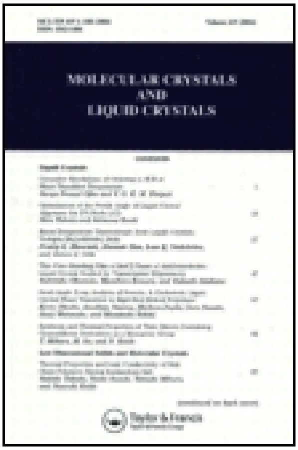

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Controlling the orientation of the columns in a DLC by irradiation with IR

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CONTROLLING THE ORIENTATION OF THE COLUMNS IN A DLC BY IRRADIATION WITH IR

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Polarized infrared photoinduced change of liquid crystal domains was investigated for a hexagonal columnar phase of a liquid crystalline triphenylene derivative. A uniform and anisotropic change of domains was observed when a polarized infrared light corresponding to the wavelength of the absorption band of triphenylene core was irradiated. IR absorption dichroism is induced as a result of the reorientation of triphenylene core. The texture observation and polarized microscopic FT-IR spectra show that a change of the molecular alignment occurred and the direction of columns depends on the polarization direction of an actinic infrared light. The technique could provide a novel technology to control the columnar alignment of supra-molecular systems.

Keywords: alignment control; columnar phase; discotic liquid crystal; infrared; polarized light

INTRODUCTION

Columnar liquid crystals, especially for discotic liquid crystals, have been drawing attention as novel organic semiconductors such as one-dimensional conductors, photoconductors, molecular wires and fibers, light

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emitting diodes and photovoltaic cells for several years [1–6]. Discotic liquid crystals have shown some interesting features for their electronic properties such as charge migration phenomena along a columnar axis [7–12]. In addition, recent studies as for photopolymerization of liquid crystals indicate such a molecular order of discotic liquid crystal could remain in polymer solid film [13], leading to a sophisticated invention of optical compensator for wider view angle of liquid crystal display [14,15]. These imply that discotic liquid crystals are good candidates for organic thin film devices if their alignment is well controlled.

In order to obtain a higher performance in molecular materials, an appropriate long-range order of molecules is an essential requirement. Uniformity of molecular alignment in the film is also an important issue in device fabrication with the thin film. However, it is well known that the control of molecular alignment is somewhat difficult to achieve for a crystalline solid and therefore liquid crystals have received much attention as materials, of which one can control the molecular alignment.

Surface effects and shear flow have often been used in order to obtain a uniformly aligned phase of discotic liquid crystals for studies of their potential application as novel optoelectronic functional materials [15–22]. Recent study on UV-vis photoalignment of discotic liquid crystals in discotic nematic phase by using photoreactive monolayer films indicates that it is possible to control the optical properties of liquid crystal devices by photons [23,24]. All the studies of photoalignment of liquid crystals have focused on the application of ultraviolet and/or visible light, since this could provide a clean and fast fabrication process for organic thin film devices [25]. However, only few results of molecular alignment controlling in columnar phases of discotic liquid crystals were reported so far, due to the higher viscosity and higher order as compared to the nematic liquid crystals.

Recently the technology of free electron lasers (FEL) has been extensively developed and this can provide some special analytical techniques to materials and their related phenomena [26]. The FEL has a specific characteristic for a laser system in that we can obtain a highly tuned pulsed laser beam with variety of wavelength from ultraviolet to far-infrared (0.3–20 μm).

In the previous work [27–29], the possibility of controlling the molecular alignment and domains of liquid crystals using infrared light, relating to selective excitation of vibrational processes, has been examined. We have found the first results on molecular alignment change for a columnar mesophase by vibrational excitation.

In this work, we show that a polarization dependent molecular alignment change for a columnar mesophase can be fabricated by vibrational excitation with polarized infrared irradiation.

EXPERIMENTAL

The compound used in this work is one of the typical columnar discotic liquid crystal, 2,3,6,7,10,11-hexahexyloxytriphenylene (C6OTP), as shown in Figure 1. Its preparation, purification and mesomorphic characterization have been presented and discussed in detail by others [30]. A hexagonal columnar mesophase appeared between the melting and clearing points (C 69°C $\mathrm{Col_h}$ 99°C Iso). C6OTP film was prepared between two BaF_2 substrates with 2-μm silica beads spacer and mounted on a hot stage (Linkam LK-600 FT-IR), which was attached to an optical polarized microscope (Olympus BH-2). The microscopic texture was recorded using a CCD camera (Keyence VH-6300C) with a commercially available S-VHS video recorder. It is found that C6OTP film shows a spontaneous homeotropic alignment in the columnar hexagonal mesophase. FT-IR spectrum of C6OTP film was measured and the absorption peak at $1615\,\mathrm{cm}^{-1}$ is assigned to an aromatic C-C stretching vibration of the triphenylene ring part.

A FEL has a complex pulse structure, which consists of a train of macropulses, which themselves contain a train of 300–400 ultrashort micropulses as shown in Figure 2(a). The width of the macropulses is about 15 μs and the repetition rate is 10 Hz. The width of a micropulse is estimated to be about 5 ps. The peak power of a micropulse is in the order of MW. Although the peak power is rather high, the duty factor is as low as 3×10^{-8}. Therefore the FEL beam average power was kept on 10 mW in this experiment. The FEL beam was focused to about 0.5 mm in diameter by ZnSe lens at the end of a FEL manipulator. The polarization property of a FEL beam intensity is shown in Figure 2(b) and it shows a linear polarization. A schematic representation of the experimental setup for a slantwise and a right above irradiation are shown in Figure 3(a) and 3(b), respectively. An IR absorption dicroism was measured by a microscopic FT-IR spectrophotometer (Horiba FTIR-520).

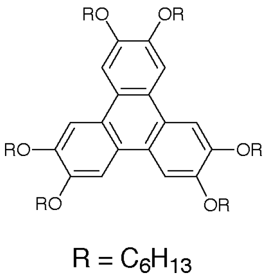


FIGURE 1 Molecular structure of C6OTP.

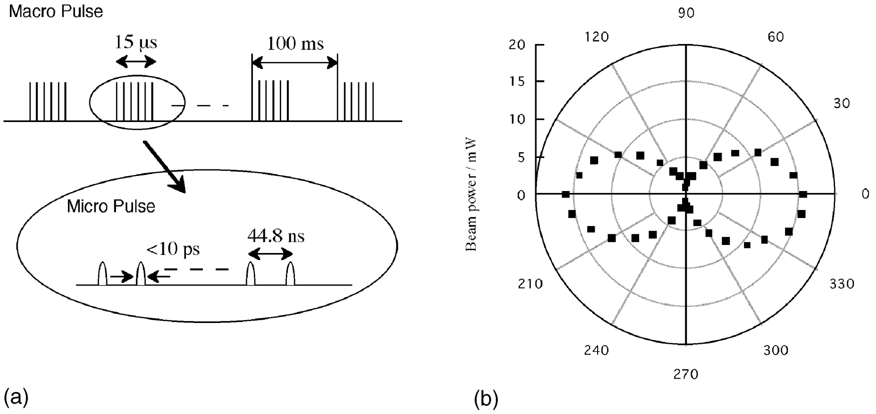


FIGURE 2 (a) The FEL temporal beam profile. The FEL has two pulse structures: micro- and macro-pulses. (b) Polarization property of an FEL beam intensity.

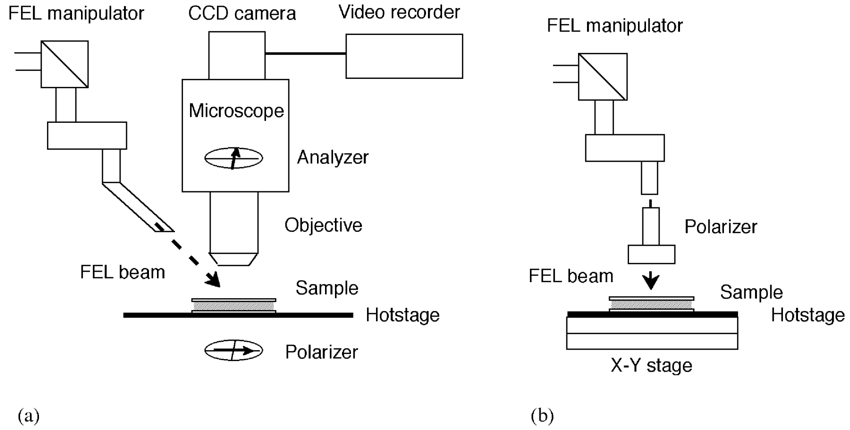
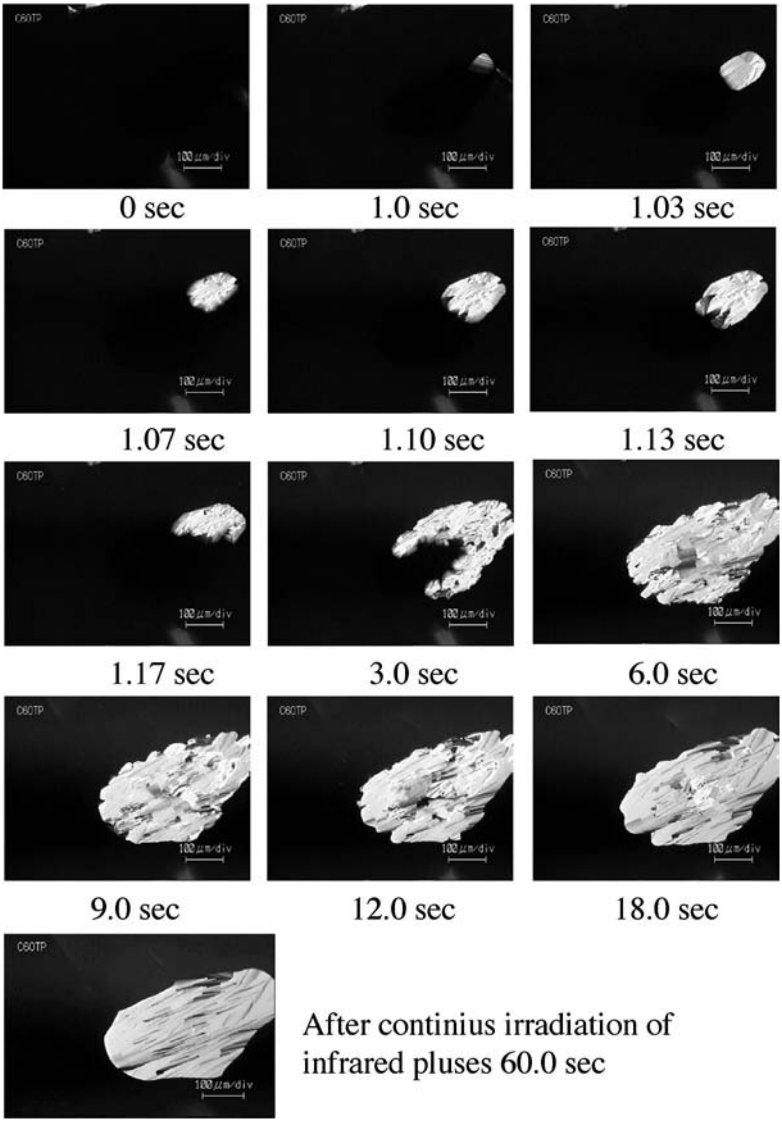


FIGURE 3 Schematic representation of setup for FEL irradiation light from (a) slantwise and (b) right vertically.

RESULTS AND DISCUSSIONS

Figure 4 shows sequentially recorded textures of C6OTP film at 97°C with slantwise irradiation (Fig. 3(a)) by the pulsed FEL beam with a wavelength of 1615 cm^{-1} (6.19 µm). When FEL irradiation started, the texture of C6OTP film slightly flickered in the dark level. After a few seconds from the beginning of the FEL irradiation, the irradiated spot in the texture



0 sec 1.0 sec 1.03 sec

1.07 sec 1.10 sec 1.13 sec

1.17 sec 3.0 sec 6.0 sec

9.0 sec 12.0 sec 18.0 sec

After continius irradiation of infrared pluses 60.0 sec

FIGURE 4 Sequentially recorded textures of C6OTP film at 97°C under FEL irradiation at 1615 cm^{-1}.

changed to bright from dark. During the FEL infrared irradiation, the bright area was incessantly and dynamically changing. In particular the central part of the bright area showed a rapidly changing texture. A dent-like structure appeared in the texture as shown in Figure 4, probably due to the Gaussian distribution of the laser-beam intensity.

This phenomena can be interpreted as the following. First, the molecules become quite mobile in the thermally disturbed domain. Following the generation of thermodynamically non-equilibrium states in the irradiated area, the molecules align in the new direction due to the irradiating infrared light in order to attain a thermodynamically more stable state by self-organization. Although the FEL beam macropulse was irradiated at intervals of 100 ms, the texture was recorded by a video tape with only 30 flames per second. This means that the following image comes up 33.3 ms after the previous one and that therefore we could not record the transient movement of the molecules during the time interval. It is assumed that the vibrationally excited state relaxes rapidly on a timescale of the order of pico second, followed by the thermal energy diffusion as a slower process. We observed only the slower process of these dynamical texture changes. The peripheral region of the irradiated spot formed a uniform texture after consecutive FEL pulse irradiation.

Further irradiation of FEL pulses created a uniform alignment of molecules. The change in polarized microscopic texture indicates that switching of the columnar axis from parallel to perpendicular or oblique to the substrate had occurred. After the FEL irradiation experiments, the phase transition temperatures of the sample were not changed at the level of our detection. This implies that the vibrational excitation and the following thermal process did not cause any significant chemical damage to the compound. The new domain created by FEL irradiation was kept on several hours in mesophase depending on temperature.

Figure 5(a) shows the textures of a C6OTP film at 94°C after right above irradiation (Fig. 3(b)) by scanning of the pulsed FEL wide area with a

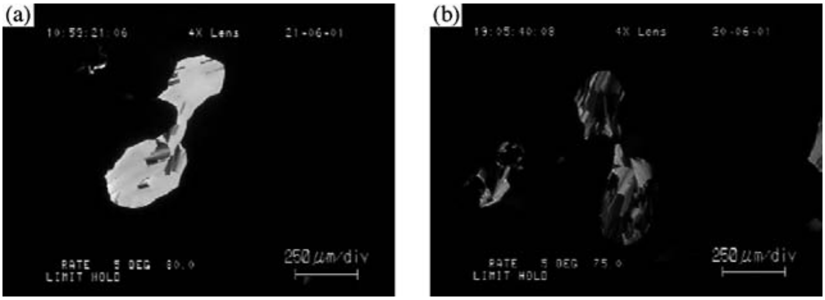
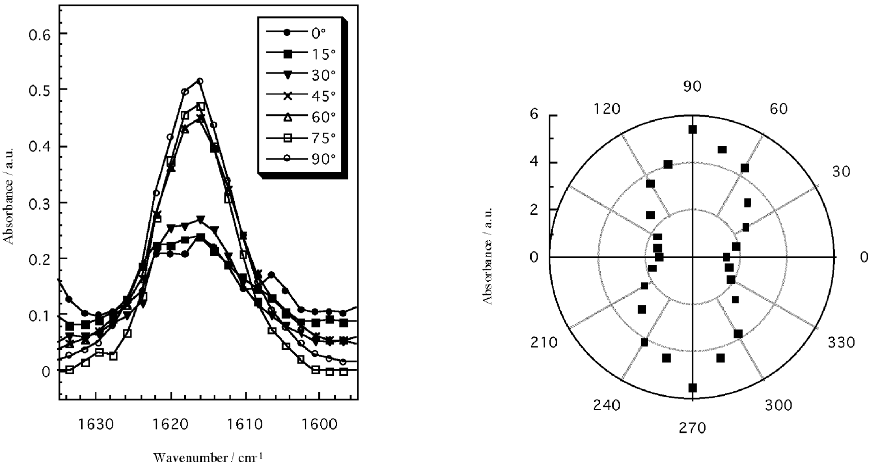


FIGURE 5 Microscopic textures observed for a C6OTP film after FEL irradiation at 94°C from right above by (a) 1615 cm^{-1} infrared pulses and (b) after rotation of the sample on the stage by 45°. The texture before FEL irradiation was one of homeotropic alignment (the columnar axis is perpendicular to the substrate).

wavelength of 6.19 μm which is absorbed by triphenylene ring. Figure 5(b) shows the texture after the sample shown in Figure 5(a) was rotated by 45° on the stage. The bright area in Figure 5(a) completely changed to the dark one in Figure 5(b). This indicates that the direction of the columnar axis changed by FEL irradiation was uniform.

Polarized microscopic FT-IR spectra of the C6OTP film for the domain changed by infrared irradiation is shown in Figure 6. The angle of the absorption maxim at the peak of 1615 cm^{-1} (assigned to the C-C stretching vibration of triphenylene ring) is perpendicular to the polarization direction of irradiated FEL beam (Fig. 3). This indicates that the plane of discotic molecules aligns perpendicular to the plane of polarization of incidence. The results indicate that the relation between the polarized direction of the actinic infrared light and the direction of the columnar axis is parallel in the film plane. These are consistent with the polarized microscopy observation.

If the columns aligned perpendicular to the polarization plane of incidence, discotic molecules would absorb infrared light and vibrational excitation leads to a thermodynamically non-equivalent state again. On the other hand, if the columns align to parallel to the polarization plane of incidence, discotic molecules would be no longer vibrationally excited by infrared light and stay same state.



(a) (b)

FIGURE 6 Polarized microscopic FT-IR absorption intensity of C6OTP film at aromatic C-C (1615 cm^{-1}) for which alignment has been changed by infrared irradiation. (•; 0°, ■; 15°, ▼; 30°, ×; 45°, △; 60°, □; 75°, ○; 90°) (b) angle dependence of polarized infrared absorption intensity.

The results clearly show that the columnar alignment of the discotic liquid crystal was changed from perpendicular to parallel to the substrate and the columnar axis is parallel to the polarization plane of actinic infrared light in the film plane. In other words, a molecular plane of the triphenylene core was changed from parallel to perpendicular to the substrate in the film. The direction of in-plane columnar axis is controlled by the angle of polarization plane of infrared incidence.

CONCLUSION

We applied infrared laser irradiation for the generation of a homogeneous alignment from a homeotropic state for a columnar mesophase of C6OTP by choosing the wavelength which is assigned to an aromatic C-C stretching vibration. The discotic molecules align perpendicular to the plane of polarization of incident infrared light. This means that the direction of the columnar axis is parallel to the plane of polarization of incident light in the film plane. In addition, it may be applicable not only for switching the columnar axis of columnar discotics, but also for precise control of liquid crystal alignment in device fabrication. For example, we may be able to make electric circuits or define optical structure in a liquid crystal film as a part of a sheet device by using infrared laser beam irradiation. The technique could provide a novel technology to control the liquid crystalline alignment in a highly cohesive system.

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