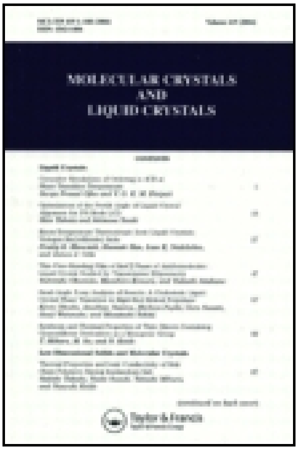

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An Infrared Technique for the Alignment Control of Liquid Crystalline Semiconductors

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An Infrared Technique for the Alignment Control of Liquid Crystalline Semiconductors

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Recently a new phenomenon was found that the change of liquid crystal alignment for hexagonal columnar (Col_h) mesophase is realized under the polarized infrared laser irradiation using an free electron laser (FEL) via *the vibrational mode excitation of a chemical bond in the mesogen. For Col_h mesophase of hexahexyloxytriphenylene (C6OTP), a new domain with a certain uniformity of molecular alignment could be obtained and one can control the director orientation based on the selected combination of the polarization direction of the incidence and the direction of the transition dipole moment for the vibrational excitation. This phenomenon could be observed only for the relatively higher-ordered liquid crystals with the higher viscosity such as Col_h mesophase not for discotic nematic as well as calamitic nematic and smectic A/C phases, meaning it could be good for the liquid crystalline semiconductors for the fabricating organic devices.*

Keywords: columnar mesophase; liquid crystalline semiconductor; molecular alignment control; organic electronic device; vibrational excitation

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INTRODUCTION

Recent studies of liquid crystalline materials have shown some of the new aspects featurized by their characteristic properties in mesophase. For example, the molecular stacking in columnar mesophase of disotic liquid crystals have been drawn much attention as an interesting architecture of self-assembled systems in terms of the efficient path for charge and energy migrations in electronic process along the axis. In particular, some compounds exhibiting columnar mesophase have shown an interesting feature as a novel electronic material of organics such as semiconductors because of the fast mobility of the charged carriers ($10^{-1}\,cm^2\,V^{-1}\,s^{-1}$) in columnar mesophase, which is comparable to that of a-silicon [1]. Also the recent studies have found novel systems of largely extended π-electronic conjugation for liquid crystalline semiconductors such as hexabenzocolonenes [2]. Furthermore, on the basis of the extensive studies on the charged carrier mobility for calamitic systems, some of the highly ordered smectic mesophases such as smectic B and E phases also show the faster mobility ($\sim 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$) [3,4].

On the other hand, the alignment control of liquid crystals is the most essential issue on the device applications because of the highly anisotropic properties of liquid crystalline materials. The alignment control of nematic liquid crystals have been extensively studied in relation to flat panel display technology and some reliable methodologies have been successfully developed [5]. Also found the development of successful techniques in the alignment control for ferroelectric liquid crystals (chiral SmC phase) [6]. However, these techniques are good only for the relatively lower ordered, thus lower viscous liquid crystals. For the more highly ordered phases, any established techniques has not yet been developed.

Therefore, it is not so difficult to imagine that one has to face with a problem in the application of these materials to functional devices, meaning a certain difficulty of the alignment control of liquid crystal domains and films arises because of the high viscosity resulting from the strong intermolecular interactions based on both of the relatively large π-electronic conjugation structure of the molecular core and the relatively higher order of molecular orientations, as compared to those of the conventional liquid crystals such as N and SmA/C phases. In fact, the recent studies show only a few successful results in obtaining a well-controlled alignment of discotic liquid crystalline semiconductors in device structure. For example, a room-temperature liquid crystalline hexabenzocolonene mesogen shows a spontaneous planar alignment behavior of molecules on a polytetrafluoroethylene (PTFE) film coated by friction transfer technique which attain to bridge the two electrodes to give the performance as Field Effect Transistor (FET) [7]. On the other hand, a novel approach of chemical structure modification of mesogens has been reported recently in which the introduction of fluoroalkylated chain into the peripheral parts of a triphenylene core to give the strong tendency of spontaneous homeotropic alignment on a variety of substrate surface for the Col_h mesophase, including ITO-coated substrate [8]. These approaches to get the well-controlled alignment of Col_h mesophase might be strongly dependent on the chemical structure as well as the mesomorphic properties of mesogen and thus, a novel technique would strongly be required to have the independent nature of such characters of mesogenic molecules.

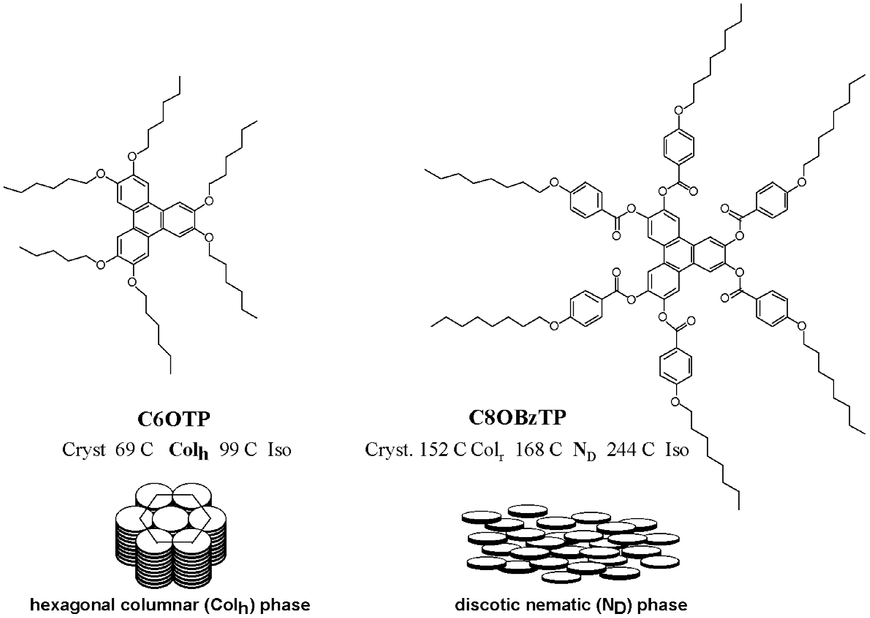
In this article, some evidences of reorientation to form liquid crystalline domains with uniform alignment of molecules under the polarizing infrared irradiation are shown to discuss the possibility of the polarized infrared technique as a novel tool for the device fabrication using highly ordered mesophases as an important component for the performance.

EXPERIMENTAL

The mesogenic compounds used in this work and their phase transition temperatures are shown in Scheme. The infrared irradiation was carried out using Free Electron Laser (FEL) in Osaka University, which is wavelength-tunable laser system based on Synchlotron radiation [9]. The incident beam power was ca. 10-8 mW as an averaged one because of some fluctuation of the generated laser beam. The beam power profile essentially has Gaussian-type distribution and for the irradiation, it was focused by ZnSe lense to give the cross section with ca. 0.5 mm of the diameter. The change of the liquid crystalline textures was observed using a polarizing microscope under crossed polarized condition and the phenomenon was recorded in video tapes as a motion picture by a video recorder. The details of the experiments are described in Ref. 15.

RESULTS AND DISCUSSION

It was found that polarized infrared laser irradiation of Col_h mesophase of a triphenylene columnar mesogen causes an alignment change to form a new domain with a certain uniformity of the alignment of which director is different from that of the surrounding area. This phenomenon is reasonably thought that the excitation of the



SCHEME

selected vibrational mode of a chemical bond is involved [10–13]. Recent studies on this phenomenon have also shown that this is a possible fabrication technique to form a certain area of a uniform domain in a Col$_h$ mesophase film [14,15].

Figure 1 shows the first observation of the texture change of the Col$_h$ mesophase of C6OTP under the successive irradiation, where the compound was sandwiched by two BaF_2 substrates. It was a new finding that between the BaF_2 substrates, C6OTP shows strong tendency to give a homeotropic alignment and after the successive irradiation of the incident beam at 1615 cm^{-1} corresponding to the absorption band of C—C stretching mode of the aromatic triphenylene ring, a new domain was formed with a almost ellipsoidal shape in the homeotropic domain. The resulting ellipsoidal shape of the new domain is due to the slantwise irradiation of the beam. The new domain has almost optical uniformity of the molecular alignment, indicated by the periodic change of the brightness in the texture under rotating the microscopic stage.

It is important to notice that this is not a phenomenon with quick formation of new domain under the irradiation. It requires a certain time (~10 sec) for the beginning of the texture change after the start

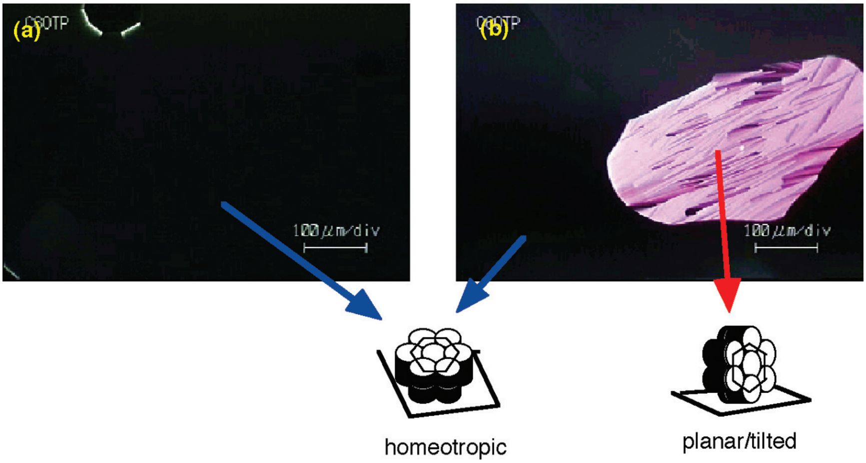


FIGURE 1 Texture change of $\mathrm{Col_h}$ mesophase for C6OTP (90°C) under the infrared irradiation to excite the C–C stretching mode of the triphenylene ring ($1615\,\mathrm{cm}^{-1}$). (a) Before the irradiation, a homeotropic alignment was spontaneously formed on cooling from the isotropic phase. The irradiation at $1681\,\mathrm{cm}^{-1}$ caused no change of domains. (b) After the successive irradiation, a new domain with an ellipsoidal shape comes out against the homeotropic area.

of irraditaion and this duration depends on the temperature at which the irradiation is carried out. Also one can see that the higher temperature for the irradiation leads to the shorter time to attain the beginning of domain change. The irradiation at $1681\,\mathrm{cm}^{-1}$ where the molecules have almost no absorption of the incident photon energy, never gives rise to any change of the domain. This means that the photon absorption to excite the vibration mode of chemical bond is necessary for the domain change of liquid crystal. This is indeed quite reasonable, considering the fact that the excited state relaxes to the ground state within a time scale of pico second order accompanied with the conversion to thermal energy which is diffused by way of through-bond and molecular collisions in a condensed matter. This strongly implies the thermal injection into the system followed by the relaxation of the vibrational excited state concerns with the formation of new domain having a uniform alignment of molecules. In addition, the change of the irradiation power affect the size of perturbed domain and the less power gets the smaller area of turbulence in the texture. This also supports that the thermal energy injection followed by the vibrational excitation is surely involved in this phenomenon.

Here, it is noteworthy to emphasize that the newly formed domain could have rather long lifetime, dependent on the temperature where the higher temperature leads to the shorter lifetime. It could range from a few minutes to several hours at least. This fact is interesting when one sees the contrast behavior in N_D phase shown by C8OBzTP. The irradiation to C8OBzTP at $1615\,cm^{-1}$, which is the wavenumber corresponding to the band of the C–C stretching mode of the aromatics, does cause only dynamic turbulence of the texture (Fig. 2) and this turbulence immediately stops to go back to the original homeotropic alignment of domain when the irradiation is cut off. The N_D mesophase exhibited by C8OBzTP also shows strong tendency for homeotropic alignment between BaF_2 substrates. For N_D phase, there was no evidence that new domains with the uniformity are formed in a stable manner like Col_h mesophase as described above. This is probably due to the far lower viscosity of N_D phase, meaning the alignment is strongly subject to the substrate surface (surface anchoring determining the alignment). This behavior was also observed for N and SmA/C phases of a calamitic liquid crystal [16].

Further experiments revealed that an interesting relation between the polarizing direction of the incident beam and the direction of

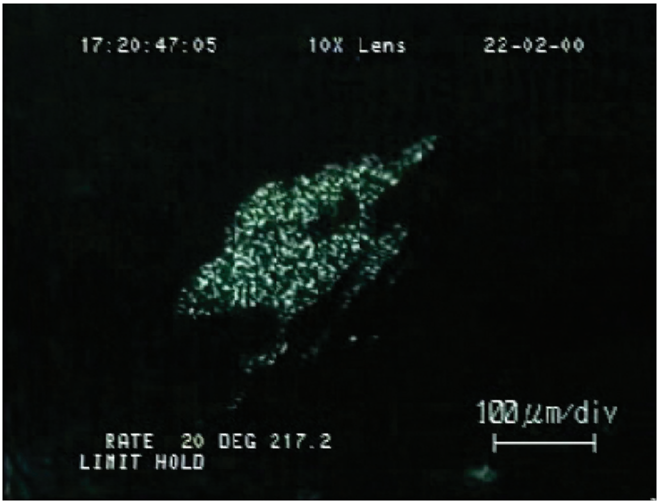
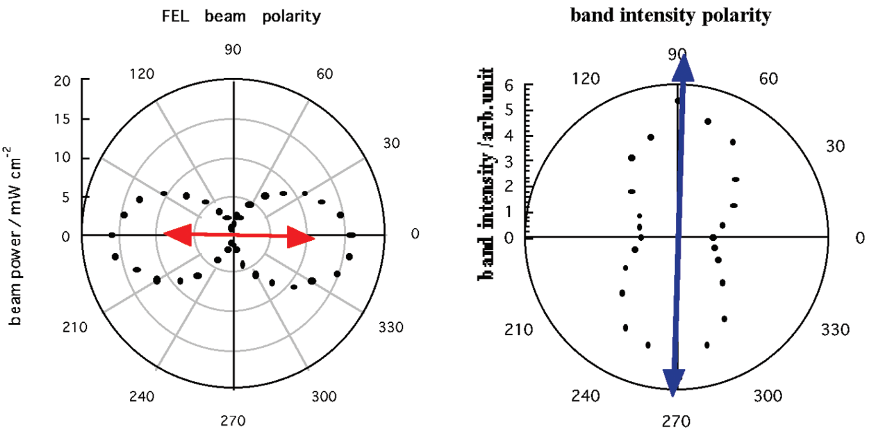


FIGURE 2 A dynamic turbulence of the homeotropic texture of N_D phase (217°C) under the irradiation at $1615\,cm^{-1}$ (C–C stretching mode of the aromatics). The bright area is a dynamic turbulence of domain texture.



polarization at 1615 cm^{-1}
(C=C str. mode of the triphenylene core)

band intensity distribution of the C-C stretching mode

FIGURE 3 The observed distribution in the band intensity of the C–C stretching mode of the triphenylene core, which directly shows the perpendicular reorientation against the polarizing direction of incident beam. The irradiation and spectral measurements were carried out at 90°C (Col$_h$ mesophase).

the transition moment of the vibrational excitation. Figure 3 shows the relation between the polarizing direction of the beam and the distribution of the band intensity for the C–C stretching mode (1615 cm^{-1}). It is clearly seen that the triphenylene mesogens align under the irradiation in a way that the molecules no longer absorb the incident photon. The new uniform domain has a planar alignment of molecules (the columnar axis parallel to the substrate surface), meaning the initial homeotropic alignment was changed to the planar one [14].

Furthermore, the irradiation at 839 cm^{-1} (C–H wagging out-of-plane mode) to the planar domain formed by the irradiation at 1615 cm^{-1} under the same direction of the incident polarization resulted in realizing the initial homeotropic alignment (return to the initial state of alignment).

These results mean this technique of polarizing infrared laser irradiation could provide a novel method to control the alignment of highly viscous liquid crystals. In our recent experiments, a H-shaped uniform domain with a planar alignment was successfully obtained in the homeotropic film of Col$_h$ mesophase for C6OTP mesogen (Fig. 4) [15]. This makes it expected that one can prepare a polymer film

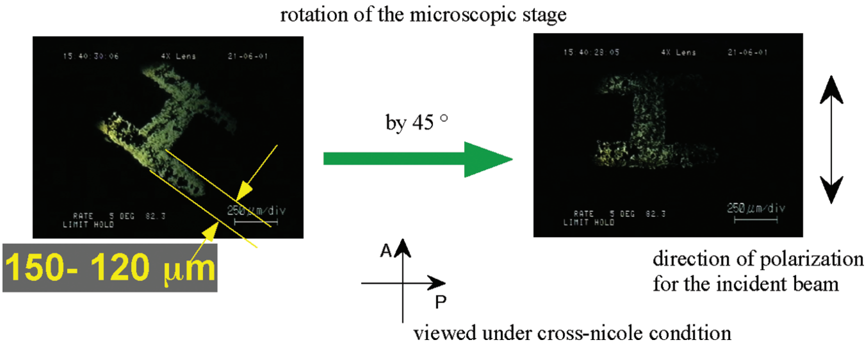


FIGURE 4 A H-shaped domain fabricated by the manual scanning of the polarized infrared beam (1615 cm^{-1}) at °C. The rotation of the microscopic stage indicates the domain has an almost uniform alignment of molecules, though some parts are not probably due to the fluctuation of beam power and quality.

with a liquid crystalline order by the following photo-polymerization after the infrared treatment, where some domains with uniformity of the molecular alignment independently exist in one sheet of the film like a circuit in a thermally stable manner (without no phase transitions in a certain range of temperature), when considering the local order parameters are changed in ca. 70% decrease of the parameter by photopolymerization in N_D mesophase [17,18]. The simple image of the novel technique is schematically drawn in Figure 5.

On the other hand, recent studies of liquid crystalline smiconductors have revealed that some of the highly ordered smectic mesophases also could have fast mobility of charged carriers. However, the same situation could be seen in the application of these materials to the functional devices as that for diacotics because of the similar property of viscosity of mesophase.

Our recent and preliminary experiments for a highly ordered calamitic system have revealed a possibility of alignment control for smectic B phase of a well-known mesogen, 8PPEP8 [19] as shown in Figure 6. The area irradiated by the polarized infrared beam shows a strong tendency to give a homeotropic alignment between BaF_2 substrates, whilst in the SmA phase, only turbulence of liquid crystalline domains was observed. It may be reasonable to think that the initially settled condition between the mesogenic molecules and substrate surface could affect the alignment behavior and it is more efficient for the highly ordered phase in the weak condition, considering the anchoring effect defined by the substrate surface.

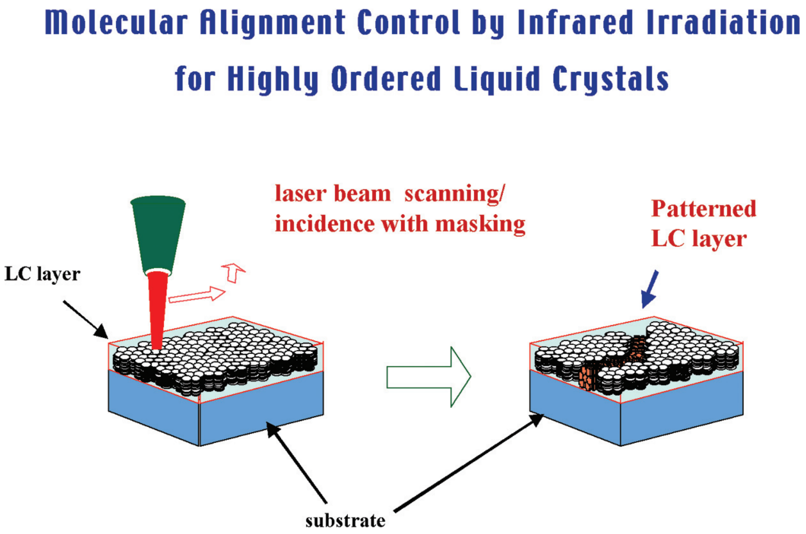
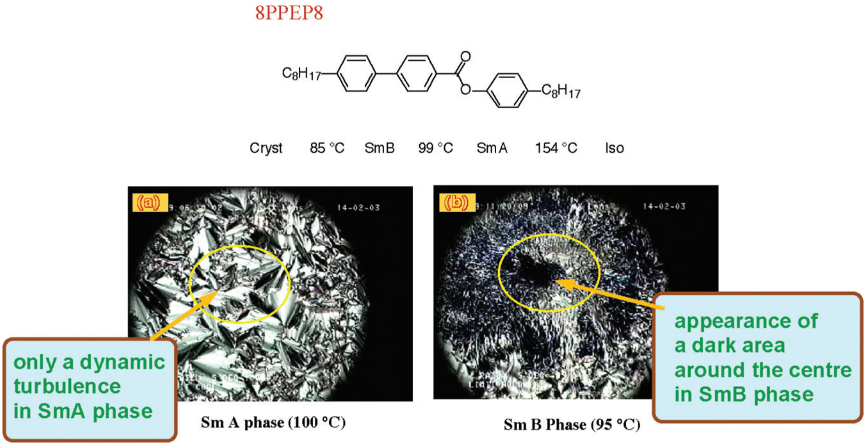


FIGURE 5 A Schematic representation of the fabrication technology using a polarizing infrared laser to control the domain shape/size with a certain uniformity of molecular alignment. The stability of the function performance might be obtained by polymerization to get a solid (soft) film in which the liquid crystalline order of molecules is being held and the fluctuation of molecules is remained to some extent.



Sm A phase (100 °C)

Sm B Phase (95 °C)

FIGURE 6 Liquid crystalline domain changes under the irradiation at 1606 cm^{-1} (C–C stretching mode excitation of vibration) for (a) SmA and (b) SmB phases with ca. 8 mW power of the incidence.

CONCLUSION

The infrared irradiation to excite a vibrational mode of chemical bond in a $\mathrm{Col_h}$ mesophase of a triphenylene discotic liquid crystal was found to induce the alignment change to form a new domain with the uniformity of the alignment of which direction could be defined by the combination of the polarizing direction of the incident beam and the direction of the transition moment of the vibrational excitation for the molecular anisotropy in shape. Also a possibility to control the alignment for SmB phase was shown as a preliminary result. This is expected to provide a novel technique for a device fabrication using highly viscous mesophase materials such as liquid crystalline semiconductors with fast mobility of charged carriers.

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