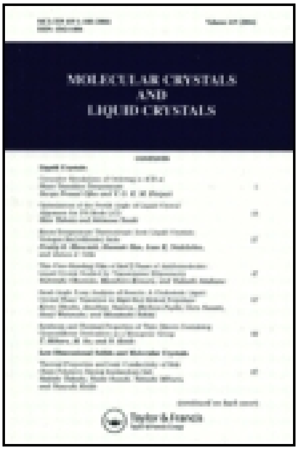

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Alignment Change of Discotic Liquid Crystal Domains by Wavelength Tunable Infrared Laser Irradiation

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Infrared photoinduced change of discotic liquid crystal domains was investigated for a hexagonal columnar mesophase of a triphenylene derivative with three wavelengths of irradiation. The formation of uniform domains was observed under the irradiation with the wavelength of certain absorption bands of the compound. The technique could provide a novel technology to control the columnar alignment of viscous mesophase materials.

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

INTRODUCTION

Discotic liquid crystal is a well-known example of supramolecular self-assembled systems [1]. The columnar arrangements of disc-shaped mesogens formed by triphenylene, porphyrin and phthalocyanine analogues have been drawing attention for their electronic properties like

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charge migration phenomena along a columnar axis as novel organic semiconductors such as one-dimensional conductors, photoconductors, molecular wires and fibers, light emitting diodes and photovoltaic cells in these years [2–9]. In addition, recent studies as for photoplolymerization of liquid crystals indicate such a molecular order of discotic liquid crystal could be remained in polymer solid film [10,11], leading to a sophisticated invention of optical compensator for wider view angle of liquid crystal display [12,13]. These imply that discotic liquid crystals are a good candidate 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 functionalization 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 a field of matter where one can control the molecular alignment. Surface effects and shear flow have often been used in order to obtain uniformly alignment of discotic liquid crystals for studies of their potential as novel optoelectronic functional materials [14–18]. On the other hand, all the studies of photoalignment of liquid crystals have been 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 [19–21]. However, only few result 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. Some experiments have been reported to get uniaxial planar and homeotropic alignment of columnar mesophases and a few successes were attained by usage of polytetrafluoroethylene (PTFE) coated by friction transfer technique [22] and the introduction of fluoroalkylated chain into peripheral parts of triphenylene [23] for planar and homeotropic alignment, respectively.

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 [24]. The FEL has a specific characteristic for a laser system and we can obtain a highly tuned pulsed laser beam with variety of wavelength from ultraviolet to far-infrared ($0.3 \sim 20\,\mu m$) including mid infrared (M-IR) light.

In the previous work, the possibility of controlling the molecular alignment and domains of discotic liquid crystals using infrared light, relating to selective excitation of vibrational processes, has been examined. We found the first results on molecular alignment change for a columnar mesophase by vibrational excitation [25–28].

In this work, infrared photoinduced alignment change of discotic liquid crystal domains was investigated for a hexagonal columnar mesophase with various wavelength of irradiation.

EXPERIMENTAL

The sample used in this work was 2,3,6,7,10,11-hexahexyloxytriphenylene (C6OTP). Its preparation, purification and mesomorphic characterization have been presented and discussed in detail by others [29]. A hexagonal columnar (Col_h) mesophase appeared between the melting and clearing points (C 69°C Col_h 99°C Iso). The chemical structure and FT-IR spectrum of C6OTP film are shown in Figure 1.

The C6OTP film was prepared in a sandwich type cell consisting of two BaF_2 substrates which have high transparency in infrared region, with 2-μm silica-beads spacer and the cell was mounted on a hot stage (Linkam LK-600 FT-IR) which was attached to an optical polarizing microscope (Olympus BX-51). The microscopic texture was recorded using a CCD camera (Olympus CS-230) with a commercially available S-VHS video recorder. The temperature of the film changed from 105°C to 50°C which is corresponding to the range between crystal and isotropic phases involving the Col_h mesophase. The cell was heated to 105°C at which the compound melts into the isotropic liquid and cooled down to 94°C to form domains of Col_h phase. It is found that the C6OTP films show a spontaneous homeotropic alignment in the Col_h mesophase between BaF_2 substrates. The infrared pulsed beam

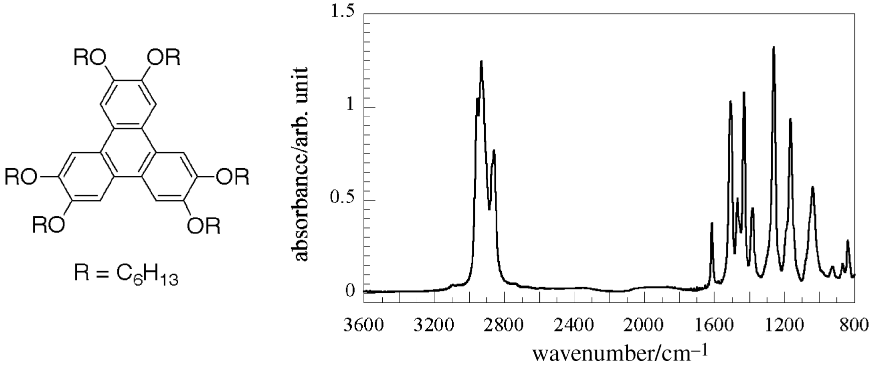

FIGURE 1 Molecular structure and FT-IR spectrum of C6OTP.

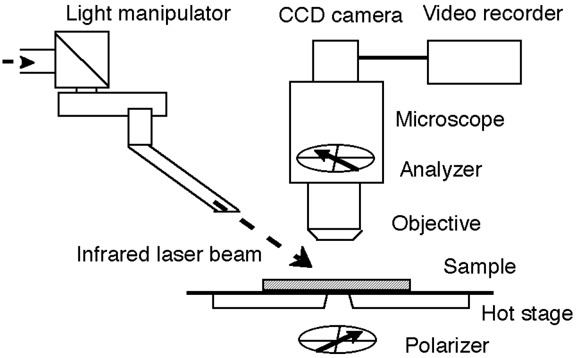

FIGURE 2 Schematic representation of the experimental setup.

was provided by FEL system in Osaka university where one can obtain a tuned beam in wavelength [24].

A schematic representation of the experimental setup is shown in Figure 2. The infrared FEL was guided through a pipe line and a mirror chamber in the experimental room from FEL emission facility. The guided M-IR FEL beam was focused in its size to about 0.5 mm in diameter by ZnSe lenses and concave mirrors. The sample on the hot stage of microscope was irradiated by the FEL beam through a multi-jointed manipulator. IR absorption spectra was measured by a polarizing microscopic FT-IR spectrophotometer (Bio-Rad FTS-3000).

RESULTS AND DISCUSSION

Figure 3(a) shows the textures of a 2-μm thick C6OTP film at 94°C after irradiation in a wavelength of 6.19 μm (1615 cm^{-1}) which is absorbed by triphenylene ring [14]. Figure 3(b) shows the texture obtained with the stage rotation by 45° of the texture in Figure 3(a). Some part of the bright area seen in Figure 3(a) changed to be dark in Figure 3(b). This indicates that the direction of the columnar axis changed by irradiation is uniform.

According to our previous work [25–28], this phenomena could be interpreted as the following. First, the molecules become quite mobile in the thermally disturbed domain as a result of the absorption of infrared light by molecules. Following the generation of thermodynamically non-equilibrium states in the irradiated area, the molecules align in the new direction by self-organization during the time before next pulse was irradiated due to the irradiating infrared light in order to attain a thermodynamically more stable state. It is assumed that

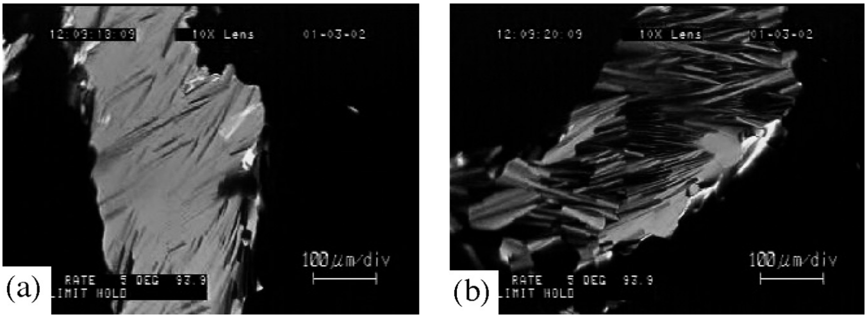

FIGURE 3 Microscopic textures observed for the Col_h phase of a C6OTP film (94°C, 2 μm-thick) after FEL irradiation at (a) 1615 cm^{-1} of infrared pulses and (b) after rotation of the sample on the stage by 45°. The texture before irradiation showed homeotropic alignment (the columnar axis is perpendicular to the substrate).

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. 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 to the substrate was attained.

Figure 4 shows the textures of C6OTP film irradiated by different two wavelength of the incident FEL beam. Figure 4(a) shows the texture after irradiation at 1509 cm^{-1} (6.63 μm), followed by the clockwise rotation of the sample by 45° on the stage as shown in Figure 4(b). The texture resulted in the irradiation at 1165 cm^{-1} (8.58 μm) was shown in Figure 4(c). Figure 4(d) shows the texture observed after 45° rotation of the sample. Some part of the bright area seen in Figure 4(a) changed to be dark in Figure 4(b) and all the part of the bright area seen in Figure 4(c) changed to be dark in Figure 4(d). This indicates that the direction of the columnar axis changed by irradiation is uniform. These results indicate that the direction of the columnar axis changed by M-IR FEL irradiation and the manner of change is the same as the previous irradiation at 1615 cm^{-1}. The absorption peak at 1509 cm^{-1} is assigned to an aromatic C−C in-plane deformation of the triphenylene ring and the peak at 1165 cm^{-1} is assigned to C−O−C asymmetric stretching vibration of the ether group. This implies that the a homogeneous alignment from a homeotropic one was attained in Col_h phase of C6OTP film by using infrared irradiation at the wavelength of the band assigned to which vibrational transition moment is parallel to the molecular plane of the rigid core.

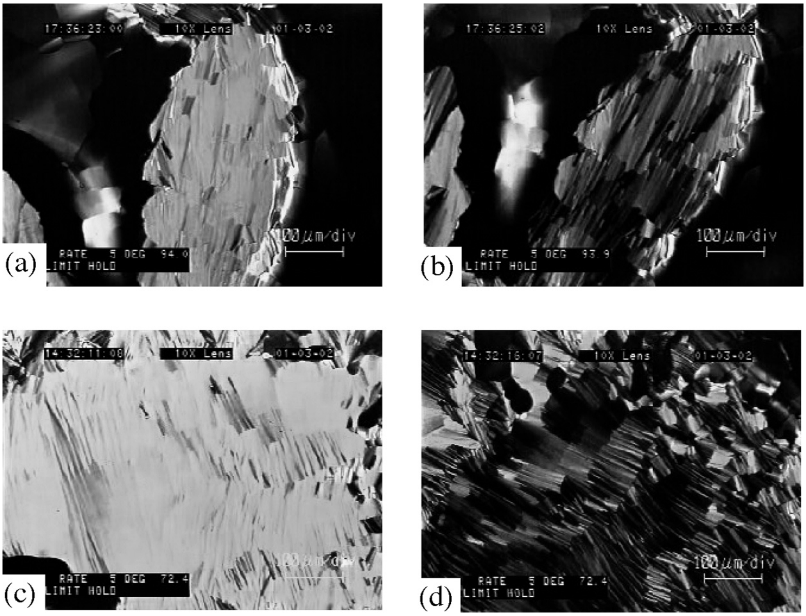

FIGURE 4 Microscopic textures observed under cross nicol condition for a C6OTP film after M-IR FEL irradiation with the wavelength of (a) 1509 cm^{-1} and (c) 1165 cm^{-1}, respectively, for 2-μm thick cells. (b) and (d) show textures after rotation of the sample on the stage by 45° of (a) and (c), respectively.

CONCLUSION

In our infrared technique for the alignment control of $\mathrm{Col_h}$ phase, it is possible to select a chemical bond to be excited by tuning the wavelength of the laser pulse for various infrared absorption bands of the mesogens. Therefore this method is expected to be good for a variety of mesophases, especially for viscous ones with a high order of molecules. The procedure seems to be applicable to obtain a completely homogeneous alignment from a homeotropic state for C6OTP by using infrared irradiation into the band assigned to which vibrational transition moment is parallel to the molecular rigid core. In addition, it may be applicable for not only switching the columnar axis of columnar discotics, but also controlling liquid crystal alignment in device fabrications such as producing a conductive line and/or some other structures in a liquid crystal film as a part of a organic sheet device.

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