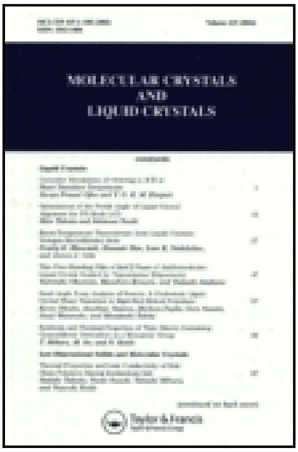

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Anisotropic Photoconduction of Triphenylene-Based DLC in Aligned Domains by Wavelength Tunable CO_2 Laser Irradiation

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Infrared induced alignment change of columnar liquid crystal domains and anisotropic electric conduction were investigated for a well-known discotic liquid crystal, 2,3,6,7,10,11-hexahexyloxytriphenylene. A uniformly aligned alignment change of domains was observed when an infrared laser corresponding to the wavelength of the aromatic C-O-C stretching vibration band was irradiated. Anisotropic photoconduction was observed for homeotropic and unidirectional planar aligned domains between in-plane two gold electrodes. Photoconductivity for unidirectional planer aligned domain was increased by 4 times compared with that for homeotropic one during dark-current was not drastically changed between two conditions.

Keywords Alignment control; discotic liquid crystal; infrared; triphenylene

1. Introduction

Columnar liquid crystals such as discotic liquid crystals (DLCs) are good candidates as organic semiconductors for electronic devices due to their potential to have the fast carrier mobility [1–4] as well as the anisotropic conduction property along the columns [5]. In fact, in a highly ordered columnar mesophase, fast carrier mobility ($\sim 10^{-1}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) by electronic process of carrier transport was found which is comparable to that of amorphous silicon [1–4]. Furthermore, DLCs are expected as a self-organized molecular ink to fabricate the organic semiconductor devices by solution process. 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 (homeotoropic alignment) for the photovoltaic solar cells and light emitting diodes, or parallel to the isolator interface (unidirectional planar alignment) for the lateral field effect transistors (FETs). The interesting results have been reported to obtain unidirectional planar or homeotropic alignment of columnar liquid crystals and a

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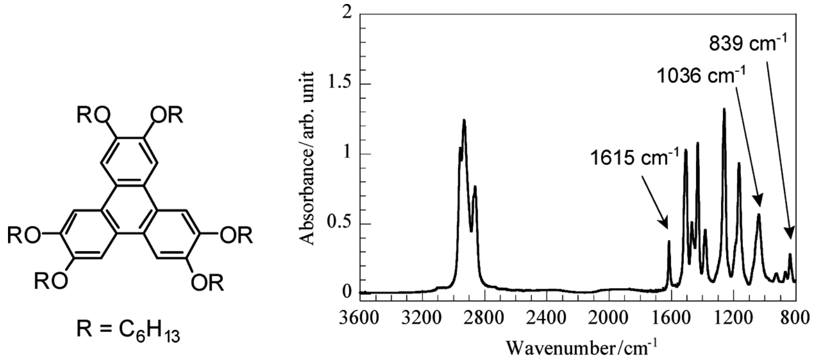
few successes were attained for planar alignment by zone-casting technique [6], polytetrafluoroethylene coating to the substrate surface by friction transfer technique [7] and applying external magnetic field with chemically modified surface [8]. On the other hand, it was found the introduction of fluoroalkylated chains into the peripheral parts of triphenylene mesogens [9] or branched alkyl chains into hexabenzocoronene mesogens [10] lead to get a strong tendency of homeotropic alignment of DLCs. Other attempts were reported control the columnar orientation in an open supported film by the kinetic growth [11]. 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 a hexagonal columnar ($\mathrm{Col_h}$) mesophase of well-known DLC, 2,3,6,7,10,11-hexahexyloxytriphenylene (C6OTP) by use of a free electron laser (FEL), we found that a homeotropic domain where the columnar axis aligns perpendicular to the substrate could be changed to a domain with a unidirectional planar alignment of columns by the excitation of C-C stretching vibration of triphenylene core in $\mathrm{Col_h}$ [12–14]. This relation can be also confirmed by the irradiation at the other wavelength which corresponds to absorption for exciting other vibrational modes or other chemical bonds such as C-O-C stretching asymmetric vibration and aromatic C-H out-of plane vibration [14–16]. This technique extended to alignment control of the highly ordered plastic columnar and helical mesophases [17–19]. 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. Furthermore, this technique extended to alignment control to get the homeotropic alignment for columnar mesophases with a circularly polarized infrared (IR) irradiation [19–21]. However, FEL is a huge instrumentation system, thus the compact setup for the alignment control of discotics was expected for using this novel technique in a production line for device fabrication. On the other hand, CO_2 laser is one of the powerful infrared light source and CO_2 laser irradiation is widely use for the material processing such as heat, fusion and ablation in commercialized manufacturing. We recently reported wavelength tunable CO_2 laser irradiation also leads to a unidirectional planar alignment change for columnar liquid crystal domains [16,22].

In this study, IR induced alignment change of columnar liquid crystal domains was investigated for C6OTP with a wavelength tunable CO_2 laser irradiation. A uniformly aligned alignment change of domains was observed when an IR laser corresponding to the wavelength of the aromatic C-O-C stretching vibration band ($1036\,\mathrm{cm^{-1}}$, $9.65\,\mu\mathrm{m}$) was irradiated. Anisotropic conduction of photo- and dark-current between in-plane two gold electrodes on BaF_2 substrate were also measured in aligned domains in the $\mathrm{Col_h}$ phase.

2. Experimental Methods

The compound used in this work is one of the typical columnar DLC, C6OTP, as shown in Figure 1(a). Its preparation, purification and mesomorphic characterization have been presented and discussed previously [23]. C6OTP exhibits the phase transition from the crystal to $\mathrm{Col_h}$ mesophase at 69°C and from $\mathrm{Col_h}$ to isotropic liquid (I) phase at 99°C. FT-IR spectrum of C6OTP film was shown in



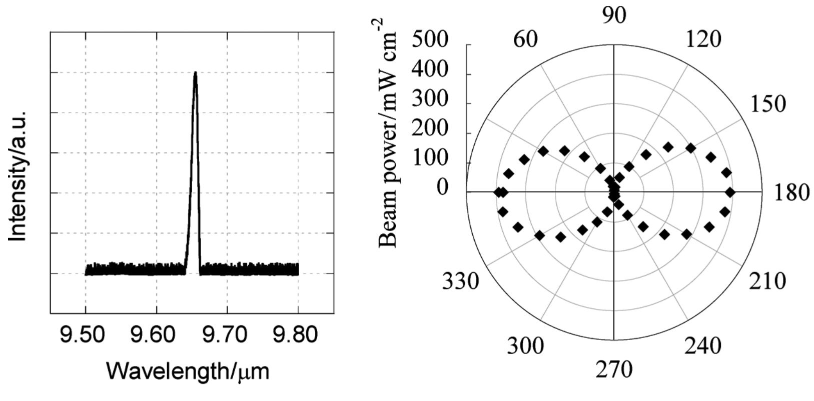
(a) (b)

Figure 1. (a) Chemical structure of C6OTP and (b) its FT-IR spectrum in Col_h (90°C).

Figure 1(b). The absorption peak at $1036\,cm^{-1}$ (9.65 μm) is assigned to an aromatic C-O-C stretching symmetric vibration of the triphenylene peripheral part [24].

A 300 nm-thick in-plane gold electrodes with 50 μm gap and 5.5 mm length was prepared on BaF_2 substrate which have high transparency in mid-IR region, by vapor deposition with a metal shadow mask. The cell consists of a BaF_2 substrate with a gold electrodes and a top cover of BaF_2 plate with 2-μm silica beads spacer (Ube-Nitto Kasei, HIPRESICA) and the cell thickness was estimated to 3 μm by interferometry. C6OTP film was filled in the cell by capillary action in I. The cell was mounted on a hot stage (Linkam, LK-600 FT-IR), which was attached to an inverted optical polarizing microscope (Olympus, GX-51). The microscopic texture was recorded using a CCD camera.

A wavelength tunable CO_2 laser (Access Laser, Merit GS) was used for IR irradiation. The standard method for wavelength selection is to use a reflective grating in the laser cavity as the dispersion element and the tunable wavelength is from 9.2 to 10.8 μm. The wavelength tunable CO_2 laser was tuned to wavelength at



(a) (b)

Figure 2. (a) The spectrum and (b) polarization property of wavelength tunable CO_2 laser beam.

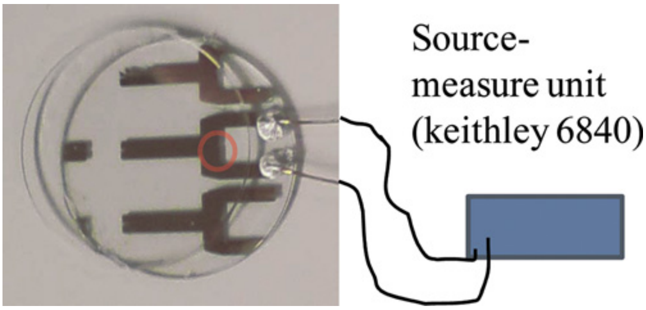


Figure 3. A schematic diagram of the BaF_2 cell configuration. (Figure appears in color online.)

9.65 µm and its spectrum is shown in Figure 2(a). Output laser beam was chopped by a mechanical chopper (Stanford Research Systems, SR540) with a handmade chopper blade (Duty ratio = 0.17) and the chopping frequency was controlled to 10 Hz. The beam intensity was controlled by neutral density filters (Janos) to 40 mW. The polarization property of a CO_2 laser beam is shown in Figure 2(b) and it shows a linear polarization. The IR beam was focused to about 0.5 mm in diameter by ZnSe lens and the sample stage was scanned with a rate of $10\,\mu m\,s^{-1}$ in one direction.

Conductivity measurement was carried out with a source-measure unit (Keithley, picoammeter 6840) by applying voltage from −50 V to 50 V with 1 V step between in-plane gold electrodes on BaF_2 substrate. Photocurrent was observed by an irradiation of UV light with a high-pressure mercury lamp (Ushio, Spoto-cure SP-7) through the top cover of BaF_2 cell. Figure 3 shows a schematic diagram of the setup.

3. Results and Discussion

3.1. *Alignment Change*

A C6OTP film shows a spontaneous homeotropic alignment in the Col_h in BaF_2 cell with in-plane two gold electrodes when it was cooled from isotropic phase. Figure 4(a) shows the microphotograph of a 3 µm-thick C6OTP film at 85°C after a scanning irradiation along the electrodes by the chopped IR laser with the wavelength of 9.65 µm which is absorbed by aromatic C-O-C stretching symmetric vibration of triphenylene peripheral part and the direction of its dipole moment is within the core plane. The polarization angle of incidence is perpendicular to the electrodes as shown in Figure 4(a). A uniformly aligned alignment change of domains was observed at the scanned irradiated area and it shows unidirectional planar alignment between gold electrodes. According to our previous work [12–22], the direction of columnar axis is parallel to the electrodes. Figure 4(b) shows a schematic representation of orientational change of DLC molecules in the cell. This newly formed domain was quite stable and could be maintained for more than several hours in the temperature range of Col_h mesophase. In addition, it was found that vapor deposited gold electrodes on BaF_2 substrate was not damaged by IR irradiation with a wavelength tunable CO_2 laser.

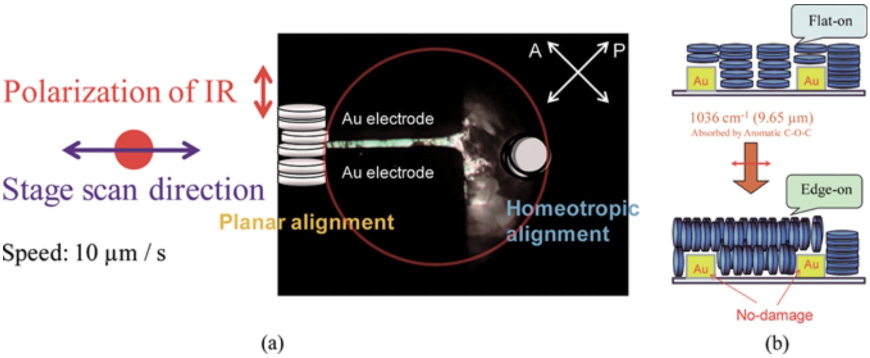


Figure 4. Microscopic textures observed for the C6OTP film at 85°C cooled from I.L. (a) after irradiation with 9.65 μm infrared chopped light at the gap of gold electrodes. The texture before infrared irradiation was one of homeotropic alignment (the columnar axis is perpendicular to the substrate). The circle is the same location in the circle in Figure 3(b). A schematic representation of the alignment change of columns in Col_h phase of C6OTP on the substrate with wavelength tunable CO_2 laser irradiation. (Figure appears in color online.)

3.2. *Anisotropic Conduction*

Figure 5(a) and 5(b) show the dark- and photo-currents for homeotopic (before IR irradiation) and unidirectional planar alignment (after IR irradiation) at 85°C in Col_h, respectively. Anisotropic photoconduction was observed between homeotropic and unidirectional planar alignment while dark-current was not drastically changed between two arrangements. Photoconduction in unidirectional planer aligned domain was increased by 4 times compared with in homeotropic one. This was probably owing to fast carrier mobility along the columnar axis between two electrodes by electronic hopping transport of photo-generated charge carriers. For dark-conductivity, there is almost same conduction path which consists of fluid alkyl

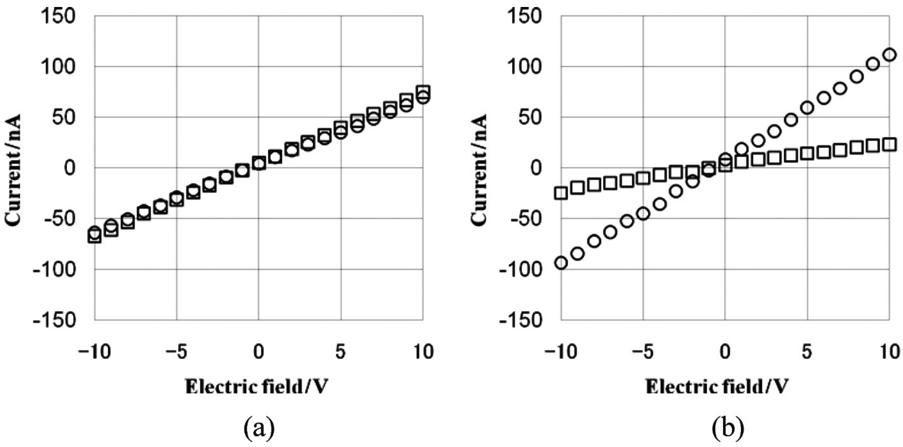


Figure 5. (a) Dark- and (b) photo-current of C6OTP between in-plane two gold electrodes for homeotopic (before IR irradiation, open square) and unidirectional planar alignment (after IR irradiation, open circle) at 85°C in Col_h.

chains of peripheral part of triphenylene for ionic carriers in $\mathrm{Col_h}$ structure for both of homeotropic and unidirectional planar arrangements [25]. Thus, if the ionic conduction was dominant for carrier transport in $\mathrm{Col_h}$, it was reasonable not observing dramatically change between two arrangements in this experiment. Anisotropic conduction ratio of observed photo-current is 4 in this experiment, although it was observed 10^3 previously reported for dark-current of a doped C6OTP film [5]. In reference [5], they use 1 mole% of $AlCl_3$ as a dopant for C6OTP and the conductivity was $\sigma \sim 10^{-3}\,\mathrm{S\,m^{-1}}$ for parallel to the axe of columns while the photoconductivity was in the order of $\sigma \sim 10^{-6}\,\mathrm{S\,m^{-1}}$ in this experiments. The deterioration of anisotropy might be caused by the inhomogeneity of DLC alignment along the long electrodes and the effect of ionic conduction of impurities in this experiment. These imply that the irradiation condition of IR might be explored for completely uniform alignment change and the higher purity of the compound was needed for higher anisotropy in electric conduction between unidirectional planar and homeotropic alignment.

4. Conclusions and Perspectives

It was found that vapor deposited gold electrodes on BaF_2 substrate was not damaged by IR irradiation with a wavelength tunable CO_2 laser. Anisotropic photoconduction was observed between homeotropic and unidirectional planar alignment domains of C6OTP. Photoconduction in unidirectional planar aligned domain was increased by 4 times compared with in homeotropic one during dark-current was not drastically changed between two conditions. In-plane anisotropy of conductivity is another interest and further studies are now in progress. These results strongly imply that the infrared irradiation of columnar liquid crystal is a possible technique for device fabrication by use of DLC semiconductors such as FETs.

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