Antiferroelectric ordering of amphiphilic glycolipids in bent-core liquid crystals

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Lipids are the main constituents of biological cell membranes, and their liquid crystalline properties play a crucial role in cell functions. We have discovered that dodecyl-β-D-glucopyranoside glycolipid layers can be electrically polarized in supramolecular structures of glycolipid and bent-core (''banana-shape'') molecules. Interestingly the glycolipid molecules, known to be excellent chiral dopants, are not able to transfer their chirality to the bent-core layers. Our observations indicate that glycolipid molecules self-assemble into pairs of tilted and antiferroelectric double layers, sandwiched between layers of bent-core molecules. These systems may provide a basis for understanding ''bioferroelectricity,'' which is important in biological cell membrane functions.

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INTRODUCTION

Liquid crystals represent a unique segment of soft matter, where the orientational order and mobility have delicate balance in determining the macroscopic properties. Various organic molecules with rod [1], disk [2], or bent-core (pyramid [3] or banana-shaped [4,5] molecules) form a great number of liquid crystalline mesophases with properties determined by the temperature. In such thermotropic liquid crystals, the orientational order is dictated by the shape of the molecules and the mobility is given by the thermal motion. Lyotropic liquid crystals that appear in the nature in living organisms [6] acquire mobility by addition of a solvent and their liquid crystalline properties are governed by the concentration of the solvent. Materials which exhibit both thermotropic and lyotropic liquid crystalline properties are called amphotropic [7,8].

Glycolipid molecules contain polar (hydrophilic) sugar head groups and apolar (hydrophobic) carbon chains, i.e., they are amphiphilic. They form liquid crystalline structures in aqueous systems depending on the concentration, as well as in their pure state depending on temperature, i.e., they are also amphotropic liquid crystals. Liquid crystalline properties of lyotropic synthetic glycolipids have been rigorously studied in the last decade [9], but so far they have not been studied as much in their thermotropic state. Glycolipid is one of the three lipids that make up the biological cell membranes. The shorter glycolipids (with 8–12 carbon atoms) mainly used as detergents [10], whereas others glycolipids involved in membrane fusion processes [11,12]. The more complex glycolipids (starting with three sugar head groups) are involved in cell surface recognition processes [13]. Most of these processes are electrical; for example, ferroelectric [14] behavior seen in nerve and muscle membranes. A better understanding of the underlining principles of these processes may provide insight into how the cells control the flow of information by recognizing signals received from other cells or, by sending electrical signals to other cells.

In this paper we describe how the glycolipid molecules (specifically alkyl glucoside, the simplest class of glycolipids with one sugar polar headgroup and an apolar carbon chain) aggregate into antiferroelectric supramolecular structures in correlation with bent-core molecules. Smectic liquid crystals of bent-core ('banana-shape') molecules recently attracted considerable interest because they have ferroelectric properties [15] and represent the first example for the formation of chiral superstructures without possessing chirality on a molecular level [16]. In mixtures of bent- and straight-core mesogenic molecules, a number of phases were detected ranging from the tilted polar smectic phase to non-polar smectic and nematic phases [17], including the biaxial smectic A phase [18]. Other studies have shown that the ferroelectric properties of the 'banana-smectic' materials can be maintained and tuned by nonpolar solvents, like xylene [19] and n-hexadecane [20].

EXPERIMENTAL RESULTS

We prepared binary mixtures of bent-core liquid crystalline molecules 4-chlorophenyline-bis [4-(4-n-tetradecyloxypheyliminomethyl)-benzoate] [21] (hereafter we will refer to it as BO14Cl), and dodecyl-β-D-glucopyranoside (hereafter we will refer to it as $C_{12}G_1$), which has a glucose polar hydrophilic head group and a hydrophobic alkyl chain with 12 carbon atoms [12]. Samples with concentrations varying continuously between 0 and 100 wt % of $C_{12}G_1$ molecules (contact preparations), and homogeneous mixtures with 20.2, 39.7, 60.5, 80.2, and 95.1 ± 0.4 wt % of $C_{12}G_1$ were prepared at 145 °C and filled in 4-μm cells from Displaytech. Inc. The cells were coated with transparent indium tin oxide (ITO) electrodes and with polyimide layers rubbed in antiparallel directions.

BO14Cl has an antiferroelectric tilted smectic C phase between 68 and 127 °C [21]. $C_{12}G_1$ has a smectic A phase between 80 and 142 °C [12]. The materials are uniformly miscible up to more than 1:1 $C_{12}G_1$:BO14Cl ratios with textures similar to that of pure BO14Cl. As the concentration of $C_{12}G_1$ increased, the clearing point of the mixtures decreased from 127 to 113 °C and the transition to the deeper smectic phase decreased from 68 to 55 °C. In addition, both the bi-

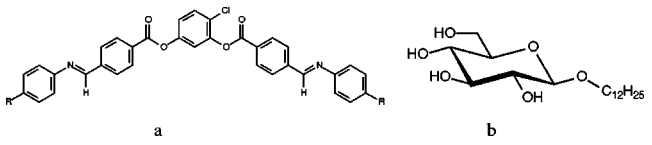

FIG. 1. The molecular structures of the components of the studied mixtures (a) Molecular structure of the bent-shape liquid crystalline compound ($R=C_{14}H_{29}$): 4-chloro-phenyline-bis [4-(4-n-tetradecyloxypheyliminomethyl)-benzoate] (BO14Cl). (b) Molecular structure of dodecyl-β-D-glucopyranoside ($C_{12}G_1$).

refringence and the resistivity decreased by an order of magnitude up to 60-wt % $C_{12}G_1$ concentration. Interestingly the bent-core molecules dominate the system and can be considered as host up to 60-wt % of $C_{12}G_1$ molecules. There is a significant change at around 3:2 $C_{12}G_1$:BO14Cl weight ratios, where the texture abruptly become similar to that of the pure $C_{12}G_1$, i.e., the $C_{12}G_1$ molecules act as host and the BO14Cl molecules are the guests (see Fig. 1).

Below about 65 wt % $C_{12}G_1$ concentrations the textures consisted of very small (2–4 μm) domains after cooling from the isotropic phase. However, after switching to the ferroelectric state by applying sufficiently strong electric field, larger (50–100 μm) and relatively uniform domains were formed. The rotation of the optic axis, as the polarity of the field was reversed, indicated chiral layer arrangements [16]. Such a field-induced racemic-chiral transition is typical of banana liquid crystals with relatively long terminal alkyl chains [22]. After switching the mixtures to the chiral states, the larger domains were broken up to left and right handed domains that alternate extinction in opposite directions. In the pure BO14Cl substance the number of left and right handed domains is about equal, whereas in the mixtures one handedness dominates, but only by about 50% even for the 60-wt % $C_{12}G_1$ mixtures. These observations are in contrast to earlier observations where only a few percentages of chiral calamitic dopant molecules [16] (or even chiral surfaces [23]) were sufficient to transfer uniform chirality into the "banana smectic." They also contradict previous studies on amphiphilic systems in which synthetic glycolipids appeared to be excellent chiral dopants for inducing chirality in nematic lyotropic liquid crystals [24].

The time dependence of the electric current under triangular voltage excitations reveals an antiferroelectric-type polarization switching of mixtures with less than 70-wt % $C_{12}G_1$ concentrations [see in Fig. 2(a)]. The temperature dependences of the polarization, as determined from the area under the polarization current peaks, are shown in Fig. 2(b).

It can be seen that above 100 °C the polarization decreases with increasing $C_{12}G_1$ concentration. This effect can be attributed to the decrease in the isotropic–smectic phase transition temperature. However, far from the phase transition, the polarization ($P_s \sim 500$ nC/cm^2) is almost independent of the concentration (the slight decrease of about 10% at the 60-wt % $C_{12}G_1$ concentration is still merely larger than the error limit of the polarization measurements). This be-

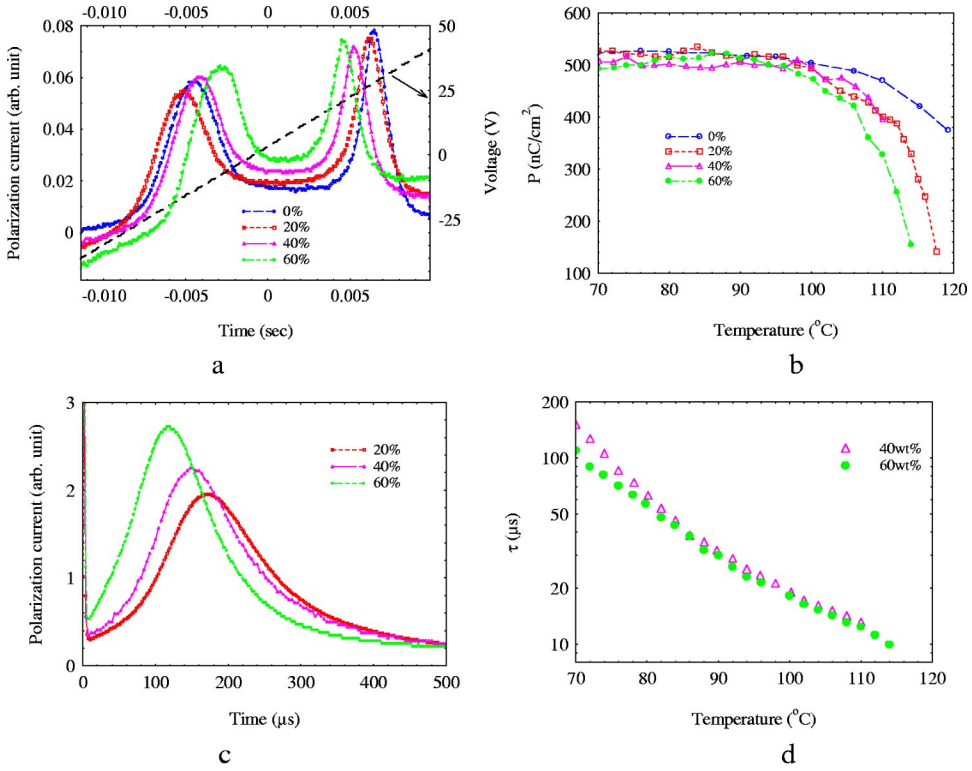

FIG. 2. (a) Polarization current curves at 70 °C of the mixtures with different concentrations under triangular fields with 10 V/μm amplitude. (b) Temperature dependence of the polarization for different concentrations of $C_{12}G_1$. (c) Time dependences of the polarization current for different concentrations after fast field reversal of $E=10$ V/μm fields. (d) Temperature dependence of the switching time for two different concentrations.

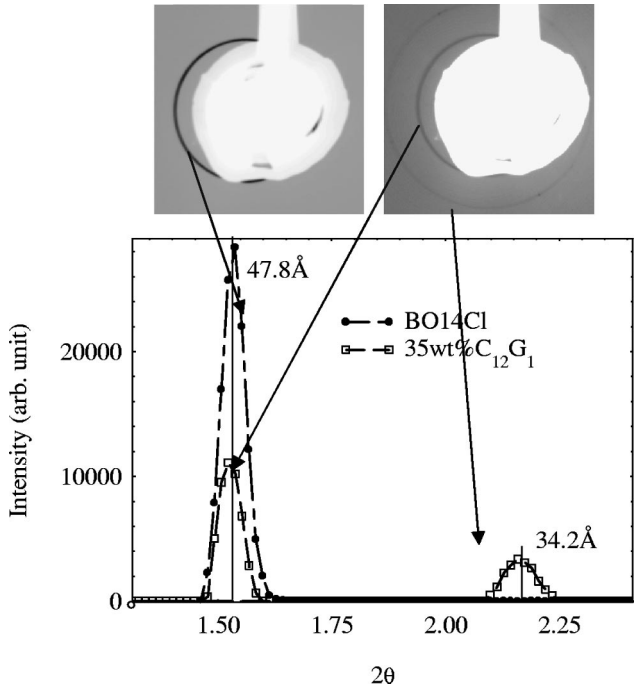

FIG. 3. Small angle x-ray pattern of the pure BO14Cl and of the 35-wt %$C_{12}G_1$+65-wt %BO14Cl mixture.

havior is quite different from previous observations made on mixtures of ''banana'' liquid crystals with non-polar solvents [19,23], and where the polarization sharply decreased with solvent concentration. As the concentration increased from 0 to 60-wt % $C_{12}G_1$ the threshold voltage required for switching decreased from 28 to 20 V at 70 °C and from 18 to 11 V at 106 °C [see Fig. 2(a)]. The switching time, as determined from the peak position of the time dependence of the polarization current under rectangular fields, also decreased with the $C_{12}G_1$ concentration [see Figs. 2(c) and 2(d)].

To elucidate the molecular arrangements in the mixtures below 60 wt % of $C_{12}G_1$ where bent-core molecules dominate the phase structure, high resolution x-ray measurements were carried out in the Midwest Universities Collaborative Access Team (MUCAT) Powder Diffraction station of the Advanced Photon Source of Argonne National Laboratory ($E=9.684$ keV, $\lambda=1.2803$ A, resolution 3450×3450 and the detector is at 378.499 mm from the sample). The measurements reveal a single small angle diffraction at $2\theta=1.53°$ in case of the pure BO14Cl and two peaks at $2\theta=1.53°$ and 2.17° for 35-wt %$C_{12}G_1$:65 wt %BO14Cl mixture. This corresponds to periodicities of 47.8 Å, which is the same as of the pure BO14Cl, and of 34.2 Å (see Fig. 3). Interestingly, this additional periodicity is the same as of the pure lipid.

Above 75 wt % of $C_{12}G_1$ content the textures resemble to that of the pure $C_{12}G_1$. In the range of about 10 °C below the transition to the isotropic phase, a smectic A phase formed and no electro-optical switching was observed. However at lower temperatures (for a 95-wt % $C_{12}G_1$ system in the range between 105 and 57 °C) a linear electro-optical switching was observed (see Fig. 4). We found that the switching angle was essentially proportional to the applied field. It is remarkable that mixtures with as low as 2-wt % BOCl14 molecules are able to render linear electro-optical switching, whereas no linear electro-optical switching is observable in pure $C_{12}G_1$ system. We note that the transition between the higher and lower temperature phases did not appear in standard DSC measurements indicating a second order transition. Preliminary x-ray observations also did not show this transition.

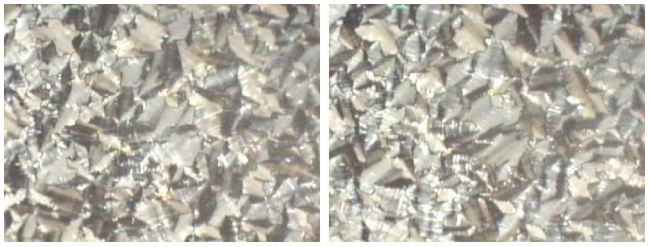

FIG. 4. Linear electro-optical switching in 95-wt %$C_{12}G_1$ +5-wt %BO14Cl system at 90 °C under positive (a) and negative (b) $E=8$ V/μm fields.

DISCUSSION

We have demonstrated that amphiphilic glycolipid and bent-core molecules can be mixed without affecting the antiferroelectric ordering of the bent-core material. Although this observation is not unexpected and can be attributed to the entropic preference associated with out-of-layer fluctuations [25], it is not a necessary scenario. First, for BO14Cl the synclinic preference is weak due to the long terminal chain. This was evident in the observation that the originally racemic antiferroelectric (synclinic) structure switched to chiral (anticlinic, antiferroelectric), and remained stable. Second, there is another viable option: to induce chiral ferroelectric state, which could keep the synclinic order. Such situations were indeed observed previously on the presently studied bent-core molecule mixed with n-hexadecane [20].

The observation that the chiral lipid molecules were not able to bias significantly the handedness of the chiral domains is however, unexpected, although it was already demonstrated previously by Nakata *et al.* [26] that molecules with chiral terminal chains still resulted in racemic ferroelectric structures.

The most interesting result of these observations is that the macroscopic polarization of the bent-core liquid crystalline material is unaffected even when it is diluted up to 60 wt % of the lipid molecules. The $C_{12}G_1$ molecules themselves form macroscopically non-polar structure where the polar sugar heads facing in opposite directions (opening angle: $\beta=180°$) in non-tilted double layer configuration. It is apparent that in the bent-core BO14Cl environment the lipid double layers adopt the tilted configuration with the polar heads tilted with respect to each other. This indicates that the polar sugar heads of the $C_{12}G_1$ molecules become tilted with respect to each other (opening angle: $\beta<180°$). To estimate this angle first we calculated (using a software CACHE) the molecular dipoles of the $C_{12}G_1$ molecules as $\mu_P=3.25\,D=1.08\times10^{-29}$ C m. Taking into account that the molecular weight of $C_{12}G_1$ is 348, and the mass density is

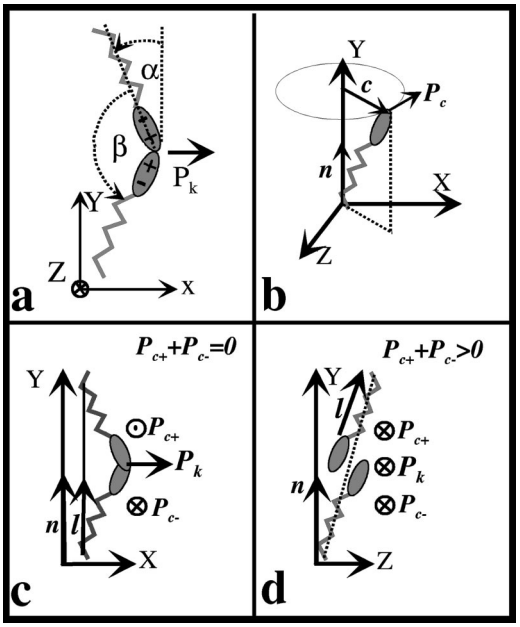

FIG. 5. Proposed model for the packing of the $C_{12}G_1$ molecules. The dodecyl-β-D-glucopyranoside molecules form bent smectic double layers mimicking the structure of the bent and tilted banana-shape molecules. The darker areas indicate parts tilted away the observer viewing the material along the smectic layers. P_k is the polarization of the glycolipids due to the kinked polar heads. (b) Polarization $\vec{P}_c \propto \vec{c} \times \vec{n}$ of tilted glycolipid layers due to molecular chirality and director tilt. (c) The direction of P_k and P_{c+} (P_{c-}) of the upper (lower) chiral lipid molecules in the SmAP configuration; The direction of P_k and P_{c+} (P_{c-}) of the upper (lower) chiral lipid molecules in the SmCP configuration.

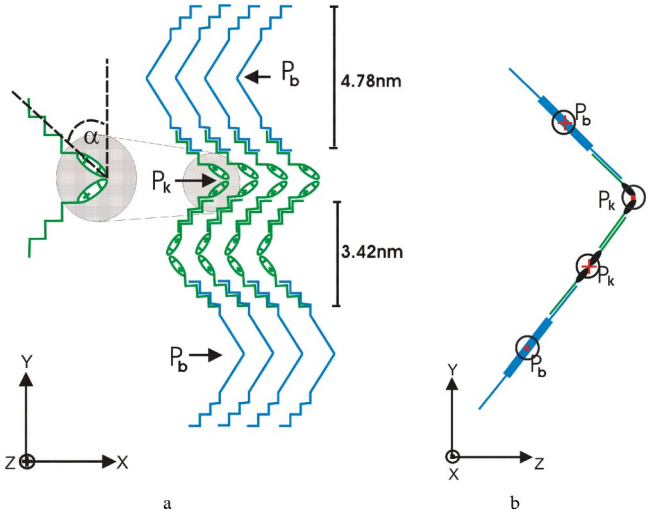

FIG. 6. Proposed model for the packing of the $C_{12}G_1$ molecules together with the BO14Cl molecules in the highest concentration ($\sim$60-wt %$C_{12}G_1$+40-wt %BO14Cl), where the bent-core molecules still dominate the phase structure. P_b is the polarization due to the polar packing of banana-shaped molecule. (a) Structure viewing normal to the kink and the bend polarization. (b) The structure viewing along the electric polarizations.

about 1 g/cm^3, we obtained that uniformly arranged dipoles would result in a polarization of $P_o = 2\times10^{-2}$ C/m^2 $= 2\times10^3$ nC/cm^2. The effective polarization of the bent double layer configuration can be given as $P_k = P_o \cos(\beta/2)$ (k stands for a kink). The observation that the contribution of the bent lipid double layers to the polarization is basically equal to that from banana-shape molecules, i.e., $P_b \sim P_k = 500$ nC/cm^2 (b stands for banana), provides that the opening angle $\beta \sim 150°$ [see Fig. 5(a)]. Considering that the molecular arrangement is not perfect due to thermal fluctuation, the actual opening angle should be smaller, probably close to the $\beta \sim 120° - 130°$ which is same as the opening angle of the bent shape BO14Cl molecules.

We have to note that by symmetry the chirality of the sugar heads, together with the tilt of the individual molecules with respect to the smectic layer normal, may result in a permanent polarization normal to the tilt plane, as it was pointed out first by Meyer [27] for SmC* materials. Therefore, as we have illustrated in Fig. 5(b), the tilt of the $C_{12}G_1$ molecules bring an additional polarization component P_c (c stands for chiral). In a SmAP-type configuration, where the director (the unit vector along the average line connecting the hydrocarbon ends of the molecules facing each other) is parallel to the layer normal, the P_c of these (facing) molecules has opposite directions, i.e., they compensate for each other [see Fig. 5(c)]. However, if the director becomes tilted following the tilt of the banana-shaped host molecules, the contribution from the individual lipids molecules adds together and points in the same direction as P_k [see Fig. 5(c)]. It is important to note that P_c is proportional to the perpendicular component of the molecular dipole moment $\mu_P^{\perp}$, and because the dipoles of $C_{12}G_1$ molecules are mainly parallel to the director ($\mu_P^{\perp} \ll \mu_P$), we estimate that $P_c \ll P_k$. Another important difference between P_k and P_c is that the latter should appear regardless of the shape of the SmC or SmC* hosts, whereas P_k is present only in bent-core hosts.

The x-ray results (the appearance of the lipid layer periodicity in addition to that of the bent-core smectics) indicate that the glucoside molecules do not pack in between the bent-core molecules within the ''banana smectic'' layers. In case of this ''intralayer packing'' the periodicity of the alkyl glucoside molecules should have been half of the banana smectic layers, which does not correspond to the x-ray results. In addition, some of the polar glucose head groups would have been in close vicinity with the alkyl chains of the BO14Cl molecules, which is not favorable. We propose therefore that the glycolipid molecules form individual smectic double layers in between the layers of the banana-shaped molecules (see Fig. 6). In this ''interlayer'' packing, the width of the $C_{12}G_1$ layers do not have to be half of the BO14Cl layers, and the flexible alkyl chains of both kinds of molecules meet only other alkyl chains, which is a much more favorable packing. We note that it is necessary to form pairs of glycolipid double layers to ensure the experimentally observed antiferroelectric ground state. Such packing means layered nanostructures where the distance between the layers of same type is determined by the concentration. Taking into account that the molecular weight of $C_{12}G_1$ is 348 and of BO14Cl is 950, in the highest ''banana'' dominating ($\sim$60-wt % $C_{12}G_1$) concentration there is only one BO14Cl

layer in between stacks of four $C_{12}G_1$ layers (see Fig. 6). For lower glycolipid concentrations each $C_{12}G_1$ stacks were separated by one or more BO14Cl layers. The observation that the periodicity of 34.2 Å is equal to that of the pure lipid, but smaller than the length of two fully stretched $C_{12}G_1$ molecules (38.4 Å), may indicate uncorrelated tilted (deVries-type) [28] smectic A phase. The tilt directions can easily become correlated in the mixtures with the bent-core molecules without involving change in the layer spacing, and thus contributing to the ferroelectric polarization. We also note that the proposed structure shown in Fig. 6 can also explain the observed weak chirality transfer, since the chiral centers, situated in the polar head groups of the $C_{12}G_1$ molecules, are not in direct contact with banana liquid crystal layers.

The suggested nanophase separated structure is different from previous observations of Schröder *et al.* [17], where only single layer spacing was observed on mixing the same BO14Cl with different calamitic molecules. This clearly shows that the interaction of BO14Cl molecules with amphiphilic lipids is different from that of with calamitic molecules.

Nanophase separation is not new in lamellar liquid crystals. It has already been observed by addition of non-polar hydrocarbon molecules to calamitic smectics [29], as well as to bent-core materials [20]. Interlamellar nanophase segregation has also been observed upon trans-cis photoisomarization of an azobenzene derivative in a smectic host [30], which basically corresponds to a segregation between bent core cis azo derivatives and calamitic molecules. An important difference however is that the azo molecules did not form a separate layer structure, but only increased the layer spacing by a few tenths of nanometer.

The observed linear-electro-optical switching in the lipid-dominating regime (larger than 75-wt % $C_{12}G_1$ concentrations) resembles to the electroclinic switching known for chiral SmA* materials above a tilted SmC* phase. However, because in our case it appears below the smectic A phase range we suggest that the bent-core molecules impose an anticlinic tilt on the lipid molecules, which becomes synclinic under strong fields. Indeed, such a situation actually was found recently in computer simulation by Maiti *et al.* [31]. Their studies show that, as low as a few percentages of bent-core molecules, is able to induce as large as 30° anticlinic tilt when the opening angle of the molecules is about 120°. These values actually are very close to our experimental observations.

Experiments are underway to study the structures in the lipid-dominated regime, and on other ''biofriendly'' banana liquid crystals (for example without chlorine atoms) and on various glycolipid derivatives. It would also be interesting to investigate whether straight-core molecules were able to impose their order into amphiphilic systems.

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