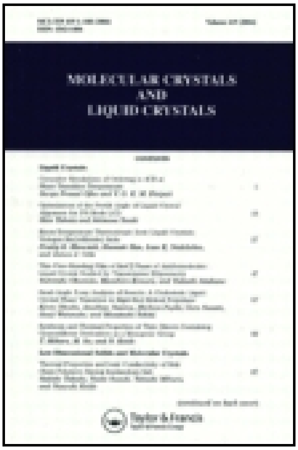

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# SPONTANEOUS FORMATION OF TWO-DIMENSIONAL SELF-ASSEMBLED POLAR ATOMIC LAYERS WITH FERROELECTRIC ORDERING OF ION PAIRS IN LIQUID-CRYSTALLINE SURFACTANT COMPLEXES

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To cite this article: Akihiko Kanazawa & Tomiki Ikeda (2001): SPONTANEOUS FORMATION OF TWO-DIMENSIONAL SELF-ASSEMBLED POLAR ATOMIC LAYERS WITH FERROELECTRIC ORDERING OF ION PAIRS IN LIQUID-CRYSTALLINE SURFACTANT COMPLEXES, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 473-482

To link to this article: http://dx.doi.org/10.1080/10587250108023988

*Mol. Cryst. and Liq. Cryst.*, 2001, Vol. 366, pp. 473-482
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

# Spontaneous Formation of Two-Dimensional Self-Assembled Polar Atomic Layers with Ferroelectric Ordering of Ion Pairs in Liquid-Crystalline Surfactant Complexes

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The unique optoelectric feature of structurally simple surfactants was presented. Phosphonium salts as a novel class of thermotropic liquid crystals were used to explore the spatial arrangement of ions in multilayer self-assemblies based on the surfactant complexes. Through the evaluation of second-order nonlinear optical property of the phosphonium self-assemblies, it was revealed that the phosphonium thin film assemblies can be regarded as a polar thin film consisting of two-dimensional ionic layers with noncentrosymmetric atomic arrangement. Such spontaneous formation of the in-plane polar structure was assumed to originate from the variety of bonding manner (*i.e.*, the characteristic electronic structure) of phosphorus atom. Furthermore, it was also found that the macroscopic polar order is enhanced by application of an external electric field.

*Keywords:* Amphiphiles; Layered Compounds; Liquid Crystals; Supramolecular Chemistry; Polar Thin Films; Second Harmonic Generation Spectroscopy

## INTRODUCTION

**Ferroelectrics, which have dielectric, piezoelectric, pyroelectric, and electro-optical properties, are widely used as active materials for**

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electronics, optoelectronics, and photonics. In recent years, the area of ferroelectric thin films is rapidly developing into a key technology with applications ranging from sensors to nonvolatile ferroelectric random access memories (FRAMs) [1-3]. Especially, FRAMs have attracted much attention for their excellent characteristics which include fatigue-free, low-voltage, and high-speed read/write operations. The ferroelectric thin films are usually prepared from inorganic layered perovskites by a variety of techniques such as chemical vapor deposition and sol-gel processing. Because of great progress of integration process technology which reduces the process damages to ferroelectric materials, the commercialization of FRAMs has begun for applications in IC card and rewritable flush memory. However, there is a problem on fabrication of FRAMs. Since the common ferroelectrics are crystalline materials, it is often difficult to prepare solid-state thin films with large uniform domains without a structural defect. The ability to control structure of organizations at the atomic levels is very important in development of more functionalized devices including high-performance FRAMs.

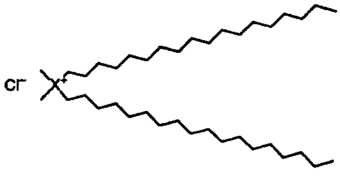
Supramolecular assemblies have been regarded as one of the most potential groups for applications in highly-functionalized materials [4-7]. Liquid-crystalline materials have self-assembly characteristics for forming various phases and provide additional features such as an ability to respond to applied external fields. The incorporation of the liquid-crystalline properties into layered materials is expected to bring about emergence of new functionalized thin films. Such liquid-crystalline materials are favorable from viewpoint of modification of the assembly structure, because their structure can be readily directed by the choice of phase. Use of the liquid-crystalline nature is also an attractive solution to the problem of structural defects. The defects could be repaired by annealing a liquid-crystalline material in the fluid phase, followed by quenching. For application of the self-organizing materials to electronic or optoelectronic devices, the key requirement is the presence of noncentrosymmetric (polar) order as well as layered structure.

Through systematic studies on applications of nonmetal (or metal) complex salts to multi-functional materials (antimicrobial agents, surfactants, phase-transfer catalysts, antistatic agents, ion exchangers, curing agents etc.), we found that phosphonium salts, which have an ion pair of positive phosphorus and negative halide atoms as well as double long alkyl segments, possess a high degree of molecular organization abilities in comparison with the common quaternary ammonium analogs with the same structure except the positive heteroatom [8-10]. Even in the bulk condition, the phosphonium salts showed an advantageous feature as a thermotropic liquid crystal in spite of the structurally simple amphiphiles [10-12]. They formed a multilayer structure based on the bilayer stacking in smectic A phase, which is built up from alternating layers of ions and alkyl segments. If such ionic liquid crystals are applied to solid-state systems, they may be regarded as a novel class of layered thin films because of the presence of polar layers showing a two-dimensional character, which are composed of pairs of positive and negative ions as an electric dipole, separated by the insulating alkyl layers. Here we present unique feature of layered thin films produced by the phosphonium liquid crystals, which was revealed through the evaluation of second-order nonlinear optical property of the phosphonium self-assembly [12,13].

## EXPERIMENTAL

### Materials and Method

To obtain information on spatial arrangement of ions in phosphonium self-assembly, the second harmonic generation (SHG) was measured which is an effective tool for evaluation of dipolar alignment in the molecular organizations. For the SHG measurement, we used the thermotropic liquid-crystalline phosphonium chloride (**P-LC**) and the quaternary ammonium analog (**N-LC**) as a reference liquid crystal. Solid-state samples retaining a smectic layer structure were readily prepared by injecting the compounds into a sandwiched cell with a gap of 15 μm in the fluid phase, followed by rapid cooling to room temperature. These



**X-LC (X = P, N)**

samples, which were colorless and transparent, showed macroscopically no optical anisotropy.

For the SHG measurements, a Q-switched Nd:YAG laser ($\lambda$ = 1064 nm, 10-Hz repetition rate, 6-ns pulse duration) was used for the exciting light source. The laser beam, the pulse energy of which was controlled with neutral-density filters, was passed through a 1/4 waveplate and a plate polarizer to convert to the laser beam polarized along the x axis or the y axis in Figure 2. The **X-LC** sandwiched cell was placed on a sample stage (in the x-y plane in Figure 2). A polarized laser beam passed through a UV-visible light cutoff filter was focused on the sample along the z axis in Figure 2. After the sample, an infrared-cut filter, an analyzer and an interference filter were used to detect only the SHG signal (532 nm) with the same polarization plane as the fundamental wave. The SHG signal was detected with a photomultiplier and processed with a boxcar integrator which was interfaced to a personal computer.

## RESULTS AND DISCUSSION

### Evaluation of Polar Order in the Phosphonium Thin Films by SHG Analysis

Figure 1 shows change in the SHG intensity observed for the **P-LC** and **N-LC** thin films. The SHG signals were clearly observed for **P-LC** (Figure 1a). On the other hand, **N-LC** with the same hydrophobic structure was inactive at all for the SHG (Figure 1b). These results indicate that the second-order nonlinear optical response of the amphiphilic organizations has relation to their liquid-crystalline properties and this phenomenon is specific for the phosphonium species. Supramolecular architecture has been recently employed to prepare second-order nonlinear optical materials in which noncentrosymmetric dipolar alignment of $\pi$-conjugated chromophores can be achieved [5-7]. However, the phosphonium assembly essentially differs from the conventional supramolecular systems because the phosphonium molecules not only possess no $\pi$-electron moieties, but also act as both supramolecular components and photoactive moieties.

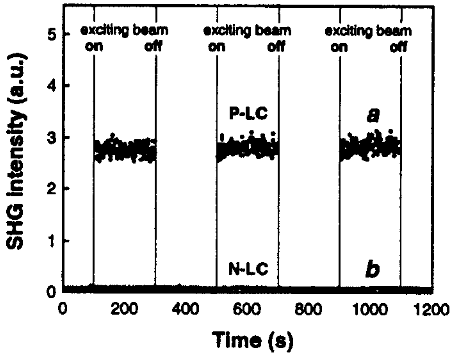


FIGURE 1 Change in the intensity of SHG signals on irradiation of the exciting beam observed for the solid-state onium assembly: (a) **P-LC**; (b) **N-LC**.

## Presumable Model for the SHG-Active Phosphonium Thin Film Assembly

Through the X-ray diffraction analysis in thin film method, the phosphonium self-assembly was confirmed to be composed of highly-ordered layer structure based on the bilayer stacking even in the solid state (Figure 2a), in which each layer is aligned parallel to the glass substrates (x-y plane). This implies that the SHG from the **P-LC** sample is due to the nonlinear polarization in the ionic layer. For the SHG, a noncentrosymmetrical molecular or atomic arrangement of the materials is required in the bulk. In the phosphonium assembly, if noncentrosymmetric macroscopic arrangement of ions in the ionic layer is induced spontaneously, the ionic layer may possess a second-order nonlinear optical property. Many polar crystals with a noncentrosymmetric structure, such as barium titanate and sodium nitrite, are known to show a second-order nonlinear optical response [1-3,14]. The spontaneous polarization (*P*s) as an overall permanent electric polarization occurs in the absence of an external electric field because of the displacement of ions or because of ordering of the dipole groups [1-3,14-16]. We propose herein a possible model for the phosphonium self-assembly: polar thin film produced by two-dimensional ionic layers with a dipolar order (Figure 2a). The *P*s occurs by the spontaneous displacement of ions in each layer plane as shown in Figure 2b. This may be namely due to the collective effect of each pair of positive and negative ions as an electric dipole. It is of interest here that the **P-LC** thin film possesses macroscopically ordered *P*s, even though each ionic layer is separated by the insulating glassy alkyl segments. In fact, the angular dependence of polarization plane of exciting beam on the SHG activity was observed. When the exciting beam polarized along the x axis was employed, the thin film assembly was most active in the SHG. In contrast, with the exciting beam polarized along the y axis, the intensity of the SHG signals decreased.

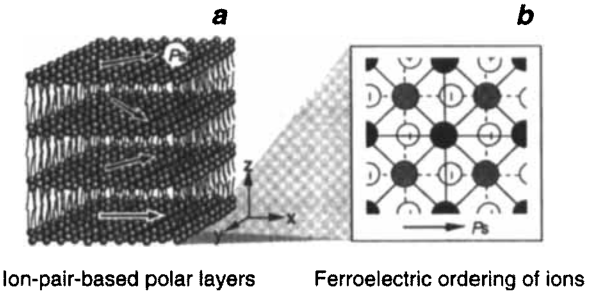


FIGURE 2 Schematic illustration of the layered thin film self-organized by the phosphonium liquid crystal (**P-LC**): (a) Two-dimensional polar layers as an SHG-active site comprising the phosphonium self-assembly, which are stacked parallel to the glass substrates (x-y plane). Arrow corresponds to a spontaneous polarization (*P*s); (b) Realized relative arrangement of ions in an ionic layer on the basis of the simplest square array model with the tetrahedral unit cell. Black and gray circles correspond to the positively-charged phosphorus atoms with the long alkyl tails above and below the lattice plane, respectively, which are located on the corners of a tetrahedron. White circles in each unit cell correspond to the chloride ions as a counter anion, which are surrounded by four cations and located in the spaces between the bilayers.

Here we need discussion why the phosphonium thin film shows the *P*s resulting from the spontaneous displacement of ions in the layer plane. The phosphorus atom is able to form pentavalent molecules, *e.g.*, $PCl_5$, in which there are more than four pairs of electrons around the central atom. This is based on the participation of 3*d* orbitals of the phosphorus atom in bond formation [17-19] or the presence of three-center four-electron bond in the molecules [20-22]. On the other hand, the nitrogen atom is unable to form such pentavalent compounds. We predicted therefore that the *P*s of the phosphonium assembly is ascribed to the intrinsic electronic structure of the phosphorus atom.

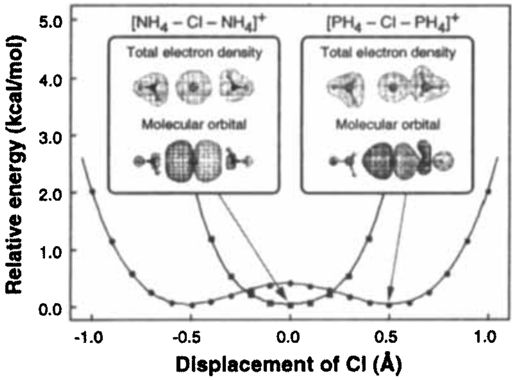


FIGURE 3 Potential energy surfaces of **X-LC**, which were obtained by theoretical calculations on the linear $[XH_4 - Cl - XH_4]^+$ model. In these molecular models, the distances between the heteroatoms were fixed, which were estimated by the X-ray measurement. To determine the most stable atomic arrangement, the degree of the displacement of Cl atom was varied, and the molecular structures were fully optimized at the DFT/Beck3LYP level of theory using the 6-31G(d) basis set and the potential energy was calculated simultaneously. Inserted figures show the total electron density and one of the most significant molecular orbital which contributes to the interaction between Cl atom and heteroatom in each molecular model. The molecular orbitals show that the orbital mixing between N and Cl atoms in $[NH_4 - Cl - NH_4]^+$ occurs out of phase (*i.e.*, antibonding manner), while that between P and Cl atoms in $[PH_4 - Cl - PH_4]^+$ is in phase manner indicating bonding combination.

The ionic layer within the layered self-assembly formed by **X-LC** is electronically neutral because the number of positive heteroatoms is equivalent to that of negative chloride ions. As shown in Figure 2b, the tetrahedral unit cell, consisting of one chloride anion and four cations, exhibits a positive trivalent state, which is significantly different from the ideal electroneutrality model. For theoretical investigation, thus, the positive univalent $[XH_4 - Cl - XH_4]^+$ model was used so as to give better approximation to the ideal model. Figure 3 shows the potential energy surface of **X-LC** calculated through the density functional method, in which the degree of displacement of Cl was varied in the linear molecular model. **P-LC** was found to give a bistable geometry with the noncentrosymmetric atomic arrangement. This result indicates that the phosphonium ion would form a weak P–Cl bond with the chloride ion as a counter anion. In contrast, **N-LC** showed only the centrosymmetric geometry. These results therefore support our hypothesis that in the two-dimensional noncentrosymmetric polar layers the spontaneous displacement of ions originates from the variety of bonding manner of phosphorus atom. The detailed mechanism of the bond formation between P and Cl ions, however, is not well understood at the present stage of research.

## Enhancement of the Polar Order by Application of Lateral Electric Field

If the phosphonium thin film assembly possesses a ferroelectric property, the *P*s directions should be changed by the external field such as an electric field and a mechanical stress. A lateral electric field was then applied to the **P-LC** thin film along the x axis by using substrates with a pattern of interdigitated electrodes, and we attempted to rearrange the ions in the layer plane. When the fundamental light polarized along the x axis was employed, the **P-LC** thin film was more active in the SHG than that before application of the electric field. In contrast, with irradiation of the fundamental light polarized along the y axis, the intensity of the SHG signals decreased outstandingly. These results demonstrate that the *P*s of the each ionic layer can be aligned by applying electric field, resulting in the enhancement of polar order in the phosphonium thin film assembly.

Ferroelectrics are characterized by the existence of polarization hysteresis loops which result from bistable states via inversion in the direction of the *P*s. Although the phosphonium thin film assembly possesses the macroscopically ordered *P*s, there is no conclusive evidence to show its ferroelectric property. Unfortunately, the polarization hysteresis loop can not be observed for the **P-LC** thin films at the present stage of research. However, it is at least true that the phosphonium thin film exhibits an electrical response and leads to the saturation of polarization. On the basis of the simplest test for the ferroelectricity, therefore, the **P-LC** thin film assembly may be regarded as "quasi-ferroelectrics" which are composed of the two-dimensional domains with the *P*s.

## CONCLUSION

We have shown for the first time that a multilayer self-assembly, which is formed by surfactants, acts as polarization-tunable polar thin films. The existence of two-dimensional self-assembled atomic layers with *P*s was revealed through the evaluation of second-order nonlinear optical property of solid-state layered thin films which are built by phosphonium liquid crystals. In an ionic layer within the multilamellar assembly, it was found that *P*s, which is an overall permanent electric polarization, occurs parallel to the ionic layer because of the spontaneous displacement of ions (*i.e.*, ferroelectric ordering of ion pairs as an electric dipole). Through the theoretical calculations, such generation of the *P*s in the layer plane was assumed to originate from the variety of bonding manner (*i.e.*, the characteristic electronic structure) of phosphorus atom. Furthermore, it could be confirmed that the intensity of SHG signals from **P-LC** increases by application of an external electric field (*i.e.*, polarization treatment), indicating the enhancement of polar order in the phosphonium thin film assembly. We predicted that the *P*s in each ionic layer can be realigned into one direction by application of an electric field.

The phosphonium self-assembly with a dipolar order essentially differs from the conventional supramolecular systems because the origin of macroscopic polarization is not due to a dipolar alignment in molecule-based organizations [4-7], but due to a noncentrosymmetrical atomic arrangement of ion pairs as an electric dipole. This finding has generated a considerable interest in an interdisciplinary field of science and stimulated the development of supramolecular devices.

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