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Hirosato Monobe^a, Hironobu Hori^a, Yo Shimizu^a & Kunio Awazu^b

^a Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan

^b Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

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Hirosato Monobe

Hironobu Hori

Yo Shimizu

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan

Kunio Awazu

Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

In this study, the alignment change with circularly polarized infrared irradiation for columnar mesophase was investigated for a liquid crystalline triphenylene derivative in order to get uniform domain with homeotropic alignment of columnar liquid crystal.

It was found that circularly polarized infrared irradiation provides alignment change to form new domain with uniformly homeotropic ("face-on") alignment and this phenomena is by way of the excitation of the selected vibrational mode of a chemical bond. The results strongly imply that the infrared irradiation is a possible technique for device fabrication by use of columnar liquid crystalline semiconductors.

Keywords: alignment control; circularly polarized light; discotic liquid crystal; infrared

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Address correspondence to Hirosato Monobe, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan. E-mail: monobe@ni.aist.go.jp

INTRODUCTION

Columnar liquid crystals such as discotic liquid crystals with a high order materials are good candidates as organic semiconductors for electronic devices due to their potential to have the fast mobility of charge carriers [1–8] as well as the anisotropic property of conduction along the columns [9]. In fact, in a highly ordered columnar mesophase, a fast carrier mobility ($\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by electronic process of carrier transport was found which is comparable to that of amorphous silicon [2,8]. Furthermore, columnar liquid crystals are expected as a self-organized molecular semiconductor to fabricate the related devices by solution process. In addition, recent studies as for photopolymerization of liquid crystals indicate that such a molecular order of discotic liquid crystal could remain in polymer solid film [10], leading to a sophisticated invention of optical compensator for wider view angle of liquid crystal display [11,12]. These results imply that discotic liquid crystals are good candidates for organic thin film devices if their alignment is well controlled.

In order to obtain the higher performance of devices, a novel technique to align the columns of the columnar liquid crystals is strongly required, by which one can obtain the alignment perpendicular to the electrode interface (“face-on”) for the photovoltaic cells and light emitting diodes, or parallel to the isolator interface (“edge-on”) for the lateral field effect transistors. The interesting results have been reported to obtain uniaxial planar or homeotropic alignment of columnar liquid crystals and a few successes were attained for planar alignment by zone-casting technique [13] and polytetrafluoroethylene coating to the substrate surface by friction transfer technique [14]. On the other hand, it was found the introduction of fluoroalkylated chain into the peripheral parts of triphenylene mesogens leads to get a strong tendency of homeotropic alignment [15]. However, the conventional techniques applied to nematic phase are not useful for the alignment control of highly ordered columnar liquid crystals.

Recently, in a series of experiments for columnar mesophases of well-known discotic mesogens, 2,3,6,7,10,11-hexaalkoxytriphenylene by use of a free electron laser (FEL), we found that the homeotropic domain where the columnar axis aligns perpendicular to the substrate could be changed to a domain with a planar alignment of columns by the excitation of C–C stretching vibration of triphenylene [16–20]. This technique extended to alignment control of the plastic columnar mesophase [21,22]. It was found that the irradiation for the excitation of the C–C stretching band of triphenylene consequently leads to the formation of a new domain with uniform alignment of molecules in the

way that the transition dipole is perpendicular to the polarization of incidence. According to this relation, the circularly polarized incidence would surely give the formation of homeotropic domains with an appropriate vibrational excitation even in the plastic mesophase.

In this work, the alignment change with linearly and circularly polarized infrared irradiation for plastic columnar mesophase was investigated for a liquid crystalline triphenylene derivative in order to get uniform domain with planar and homeotropic alignment of plastic columnar mesophase via vibrational excitation process, respectively.

EXPERIMENTAL

The compound used in this work is a typical columnar discotic liquid crystal, 2,3,6,7,10,11-hexabutyloxytriphenylene (C4OTP), as shown in Figure 1(a). Its preparation, purification and mesomorphic characterization have been presented and discussed in detail by others [2,23,24]. A plastic hexagonal columnar (Col_{hp}) mesophase appeared between the melting and clearing points ($\text{C } 90^\circ\text{C } \text{Col}_{\text{hp}} \text{ } 145^\circ\text{C Iso}$). C4OTP film was prepared between two BaF_2 substrates which have high transparency in infrared region, with 2- μm silica beads spacer and mounted on a hot stage (Linkam LK-600 FT-IR), which was attached to an inverted optical polarized microscope (Olympus IX-51). The BaF_2 substrates used were polished substrates and no surface treatment was used in this study. The microscopic texture was recorded using a CCD camera (Keyence VH-6300C) with a commercially available S-VHS video recorder. FT-IR spectrum of C4OTP film at 140°C was shown in Figure 1(b). The absorption peak at 831 cm^{-1} is assigned to an aromatic C–H out-of-plane vibration of the triphenylene.

The pulse sequence of infrared FEL consists of a train of macropulses which themselves contain a train of 300–400 ultrashort micropulses. The width of the macropulses is about $15\text{ }\mu\text{s}$ and the repetition rate is 10 Hz. The width of a micropulse is estimated to be about 5 ps. The average power of FEL beam was ca. $2\sim 5\text{ mW}$ in this experiments. The beam was focused to about 0.5 mm in diameter by ZnSe lens. A polarizer (II-VI, PAZ-20) and a tunable zero-order $\lambda/4$ plate (Alphas) was used to obtain circularly polarized infrared light. The polarization property of a FEL beam intensity shows a linear polarization before light through the $\lambda/4$ plate and a circularly polarized after it through the waveplate as shown in Figure 2(a) and 2(b), respectively. A schematic representation of the experimental setup for a right above irradiation are shown in Figure 3. The position of the irradiating

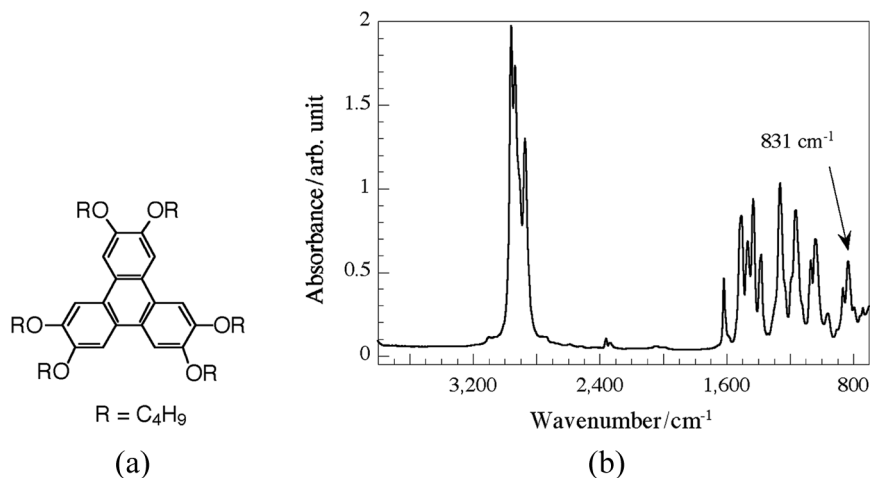


FIGURE 1 (a) Molecular structure of hexabutyloxytriphenylene (C4OTP) and (b) its infrared absorption spectrum in Col_{hp} phase (140°C).

FEL beam spot was confirmed by color change of a thermosensitive paper on the stage.

RESULTS AND DISCUSSIONS

The microscopic observations of a Col_{hp} phase emerge as a multi-domain mosaic texture under the crossed Nicol condition when a 2-μm thick C4OTP film is cooled from isotropic phase to 141°C as shown in Figure 4(a). A rotation of the microscopic stage gave rise to an alternately and periodic appearance of darkness for the domains under crossed Nicol condition by every 45° as shown in Figure 4(b). This means that it is almost planar (edge-on) alignment where the columnar axis lies on the substrate surface in the center area of Figure 4.

Figure 4(c) shows the texture of C4OTP film after irradiation by the infrared FEL with a wavelength of 831 cm⁻¹ which is absorbed by C–H out-of-plane vibration of triphenylene. The plane of polarization of the IR radiation was perpendicular to the substrates and parallel to the abscissa in the Figure 4(c). A rotation of the microscopic stage gave rise to an alternately and periodic appearance of darkness for the newly formed domain under crossed Nicol condition by every 45° as shown in Figure 4(d). This means a uniform alignment of columns is obtained in this newly formed domain. Only in the central part of

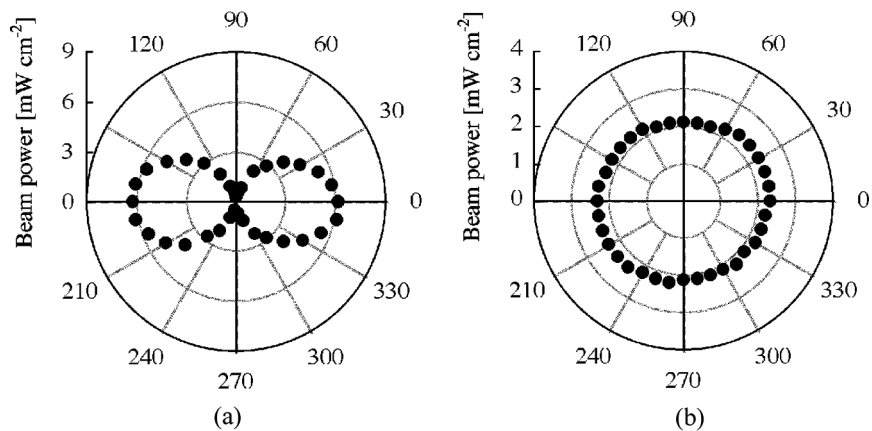


FIGURE 2 Polarization property of a FEL beam (a) original and (b) with $\lambda/4$ waveplate.

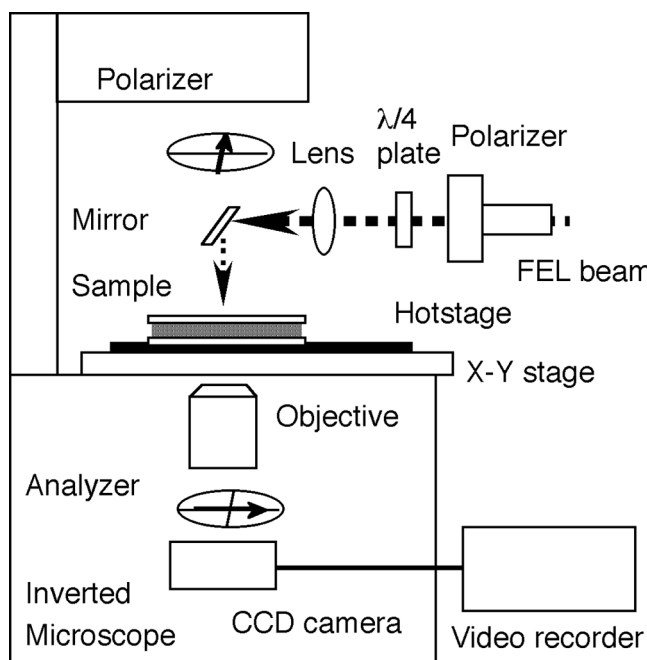


FIGURE 3 Schematic representation of setup for FEL irradiation.

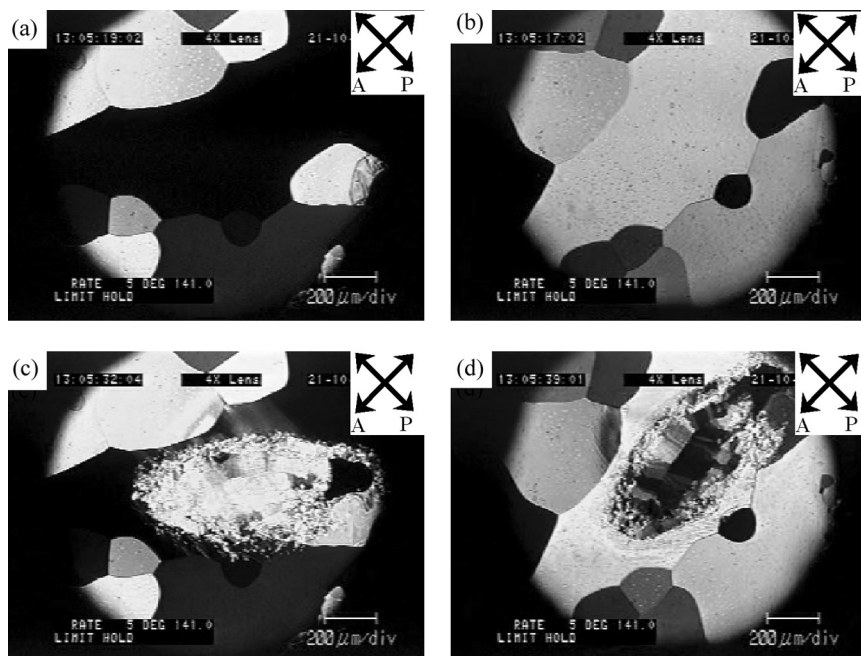


FIGURE 4 Microscopic textures observed for a C4OTP film at 141°C cooled from I.L. (a) before and (c) after linearly polarized IR irradiation. (b) and (d) show textures after rotation of the sample on the stage by 45° counterclockwise for (a) and (c), respectively.

domain shows completely uniform alignment change, this was probably caused by less quality of FEL beam of surrounded area.

Figure 5(a) and 5(b) show a multi-domain mosaic texture under the crossed Nicol condition of C4OTP film which was cooled from isotropic phase to 140°C and it is almost a planar (edge-on) alignment where the columnar axis lies on the substrate surface in the center area. The viewed sample area in Figure 5 was different from that in Figure 4.

Figure 5(c) shows the texture of C4OTP film after irradiation by circularly polarized infrared FEL with a wavelength of 831 cm^{-1} which is absorbed by C–H out-of-plane vibration of triphenylene. A rotation of the microscopic stage gave no change of an appearance of darkness for newly formed domain under crossed Nicol condition by every 45° as shown in Figure 5(d). This means a homeotropic alignment of columns is attained in this newly formed domain. The sample position was slightly moved to the upper part in the pictures between Figure 5(a) and 5(c). There are possibility that IR light heats up the

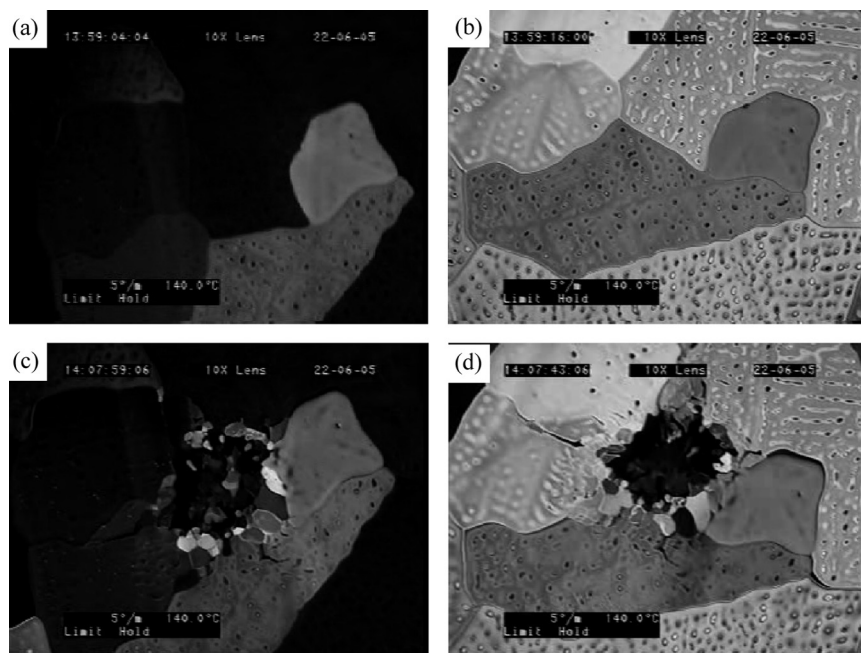


FIGURE 5 Microscopic textures observed for a C4OTP film at 140°C cooled from I.L. (a) before and after (c) circularly polarized IR irradiation. (b) and (d) show picture after rotation of the sample on the stage by 45° counter-clockwise for (a) and (c), respectively.

sample locally, which could cause a change from homogeneous to the energetically favored homeotropic alignment. Indeed, other alkoxy-triphenyls with longer alkoxy chains shows spontaneous homeotropic alignment cooling from the isotropic phase to the hexagonal columnar (Col_h) mesophase [25]. However, in Col_{hp} mesophase which is more rigid mesophase than Col_h , C4OTP cell does not show the spontaneous alignment behavior in the homeotropic way when cooling from the isotropic liquid. This implies that the switching of columnar axis is not only arisen from the energetically favored homeotropic alignment by locally heating with IR irradiation. This newly formed domain was quite stable and could be maintained for more than several hours in the mesophase. The sample used in this experiments did not show any change of the phase transition temperatures checked by polarized microscope observation. This implies that the vibrational excitation and the following thermal process did not cause any significant chemical damage of the compound.

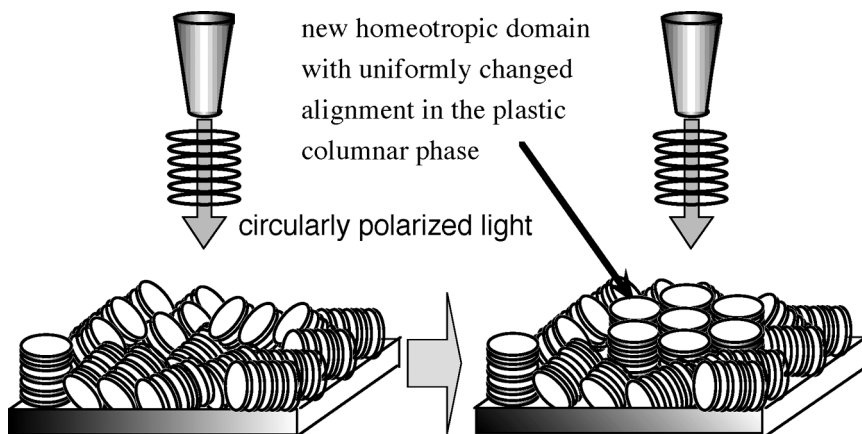


FIGURE 6 Schematic representations of alignment change of C4OTP with the circularly polarized IR irradiation.

These results indicate that the plane of discotic molecules aligns parallel to the plane of polarization of incidence (“edge-on”) with linearly polarized infrared irradiation. This indicated that the direction of the vibrational transition moment of the excited band aligns perpendicular to the plane of polarization and the propagation direction of incidence as same manner as previous work [17,18,20]. On the contrary, The change in polarized microscopic texture indicates that the irradiation with the circularly polarized light provides an alignment change to a homeotropic state. This indicates that the plane of discotic molecules aligns parallel to the substrate (“face-on”) and perpendicular to the propagation direction of incidence as shown in Figure 6. In other words, the relation between the propagation direction of the incidence is parallel to the direction of the vibrational transition moment of the excited band after the irradiation with circularly polarized infrared light. The direction of in-plane and out-plane columnar axes is controlled by choosing the polarization property of infrared incidence for the plastic columnar mesophase.

CONCLUSION

It was found that infrared laser irradiation of Col_{hp} mesophase shown by a typical triphenylene mesogen causes alignment change to form a new domain with uniformity of alignment and this phenomena is by way of the excitation of the selected vibrational mode of a chemical bond. Switching to “edge-on” and “face-on” arrangements could be

observed by vibrational excitation of the aromatic C–H vibration band of triphenylene with linearly and circularly polarized infrared irradiation, respectively. Recent studies on this phenomenon have also shown that a relationship was found for the directions of the polarization of incidence and the transition moment of the vibrational excitation. The results strongly imply that the infrared irradiation is a possible technique for device fabrication using highly viscous mesophase materials as a liquid crystalline semiconductor.

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