state with the oxygen 2p level,[1] the narrow range of composition that gives rise to superconductivity for this new material can be interpreted as indicating a very narrow range where the 6s state of the Tl, Bi, and Pb overlap sufficiently with the 2p level of oxygen. Although the 6s energy levels of Pb and Bi are nearly identical, that of Tl is considerably higher than that of Bi or Pb. Therefore, superconductivity in this system is not critically dependent upon the density of states of the Fermi surface as predicted by BCS theory, but rather upon the degree of overlap of the three different 6s states with that of the oxygen 2p level.

Band structure calculations for these materials may indicate why their electronic structure is so sensitive to slight variations in the thallium content and thereby help to elucidate the origin of the anomalous properties of these superconducting materials.

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2-(Pentacosa-10,12-diynylamino)-5-nitropyridine: A New Polymerizable Amphiphile for Nonlinear Optical Langmuir–Blodgett Films

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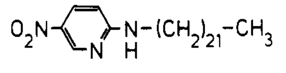
Recently we have shown that long-chain-substituted 2-(alkylamino)-5-nitropyridines such as 1 are excellently



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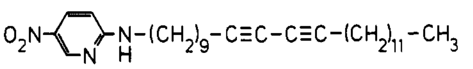

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suited for optical second harmonic generation in Langmuir–Blodgett (LB) films.[1-3] Optical nonlinearities are due to the donor–acceptor-substituted pyridine headgroup and the noncentrosymmetric arrangement of the molecules in a polar Y-type (herringbone) structure (Figure 1).

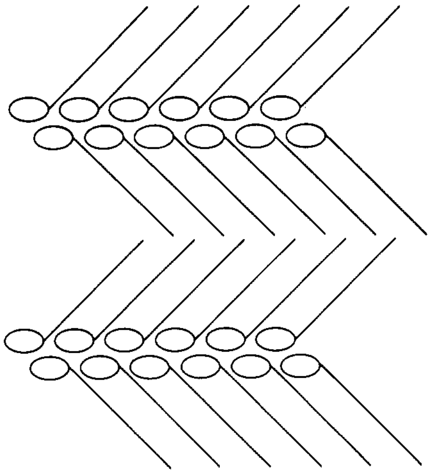

Figure 1. Structural model for polar Y-type structure (straight lines are alkyl chains, ovals represent chromophores).

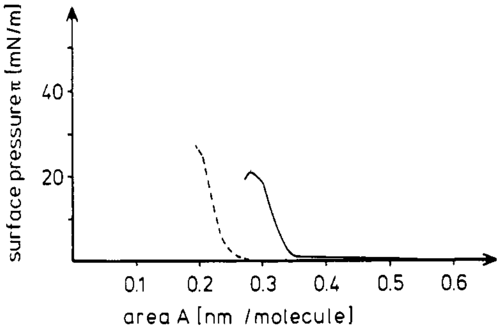

Figure 2. π/A isotherms of 2 (—, subphase, pure water, T = 7.7 °C) and a 1:1 mixture of 2 and 3 (---, subphase, 3×10^{-4} M $CdCl_2$ solution, pH 6.6, T = 10 °C).

Compounds such as 1 are superior to other donor–acceptor-substituted amphiphiles[4-6] with regard to film-forming properties and ease of formation of the acentric structure.

The purpose of the present investigation was to further improve the stability of the LB films by using polymerizable amphiphiles. We therefore synthesized 2-(pentacosa-10,12-diynylamino)-5-nitropyridine (2) containing a diacetylene group in the alkyl chain. The diyne units can be polymerized in a solid-state 1,4-addition reaction upon UV or high-energy radiation.[7] In the following, film-forming properties, polymerizability, and optical second harmonic generation from LB films based on 2 will be described.

2 (mp 55–57 °C) was prepared by nucleophilic substitution of 2-chloro-5-nitropyridine with 1-aminopentacosa-10,12-diyne[8] in about 40% of the theoretical yield. The crude product was purified chromatographically (silica gel, hexane/ether 1:1) and recrystallized from ethanol. Spreading of 2 at the air–water interface (Lauda film balance equipped with a film lift FL-1; Milli-Q water) results in the formation of a monomolecular film with solid condensed behavior. As shown in Figure 2, the collapse

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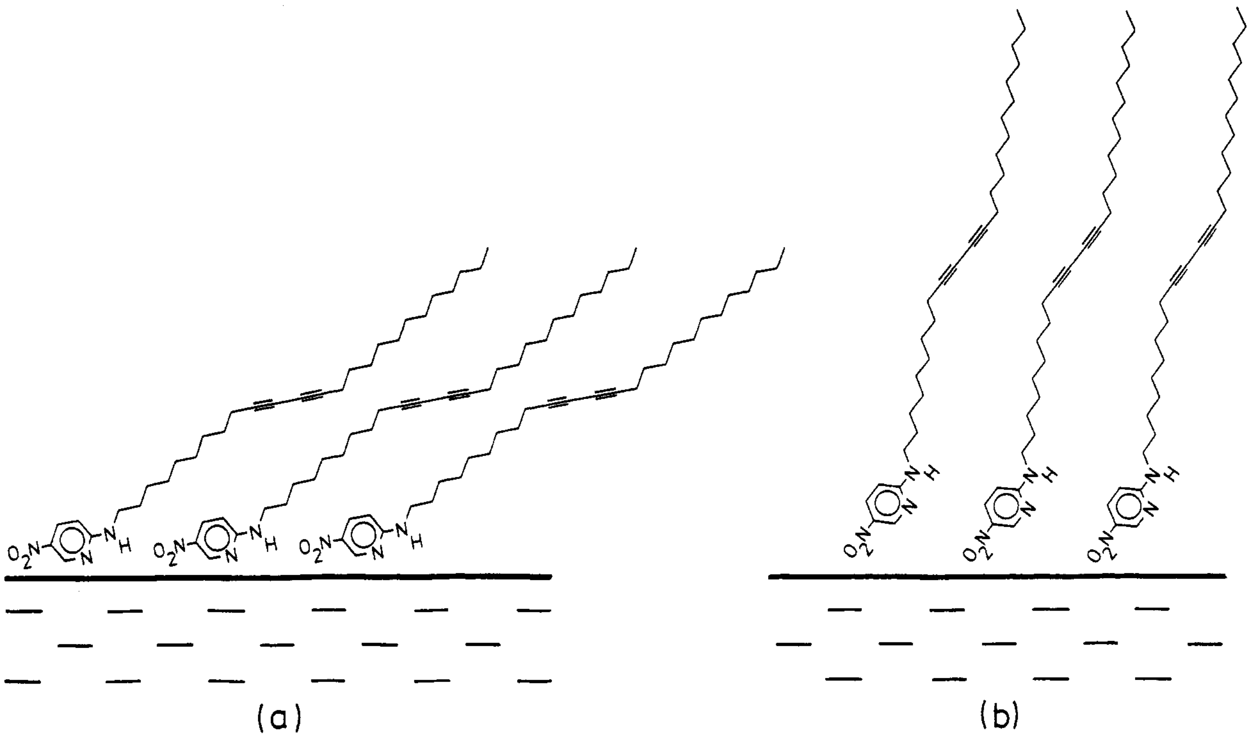

Figure 3. Suggested orientations of **2** in (a) pure and (b) mixed monolayers.

pressure π_c of the condensed phase is 18 mN/m (T = 10.6 °C), and the packing density A_c at film collapse is 0.30 nm^2/molecule. This value is relatively large and compares well with the A_c value observed for **1**. We therefore assume that the molecular arrangement of **2** at the air–water interface is similar to that of **1**, i.e., the substituted pyridine rings are oriented nearly parallel to the water surface, and the alkyl chains are strongly tilted with regard to the surface normal.[1] A proposed orientation of the molecules is shown in Figure 3a.

Mixed monolayers of **2** and the cadmium salts of pentacosa-10,12-diynoic acid (**3**, mixture I) or arachidic acid (**4**, mixture II) exhibit a higher collapse pressure and a smaller collapse area than monolayers of pure **2**. For example, a monolayer of mixture I containing the two compounds in equimolar ratio exhibits a collapse pressure of 25 mN/m, and an A_c value of 0.22 nm^2/molecule (subphase: 3 × 10^{-4} M $CdCl_2$ solution, pH 6.6; T = 10 °C). These values suggest a more upright position of **2** in the mixed films as indicated in Figure 3b.

Monolayers of pure **2** as well as mixed monolayers could be easily transferred onto various hydrophobic substrates (quartz, glass, germanium, or silicon silanized with trichlorooctadecylsilane) at a surface pressure of about 10 mN/m and a subphase temperature of 10 °C or lower. For deposition the substrates were dipped perpendicularly through the monolayer. Film transfer occurred on both down- and up-stroke, suggesting the formation of head-to-head and tail-to-tail (Y-type) arrangement of the molecules. Mixed LB films of a thickness of about 20 bilayers did not show any defects detectable with the naked eye, whereas films of pure **2** already became inhomogeneous if more than 10 bilayers were deposited.

LB films of **2** are pale yellow with an absorption maximum at 410 nm. In mixed LB films the maximum is shifted to about 390 nm, which can originate from a different orientation of the pyridine chromophores in the LB film. The absorption coefficient α at the maximum wavelength λ_{max} = 410 nm is about 15700 cm^{-1}. Upon UV irradiation of the LB films (λ = 254 nm) the diacetylene

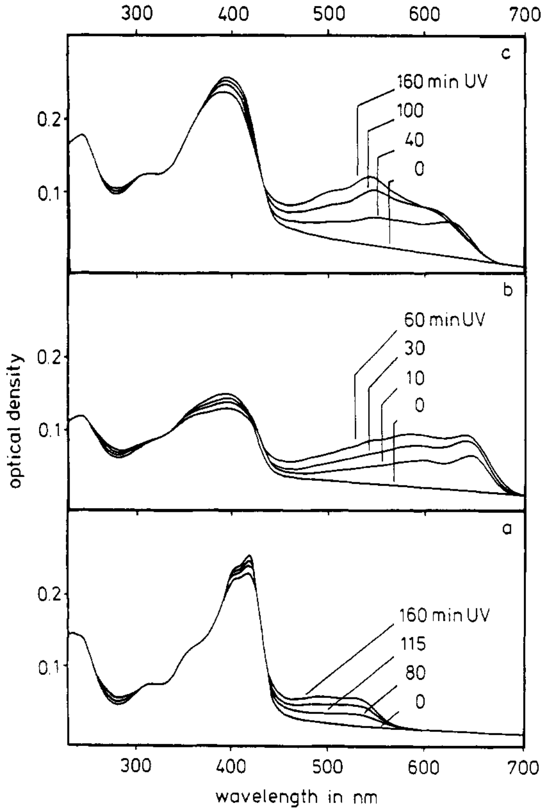

Figure 4. Optical absorption spectra of LB films of (a) **2**, (b) a 2:1 mixture of **2** and **3**, and (c) a 2:1 mixture of **2** and **4**. Spectra were monitored prior to UV exposure and after different irradiation times (20 double layers).

units polymerize under formation of a fully conjugated polymer backbone, which strongly absorbs in the visible.[9] Optical absorption spectra monitored after different UV exposure times (Figure 4) show a gradual increase in op-

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Table I. Normalized SH Intensities of LB films Containing Compounds 1–4 (Thickness, 10 Double Layers)

composition of LB film	$I^{2\omega a}$	composition of LB film	$I^{2\omega a}$
1	1	**2/3** (2:1)	5×10^{-5b}
2	1×10^{-3b}	**2/4** (2:1)	no effect obsd

[a] Experimental values are normalized to $I^{2\omega}$ of 10 double layers of 1. Nonlinear optical susceptibilities of **1**: $d_{333} = 6.8 \pm 1.2$ pm/V, $d_{311} = 0.9 \pm 0.2$ pm/V.[2] [b] No differences were found prior and subsequent to UV polymerization of **2**.

tical density due to the progressive polymer formation in the sample. In the mixed film, the increase is faster and the integral optical density reached after prolonged UV exposure is higher, indicating a more rapid polymerization and a higher conversion to polymer than in films of pure **2**. In mixture I, this can originate from a polymerization of either compound, whereas in mixture II the high photoreactivity must be due to another molecular packing of **2**. According to a previous study on mixed LB films of diacetylenes,[9] the occurrence of the photopolymerization is a strong indication for a phase separation of the individual compounds in the mixed film.

As indicated by small-angle X-ray scattering (SAXS), the LB films containing either pure **2** or a 1:1 mixture of **2** and **3** exhibit bilayer spacings of 3.99 and 5.16 (±0.04) nm, respectively. Since the maximum length of **2** in the fully extended conformation is shorter than the observed layer spacing, a head-to-tail (X- or Z-type) structure can be ruled out. Instead it must be concluded that the LB films are Y-structured, the molecules being tilted with regard to the layer plane. The different layer spacings observed for either the pure or mixed films most likely originate from different molecular arrangements, which may be similar to those in monolayers at the air–water interface (Figure 2).

Optical second harmonic generation (SHG) was studied on pure and mixed LB films containing **2** as monomer and polymer. A Q-switched Nd:YAG laser beam (BMI 501 DNS: wavelength $\lambda = 1064$ nm, pulse width $\tau = 25$ ns, repetition rate $f = 30$ Hz) was focused perpendicularly onto the sample. The second harmonic (SH) signal was detected as described previously.[10] In Table I the SH intensities $I^{2\omega}$ are listed. Data are normalized to the SH intensity of a corresponding LB film of pure **1** for both fundamental and SH wave polarized parallel to the dipping direction. As shown by the table, **2** exhibits a much lower SH intensity than **1**. In mixed films of **2** and the cadmium salt of **3**, nonlinear optical effects are even further diminished. Since in these cases the intensity was very close to the damage threshold of the glass, damage mechanisms may also have caused the nonlinearity. In mixed films of **2** and the cadmium salt of **4** nonlinear optical effects have not been observed. In the active films, the SH signal is always strongly polarized in the dipping direction, indicating a preferential alignment of the aromatic headgroups along this direction. The alignment is known to occur during LB-type transfer of the monolayers onto the substrate.[11]

Since the LB films are highly ordered, it can be inferred that the optical nonlinearity is a property of the film and most likely originates from a polar Y-structure (Figure 1).[1-3] The poor SH intensity observed for the mixed LB films is likely due to a more upright position of **2**, giving rise to a less polar structure. In addition, the SH intensity can be diminished by a more random orientation of the herringbone domains of **2** in the phase-separated mixed film.

In conclusion, we prepared a novel polymerizable amphiphile and observed optical second harmonic generation in Langmuir–Blodgett films of this material. Unfortunately, LB films based on this compound exhibit either a high photoreactivity and poor optical SHG or vice versa but not both effects at the same time.

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Organo Clay Assemblies for Triphase Catalysis

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Triphase catalyst systems for organic nucleophilic displacement reactions consist of a dispersed solid phase and two immiscible liquid phases that contain the electrophilic and nucleophilic reagents.[1] Reaction occurs by transfer of the reagents from the liquid phases to the solid phase. Normally, the triphase catalyst is a functionalized organic polymer[1-6] or inorganic support[7-10] that contains immobilized organo cations, including quaternary ammonium ions analogous to those used for conventional liquid–liquid phase-transfer catalysts.[11]

Although triphase catalysis greatly simplifies the recovery of the catalyst and provides opportunities for selective chemical conversions based on substrate size or polarity, the technique is not without limitations.[12-14] Polymer-supported triphase catalysts have yet to find industrial applications, in part because of their diffusion limitations and mechanical or chemical instability.[14] Several inorganic supports, including metal oxides,[7] clays,[8,9] and zeolites,[10] have been used in place of polymers, but these generally suffer similar disadvantages of low reactivity or structural instability under sustained reaction conditions. Thus, new materials for improved triphase catalysis are desirable.

We report here a promising new family of triphase catalytic materials based on alkylammonium exchange

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