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[11] To obtain conductivities the coverage on the electrodes were determined by profilometry and are related to that of poly(3-methylthiophene), $\sigma = 60\,\mathrm{S\,cm^{-1}}$ to correct for non-uniform coverage. This method has been established to provide a reliable measurement of a number of electropolymerizable monomers.[12, 13]

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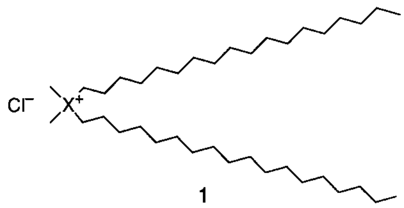
Polar Thin Films Produced by Phosphonium Liquid Crystals: Two-Dimensional Self-Assembled Ionic Layers with Spontaneous Polarization**

Akihiko Kanazawa, Tomiki Ikeda,* and Jiro Abe

The area of thin film assemblies that have layer structures is rapidly developing into a key technology with applications ranging from chemical sensor systems to electronic materials (dielectrics, semiconductors, superconductors, optoelectronics, magnetic substances, and so forth).[1] The layered thin films are usually prepared from organic or inorganic materials by a variety of physical and chemical techniques (including, among others, laser ablation, evaporation, sputtering, chemical vapor deposition, the Langmuir–Blodgett technique, and sol–gel processing).[1a,b, 2] For solid-state thin films, however, it is often difficult to control the layer structure and the molecular (or atomic) arrangement. Since crystalline materials are mainly used as sources for the thin film assemblies, the assembly structures are limited by the intrinsic single-crystal structures of these sources. Clearly, the ability to control of organizational structure at the molecular or atomic levels is very important in development of new functionalized materials. Recently, supramolecular assemblies have been regarded as one of the most promising systems for applications in highly functionalized materials.[3] Liquid-crystalline materials have self-assembly characteristics for forming various phases and provide additional features such as the ability to respond to applied external fields. The assembly structures are directed by the choice of phase, so that the structurally controlled thin films could be prepared by quenching from the appropriate fluid phase into the solid state.[4] The incorporation of the liquid-crystalline properties into layered materials may be expected to bring about emergence of more functionalized thin films with characteristic structural features.

Through systematic studies on the applications of ionic amphiphiles to multifunctional materials (for example: antimicrobial agents, surfactants, phase-transfer catalysts, antistatic agents, ion exchangers, curing agents), we found that phosphonium salts, which are composed of an ion pair of positive phosphorus and negative halide atoms as well as two long alkyl segments, **1** (X = P), possess a high degree of molecular organization abilities in comparison with the common quaternary ammonium analogs, **1** (X = N), with the same structure except for the positively charged heteroatom.[5]



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Even in the bulk state, the phosphonium salts showed an advantageous feature as a thermotropic liquid crystal in spite of being structurally simple amphiphiles.[5c, 6] These salts formed a multilayer structure based on the bilayer stacking of the 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 two-dimensional polar layers, which are composed of pairs of positive and negative ions forming an electric dipole, separated by the insulating alkyl layers. Here we present unique feature of self-assembled layered thin films produced by the phosphonium liquid crystals, which was revealed through the evaluation of the second-order nonlinear optical properties (Figure 1).

To determine the spatial arrangement of ions in the layers 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 sandwiching cell with a gap of 15 μm in the isotropic phase, followed by rapid cooling to room temperature. These samples were colorless and transparent. Figure 2 shows changes in the SHG intensity observed for the P-LC and the N-LC films. The polarized exciting beam was introduced along the *z* axis (Figure 1b). Second-harmonic generating signals were clearly observed for P-LC (Figure 2a). On the other hand, N-LC with the same hydrophobic structure was SHG-inactive (Figure 2b). These results indicate that the second-order nonlinear optical response of the

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[*] Prof. Dr. T. Ikeda, Dr. A. Kanazawa
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5275
E-mail: tikeda@res.titech.ac.jp

Dr. J. Abe
Faculty of Engineering, Tokyo Institute of Polytechnics
1583 Iiyama, Atsugi 243-0297 (Japan)

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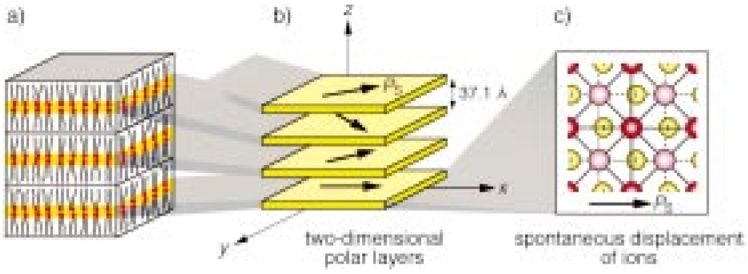

Figure 1. Schematic illustration of the self-organized layered thin film of the phosphonium liquid crystal (P-LC). a) Molecular alignment in the solid-state P-LC sample retains a bilayer structure, which was evaluated by the X-ray diffraction analysis using thin film methods. The diffraction patterns gave several higher-order Bragg reflections and the layer spacing (37.1 Å) is equal to twice the 18.5 Å molecular length. b) Two-dimensional polar layers, as an SHG-active site comprising the self-assembled phosphonium molecules, are aligned parallel to the glass substrates (*x*,*y* plane). Square plates and arrows correspond to an ionic layer and a spontaneous polarization (P_s), respectively. c) Realized relative arrangement of the phosphonium ions in a layer on the basis of the simplest square-array model with a tetrahedral unit cell. Dark- and light-red circles correspond to the positively charged phosphorus atoms with the long alkyl tails above and below the lattice plane, respectively, located on the corners of the tetrahedral cell. Yellow circles in each unit cell correspond to the chloride anions located in the spaces between the bilayers and are surrounded by four cations.

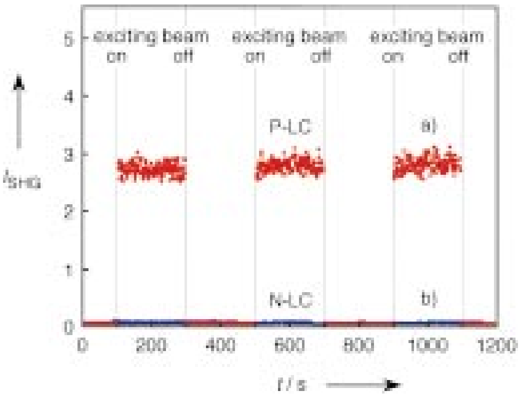

Figure 2. Change in the intensity of SHG signals on irradiation of the layered thin samples with the exciting beam: a) P-LC; b) N-LC. A Q-switched Nd:YAG laser ($\lambda = 1064$ nm, 10 Hz repetition rate, 6 ns pulse duration) was used for the exciting light source. The pulse energy of laser was controlled with neutral-density filters, then passed through a ¼ waveplate and a plate polarizer to polarized the beam along the *x* or *y* axis (see Figure 1). The sample sandwiched in the cell was placed on a sample stage in the *x*,*y* plane. The polarized laser beam passed through a UV-Vis cutoff filter and was focused on the sample along the *z* axis. After the sample, an IR filter, an polarization analyzer, and interference filter were used to remove all but the SHG signal (532 nm) with the same plane polarization as the fundamental wave. The SHG signal was detected with a photomultiplier and processed with a boxcar integrator interfaced with a computer.

amphiphilic organizations is related to their liquid-crystalline properties and this phenomenon is specific for the phosphonium species.

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 1 a). This implies that the SHG from the P-LC sample is due to the nonlinear polarization in the ionic layer. For SHG, a noncentrosymmetrical molecular or atomic arrangement of the materials is required in the bulk phase. In the phosphonium assembly, if noncentrosymmetric macroscopic arrangement of ions in the ionic layer is induced spontaneously, the ionic layer may possess second-order nonlinear optical properties. Many polar crystals with a noncentrosymmetric structure, such as barium titanate and sodium nitrite, are known to show a second-order nonlinear optical response.[1a,b, 7] 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, 7, 8] We propose herein a possible model for the polar thin film produced by the self-assembly of two-dimensional ionic phosphonium layers (Figure 1 b). The P_s occurs by the spontaneous displacement of ions in each layer plane as shown in Figure 1 c. This may be due to the collective effect of each ion pair as an electric dipole. It is of interest that the P-LC thin film possesses a macroscopically ordered P_s, even though each ionic layer is separated by insulating glassy alkyl segments. Further, the angular dependence of the polarization of the 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.

Here we must clarify 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, for example PCl_5, in which there are more than four electon pairs around the central atom because of the participation of 3d orbitals participating in bonding[9] or the presence of three-center four-electron bonds.[10] On the other hand, the nitrogen atom is unable to form such pentavalent compounds. We predict therefore that the P_s of the phosphonium assembly is attributed to the electronic structure of the phosphorus atom. Figure 3 shows the potential energy surfaces of the liquid crystals calculated through the density functional method, in which the chlorine displacement in linear $[XH_4{-}Cl{-}XH_4]^+$ ($X = N$, P) was varied.[11] The P-LC sample was found to give a bistable geometry with the noncentrosymmetric atomic arrangement. This result indicates that the phosphonium cation would form a weak P–Cl bond with the chloride 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 of the phosphorus atoms. The detailed mechanism of the bond formation between phosphonium and chloride ions, however, is not well understood at the present stage of research.

The phosphonium self-assembly with a polar 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,[3c–l] but due instead to a noncentrosymmetrical atomic arrangement of ion pairs as an electric dipole.[12]

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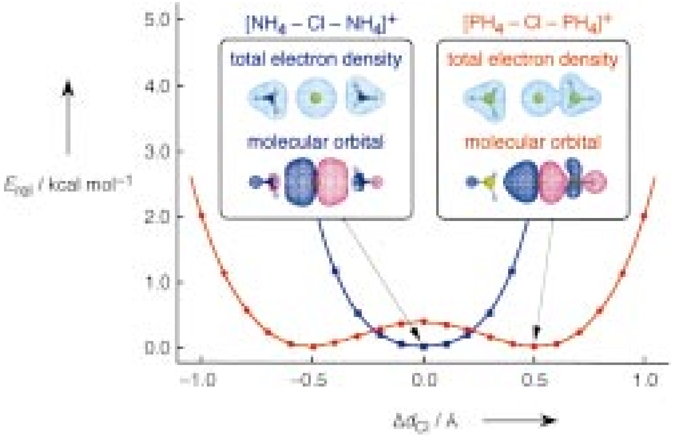

Figure 3. Potential energy surfaces of the **LC** samples, which were obtained by theoretical calculations on the linear $[XH_4{-}Cl{-}XH_4]^+$ (X = N, P) model. In these molecular models, the distances between the heteroatoms were fixed; 7.0 and 6.6 Å for P-LC and N-LC, respectively, which were estimated by the X-ray measurement. To determine the most stable atomic arrangement the degree of the displacement of the chlorine atom was varied and the molecular structures were fully optimized at the DFT/Beck3LYP level of theory using the 6-31G(d) basis set. 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 the chloride atom and heteroatom in each molecular model. The contour level is 0.015 au. The molecular orbitals show that the orbital mixing between nitrogen and chlorine atoms in $[NH_4{-}Cl{-}NH_4]^+$ occurs out of phase (i.e., antibonding manner), while that between phosphorus and chlorine atoms in $[PH_4{-}Cl{-}PH_4]^+$ is in phase and indicates bonding.

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[11] The ionic layer within the layered self-assembly formed by the samples is electrically neutral. As shown in Figure 1c, 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. Thus, the positive univalent $[XH_4{-}Cl{-}XH_4]^+$ model was used to approximate the ideal model.

[12] The interaction of the molecule with an electromagnetic field is described as the perturbation Hamiltonian. The interaction Hamiltonian can be written as a multipole expansion by a canonical transformation $\mathscr{H}_1 = -(\mu \times E + m \times H + Q \times \nabla E + \ldots)$, where μ, m, and Q correspond to the electric dipole, magnetic dipole, and electric quadrupole moments of the molecules, respectively.[13a] Within the electric dipole approximation, SHG is allowed in a molecular organization with dipole symmetry (dipolar order) but forbidden in one with quadrupole symmetry (e.g., an antiparallel array of the dipolar molecules). In the latter case, SHG should be dominated by electric quadrupole and magnetic dipole contributions. The conventional cyanobiphenyl-based liquid crystals, possessing dipole moments along the molecular long axis, have been reported to show an SHG activity in the smectic A phase.[13b] It has been concluded that the nonlinear optical response is due to the antiparallel orientational order of the molecules in each layer, that is, the smectic A films have quadrupole rather than dipole symmetry.[13b] In the case of molecular assemblies with quadrupole symmetry, the SHG can be observed even in the fluid phase possessing a centrosymmetric macroscopic structure. On the other hand, if an electric dipole process contributes to the SHG, the materials should exhibit no SHG activity in the fluid phase because of the disruption of polar ordering of dipoles (i.e., noncentrosymmetric structure). In the usual polar crystals with a noncentrosymmetric structure, it is known that the macroscopic polarization disappears at a certain (Curie) temperature resulting from the increase of lattice vibration through order–disorder solid–solid phase transition.[1d] A similar phenomenon was observed also for the solid-state P-LC film. We confirmed that P-LC shows no SHG activity in the temperature range of 75–82 °C not only in the smectic A phase but also in the solid phase retaining a smectic layer structure. This indicates disruption of dipolar order in the ionic layers occurs earlier than the solid to liquid-crystalline phase transition. Additionally, if the P-LC film is truly composed of the two-dimensional domains with P_s based on the dipolar order, their P_s directions are assumed to be changed by the external field such as an electric field and a mechanical stress. A lateral electric field was then applied to the sample film along the x axis by using substrates with a pattern of interdigitated electrodes. When the exciting beam polarized along the x axis was employed, the P-LC film was more active in the SHG than that before application of the electric field. In contrast, with irradiation of the exciting beam polarized along the y axis, the intensity of the SHG signals decreased outstandingly. This result implies that the P_s of the ionic layers can be aligned macroscopically by application of the lateral electric field. If the SHG from P-LC is due to the alternate

arrangement of the positive and negative ions in each layer plane (quadrupole symmetry), such modulation of the polar order may not be observed. In fact, the N-LC film, possessing quadrupole symmetry in the ionic layers, was inactive at all for the SHG under the same experimental condition. On the basis of these preliminary results, therefore, we concluded that the SHG from the P-LC film may be governed by the customary electric dipole process rather than the electric quadrupole process.

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Global Chirality in Rigid Decametallic Ruthenium Dendrimers[**]

Mahn-Jong Kim, Frederick M. MacDonnell,[*]
Mary E. Gimon-Kinsel, Thomas Du Bois,
Niloofar Asgharian, and James C. Griener

One hallmark of dendrimer chemistry is the ability to construct nanometer-sized assemblies with discrete architectures and defined connectivity.[1] In many cases, however, the ability to control the primary structure does not translate into the ability to control the global structure with high spatial organization and fidelity. Conformational flexibility within the dendrimer often leads to compact "molten globule" tertiary structures despite the composition. The incorporation of rigid monomers and linkages has led to shape-persistent dendrimers with restricted conformations, however, some rotational motion prevents complete spatial control.[2] A related, but heretofore elusive, goal is the construction of dendrimers that exhibit a global chiral topology.[3] Efforts to impart such a "tertiary" structure have focused predominantly on the incorporation of chiral carbon centers (C_1 symmetric) into the "primary" structure of the dendrimer.[4] While interesting chirooptic effects are observed in several cases, none show adoption of a preferred global chiral structure.

In contrast, spatially well-defined nanoscopic molecules, such as helicates, rings, squares, and boxes, are readily assembled by using metal-directed self-assembly methods.[5] Many such structures exhibit macroscopic chirality and several have even been prepared in enantiopure form through the use of chiral ligands.[6] The self-assembly approach has one drawback, in that the high lability of the metal ions required for such facile assembly typically makes such structures equally susceptible to decomposition or reorganization under conditions far milder than observed for most dendrimers.

We describe herein the synthesis of chiral, conformationally rigid metallodendrimers, which rival organic dendrimers in robustness and self-assembled structures in spatial fidelity. The $[\mathrm{Ru(diimine)_3}]^{2+}$ unit is our basic chiral synthon for supramolecular synthesis. This unit has enjoyed considerable attention as a building block for metallodendrimers largely because of its favorable room-temperature luminescence and redox properties, as well as its excellent chemical stability.[7] Until recently, however, the lack of stereospecific synthetic methods in the preparation of multimetallic assemblies has meant that such dendrimers are diastereomeric mixtures.[8] We have developed a stereospecific synthetic strategy for assembling such units into dendritic arrays and now demonstrate the power of this method to direct the tertiary structure of a nanosized molecule.

The homochiral decamer $\Lambda_6\Lambda_3\Lambda$-**Ru$_{10}$** was prepared in enantiopure form following the divergent synthetic route shown in Scheme 1. The notation used, $\Lambda_6\Lambda_3\Lambda$-**Ru$_{10}$**, gives first the stereochemistry of the outermost shell of ruthenium atoms, then the stereochemistry of the next outermost ruthenium sites, and then of the core atom. Central to this strategy is the use of substitutionally inert ruthenium trisdiimine complexes as chiral synthons which are connected by the condensation reaction between quinone and diamine functional groups at the periphery. The ruthenium tetramer $[\Lambda\text{-Ru}\{\Lambda\text{-(tpphz)Ru(phen)}_2\}_3]^{8+}$ (tpphz = tetrapyrido[3,2-*a*: 2′,3′-*c*: 3″,2″-*h*: 2‴,3‴-*j*]phenazine) ($\Lambda_3\Lambda$-**Ru$_4$**) was prepared by this method[9] and can act as the core for further dendritic growth after oxidation of the terminal phenanthrolines to the quinone product $\Lambda_3\Lambda$-**Ru$_4$one** (Scheme 1). In this manner, the parent hydrocarbon acts as the protected form of the quinone and permits a controlled growth scheme. This reaction gives 67% yield of the desired quinone and proceeds with retention of stereochemistry, despite the harsh reaction conditions, as determined by circular dichromism (CD) and by analogy to a model study of this reaction on mononuclear chiral complexes.[10] Addition of excess Λ-[Ru(phen)$_2$(phendiamine)]$^{2+}$ produces the decamer in ≈20% yield after purification by alumina- and gel-packed column chromatography. The diastereomeric decamer $\Lambda_6\Delta_3\Lambda$-**Ru$_{10}$** was prepared in a similar manner from $\Delta_3\Lambda$-**Ru$_4$one** and Λ-[Ru(phen)$_2$-(phendiamine)]$^{2+}$. Both show excellent solubility in acetonitrile or dimethyl sulfoxide as the hexafluorophosphate salt, or in water as the chloride salt. These complexes are robust and show good stability even under harsh conditions (heat, concentrated acids and bases) and are stable to racemization in the absence of intense irradiation.[11]

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[*] Prof. F. M. MacDonnell, M.-J. Kim, Dr. N. Asgharian
Department of Chemistry and Biochemistry
The University of Texas, Arlington, TX (USA)
Fax: (+1) 817-272-3808
E-mail: macdonn@uta.edu

Dr. M. E. Gimon-Kinsel
Sensar Corporation, Provo, UT (USA)

Prof. T. Du Bois
Department of Chemistry
University of North Carolina, Charlotte, NC (USA)

Dr. J. C. Griener
Department of Pediatrics
The University of Texas Southwestern Medical Center,
Dallas, TX (USA)

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