum of the **KZ16-salt**, argues most for the second explanation, a preferred tilt of 55° . This will be discussed further later on in this paper.

As an extra check the reflection spectra of a sample with 9 layers of the **KZ16-salt** are given in Figure 6.5. Figure 6.5 (A) shows the GIR (grazing angle incidence reflection) spectrum from KZ16 as deposited and spectrum B is the result when the sample is heated for 10 minutes at 185°C and cooled down to room temperature. The relative changes of the bands associated with the CH_2 chain are opposite of those observed in the transmission spectra. The information derived from the GIR corresponds with the orientation already revealed by the transmission spectra.

Figure 6.6 shows the transmission spectra of a multilayer sample of the **KZ16-salt** measured with polarized light. Spectrum A was measured with light parallel to the dipping direction and spectrum B perpendicular to the dipping direction. The difference spectrum (Fig. 6.6[C]) indicates no preferred orientation of specific modes in the dipping direction. An other way of saying: there is no flow induced orientation, these measurements indicate an isotropic structure in the plane of the film.

Spectrum A Fig.6.7 represents the spectrum of a sample of 18 layers **KDEZ16** as deposited and spectrum B is the result after heating the sample to 160°C for 10 minutes and cooling down to room temperature. Spectrum C is the difference spectrum of these two. Also these spectra can be divided into two regions of interest, the region of the modes of the aliphatic chains ($3200\text{-}2800\text{ cm}^{-1}$) and the region of the absorption of the chromophoric unit of the dye. The $\nu_a \text{CH}_2$ (2921 cm^{-1}) and the $\nu_s \text{CH}_2$ (2852 cm^{-1}) are relatively strong in spectrum A compared to the heated layer in spectrum B. If we assume a random orientation after the heating cycle, a tilted alkyl chain at an angle smaller as 55° with the surface normal, is revealed for the "as deposited" layer. The relative intensities of the vibration bands in the bulk spectrum (spectrum 7D) and in the spectrum of the heated sample correspond well, making the assumption of a random orientation of the heated sample reasonable.

The carbonyl vibrations of the ester groups (1743 cm^{-1}) and of the carboxylic acid (1696 cm^{-1}), also show **dichroism**. The ester carbonyl shows a preferred orientation parallel to the substrate surface whereas the carbonyl vibration of the acid is oriented more perpendicular

to the substrate surface. The transition moment of the vibration at 1603 cm^{-1} , the C=C vibrations of the benzene ring, lies parallel to the longest molecular axis. Spectrum A, compared to spectrum B in Figure 6.7 reveals an orientation of the C=C band more parallel to the surface normal. Because of the preferred orientation of the C=C bands, the main axis of the chromophore has to be tilted in the same way. The oriented vibration at 1380 cm^{-1} arising from the $\text{C}_{\text{aromatic}}\text{-N}$ stretch vibration supports this suggested tilt of the chromophore unit. Other oriented vibrations have transition moments with unknown direction and therefore are of less interest.

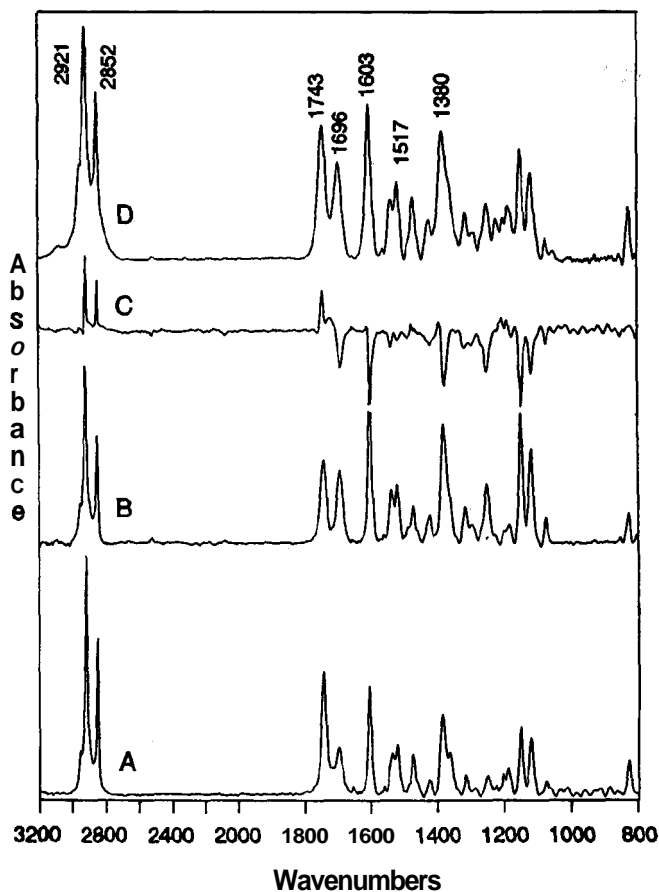


Figure 6.7 Transmission FT-IR spectra of KDEZ16. A = 18 layers of KDEZ16 on ZnS as deposited, B = same layer after heating to 160°C for 10 minutes, C = difference spectrum before and after heating (A-B), D = bulk spectrum of KDEZ16 in a KBr pellet.

Figure 6.8 shows the transmission spectra measured with polarized light. The difference of the spectra with light polarized parallel (A) and perpendicular (B) to the dipping direction, shows a small orientation of the aliphatic chains along the transfer direction, implying a non isotropic arrangement of the molecules in the plane of the substrate.

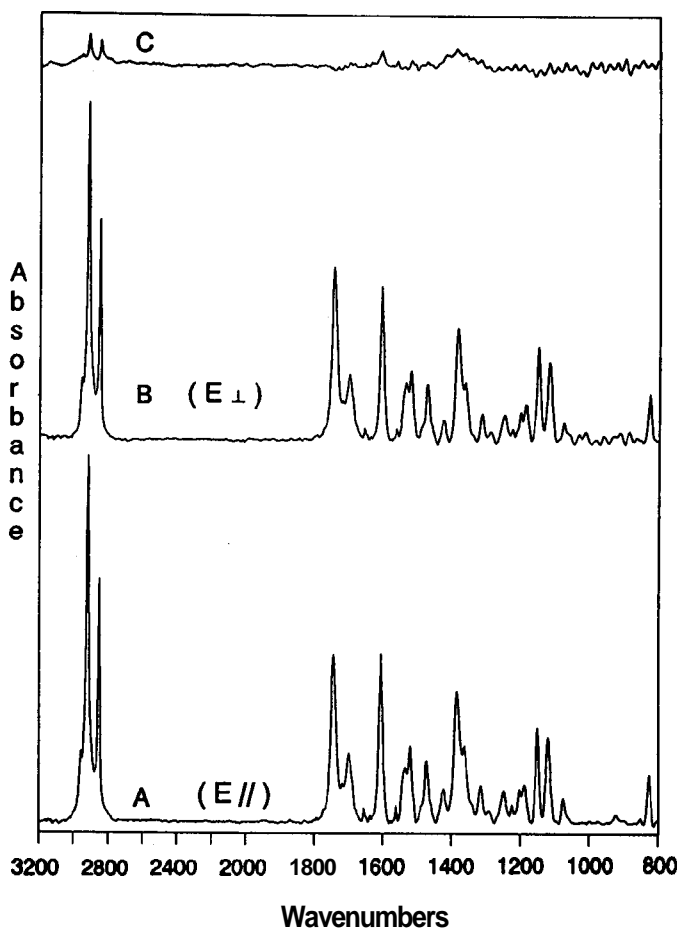


Figure 6.8 Polarized transmission spectra of a multilayer of KDEZ16 (18 layers). A = polarized light parallel to the dipping direction. B = polarized light perpendicular to the dipping direction, C = difference spectrum (A-B).

Structure and SHG of KZ16 and KDEZ16

The multilayers of KZ16 and KDEZ16 were also characterized by UV-visible light spectroscopy. The spectra of the dyes in chloroform and of multilayers on glass slides are shown in Figure 6.9. The samples on glass were measured with normal incidence light. The maximum absorption in solution is found at 472 nm for KZ16 and 460 nm for KDEZ16. The maximum absorption of the multilayers on glass are shifted to 436 nm and 444 nm respectively. The shape of the absorbance curve of the dyes does not indicate any formation of aggregates. When the absorbance is measured as a function of the number of transferred layers onto glass, a linear relationship is found, indicating a uniform transfer process.

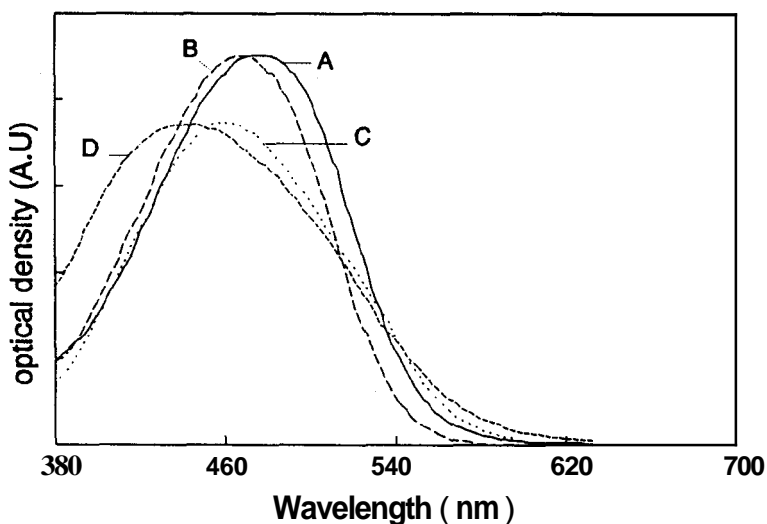


Figure 6.9 UV/visible light spectra of KZ16 and KDEZ16. A = solution of KZ16 in chloroform, B = Solution of KDEZ16 in chloroform, C = multilayer of KDEZ16 on glass, D = multilayer of KZ16 on glass.

The calculated molecular lengths in the extended conformation is 34.5 Å for both dye molecules. To fit these lengths of the molecules with the observed spacings for Y-type layers of KZ16 and KDEZ16, a tilt of approximately 48° (KZ16) and 33° (KDEZ16) is required. These required tilts correspond with the orientation of the molecules deduced from FT-IR spectroscopy. Combining the results of the X-ray measurements and the IR-measurements of the KZ16 multilayers, a preferred tilt of the chromophore unit of 55° to the surface normal seems the most realistic explanation for the unchanged intensities comparing the

heated and unheated sample in Figure 6.4 (A) and (B). The aliphatic chain must be tilted about 35° to the surface normal regarding the spacing found for the KZ16 multilayers.

Combining the results of the FT-IR and X-ray measurements of KDEZ16 multilayers a tilt angle of the molecules in the multilayer of 35° to the surface normal is found.

In an accompanying study, the tilt angles of KZ16 and KDEZ16 monolayers on glass have been determined by SHG in relation to local field factors¹⁵. The tilt angle of a KZ16 molecule in a monolayer on glass was determined to be 50° , similar to the values found in this study. KDEZ16 molecules in a monolayer on glass were found to have a tilt angle of 60° with the surface normal. Apparently the tilt angle changes on going from a monolayer to a multilayer. Crystallization of the aliphatic chains might cause this behaviour and might be also responsible for the anisotropic orientation of the chains of KDEZ16 in the plane of the film.

A schematic representation of the orientation of the molecules KZ16 in the multilayer is given in Figure 6.10.

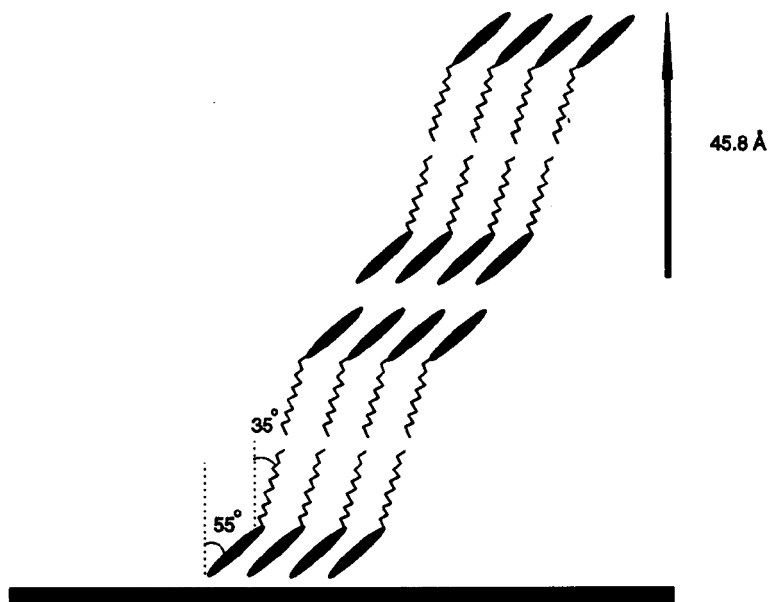


Figure 6.10 Schematic representation of the orientation of the KZ16 molecules in a multilayer.

Structure and SHG of KZ16 and KDEZ16

SHG (second harmonic generation) is a process in which light of a fundamental frequency (ω) is partially converted into light at frequency (2ω). Normally when the **SHG** activity of LB-multilayers is measured the layer is treated as a thin dielectric sheet characterized by an optical constant ϵ_m and an integrated (per unit area) **SHG** susceptibility tensor $\chi_m^{(2)}$ ⁹. The net second harmonic radiation generated in the LB-film is a superposition of that generated in each asymmetric LB-layer. If the thickness of one layer is much smaller than the coherence length, the **SH** waves generated in each layer are roughly in phase with one other, so we may approximate the net **SHG** response by an integrated film susceptibility:

$$\chi^{(2)}(\text{film}) = n\chi^{(2)}(\text{monolayer}) \quad n = \text{number of monolayers.}$$

When the film is isotropic in the x-y plane (z is the direction perpendicular to the surface) and using the **Kleinmann** symmetry²⁴, $\chi^{(2)}$ is reduced to only two independent tensor elements:

$$\chi^{(2)}_{zzz} \text{ and } \chi^{(2)}_{zxx} = \chi^{(2)}_{xxz} = \chi^{(2)}_{xzx} = \chi^{(2)}_{zyy} = \chi^{(2)}_{yyz} = \chi^{(2)}_{yzy}$$

Regarding our experimental set up this would give **SHG** in the **I_{sp}** and **I_{pp}** mode.

In ideal Z-type LB-films or in alternating layers, the polar layers are expected to show constructive interference, yielding n^2 dependence. Y-type LB-layers interfere destructively and cause a cancellation for even n and a residual monolayer contribution for odd n .

We have focused the **SHG** measurements on the **KZ16** mono and multilayers because of the isotropic arrangement of the molecules in the x-y plane. Table 6.111 shows the **SHG** of different composed mono- and multilayers of KZ16 and arachidic acid. Irradiation with the fundamental beam at 45° incidence generates p polarized **SH** signals. This finding confirms the IR-experiments where also an isotropic structure in the plane of the substrate was found (Fig. 6.6). The **SHG** values in table 6.111 were calculated according to the following equations:

$$\mathbf{P}(2\omega) = \chi^{(2)} \mathbf{E}(\omega) \mathbf{E}(\omega) \quad (1)$$

$$I^{2\omega} \propto |\mathbf{P}(2\omega)|^2 = |\chi^{(2)}|^2 * I_0^{2\omega} \quad (2)$$


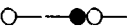
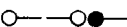
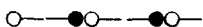




$$\chi^{(2)} = (I^{2\omega} / I_0^{2\omega})^{1/2}$$

$I^{2\omega}$ = **SHG** of the sample.

$I_0^{2\omega}$ = **SHG** of the reference **KDP** crystal.

Table 6.III shows the measured second harmonic intensities detected in the polarization sets sp and pp. $Q_{sp} = I_{sp}^{2\omega} / I_0^{2\omega}$ and $Q_{pp} = I_{pp}^{2\omega} / I_0^{2\omega}$.

Table 6.III SHG of KZ16 layers

Layer architecture	Q _{SP}	Q _{PP}
KZ16 	0.48	0.30
KZ16 	0.49	0.31
KZ16 	0.50	0.31
KZ16 2L 	2.43	1.91
KZ16 2L 	0	0
KZ16 3L 	0.60	0.23
KZ16.		
Arachidic acid.		

The intensities of the SHG reported here are calibrated on a monolayer of a hemicyanine dye with a known SHG²⁵. A $\chi_{zyy}^{(2)}$ value of $2.2 \pm 0.2 \cdot 10^{-6}$ esu was found for a monolayer of KZ16 on glass.

An Y-type double layer of KZ16 with a symmetric alignment does not show any **SHG**. The symmetric alignment in a bilayer of KZ16 cancels the second order non linearity completely.

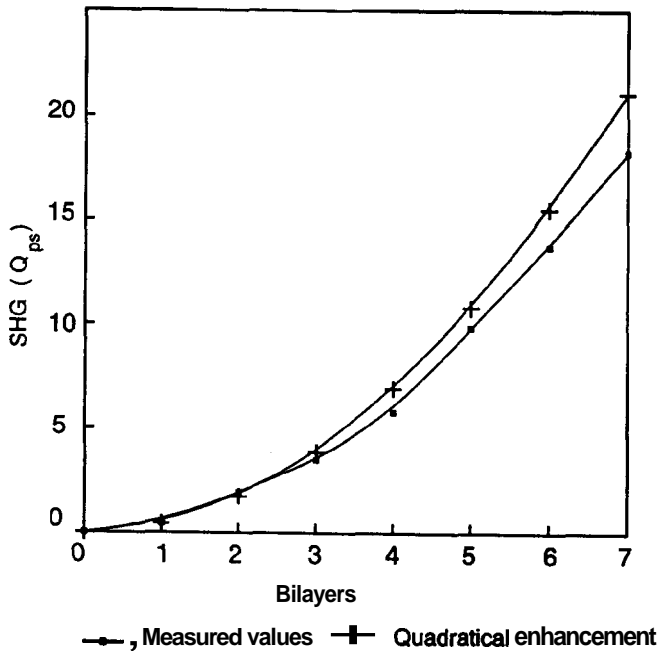


Figure 6.11 *Intensity of the second harmonic generation versus the number of alternating layers of arachidic acid and KZ16.*

This indicates that in this case the stereogenic center in the KZ16 molecule does not contribute to any measurable extent to a non linear behaviour. The mono- and alternating bilayer behave according to the general accepted theory of **SHG** of Bloembergen and Pershan ⁸.

Figure 6.11 shows the dependence of the intensity of the SHG (Q_{sp}) on the number of alternating bilayers. As can be seen a nearly quadratic (ideal) behaviour of the alternating layers of KZ16 with arachidic acid is obtained.

After heating the layers above the melting point and cooling down, no significant **SHG** can be detected anymore, indicating there is no self organization of the multilayer in a **non-centro-symmetric** way.

CONCLUSIONS

The Langmuir-Blodgett properties and structure of multilayers from two new amphiphilic NLO-materials with stereogenic centers, 4-[4'-[(3R)-palmitoylpyrrolidine-1]-phenylazo]-3-nitro-benzoic acid (**KZ16**) and 4-[4'-[(3R,4R)-dipalmitoylpyrrolidine-1]-phenylazo]-3-nitro-benzoic acid (**KDEZ16**) have been studied. KZ16 multilayers gave homogeneous structures in the plane of the film and could be used as a model compound to study second order non linearity of a Y-type ordered bilayer. The tilt angle of the chromophore part of the KZ16 molecule is 55° to the surface normal whereas the aliphatic chain is tilted 35° with respect to the surface normal in a multilayer. An Y-type bilayer does not show any SHG, indicating a complete destructive interference of the oppositely packed molecules. The stereogenic centers in the bilayer do not contribute to any measurable extent to a non centro symmetric structure.

Regarding the previous study^{4,5} of a less conventional LB-material with similar stereogenic centers compared to the compounds studied here, a completely different second order non linear behaviour was found. Chirality of the dye molecules seems to contribute to a non centro symmetric structure only when the molecules are arranged in special aggregates.

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