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## Liquid Crystals

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# Self-constructed stable liquid crystal alignment in a monomer-liquid crystal mixture system

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#### Self-constructed stable liquid crystal alignment in a monomer-liquid crystal mixture system

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Here, we demonstrate excellent liquid crystal (LC) vertical alignment without using an alignment layer printing process by introducing octadecyltrichlorosilane (OTS) into the LC mixture. Further, we investigated the alignment mechanism by analysing the surfaces of the substrates. The optimum concentration of OTS was found to be about 0.03 wt%, which is 1/100 of that in the previously reported polyhedral oligomeric silsesquioxane (POSS)–LC system. Moreover, the OTS–LC system exhibited a more stable LC alignment compared with the POSS–LC system. These differences may arise from the different strengths of surface–dopant interactions; that is, the covalent bond in the OTS–LC system and the van der Waals interactions in the POSS–LC system. We also demonstrated that the method can be used in a capillary tube, which may serve as a new method facilitating the application of LCs with curved surfaces.

Keywords: LC alignment; nanoparticle-doped LC; alignment layer free; monolayer

#### 1. Introduction

Although liquid crystals (LCs), which are the most common organic materials used in electro-optical devices [1], exhibit self-assembled microscopic molecular orientation, macroscopic uniform LC alignment is necessary and can be accomplished by means of surface confinement in solid substrates. Substrates confining LCs commonly contain an alignment layer on the surface, such as a buffed polymer layer [2] or a UV-irradiated photo-sensitive organic layer [3]. Hence, the LC alignment process using a polymer layer is considered essential in LC device manufacturing.

An alignment layer-free process employing a nanoparticle-doped LC mixture was introduced by Jeng et al. [4]. They observed that an LC mixture with polyhedral oligomeric silsesquioxanes (POSS) exhibited vertical alignment without using an alignment layer [4], and the electro-optical characteristics were analysed [5]. The POSS-LC system was applied to ferroelectric LC cells [6], polymer-dispersed LCs [7], cholesteric LCs [8], mixtures with active reactive mesogens [9], a guest-host system [10] and planar alignment [11]. The advantages of the method are apparent; from an industrial point of view, it reduces the number of manufacturing steps, thereby decreasing the manufacturing cost. From a technological point of view, this method provides a uniform LC alignment even in a closed cavity or on a curved surface, where the conventional method cannot be applied. However, the actual application of the system may require extensive study

in order to secure the reliability required for mass production.

In this paper, we introduce LC-trichlorosilane derivative mixtures instead of POSS, and investigate the corresponding alignment mechanism. We made nematic LC mixtures with a small amount of octade-cyltrichlorosilane (OTS); its chemical structure is shown in Figure 1(a). Unlike the POSS–LC system, which requires about 3 wt% POSS for quality alignment, the OTS–LC requires only 1/100 that of POSS. The OTS–LC forms a uniform, stable monolayer on the substrate, and the cell exhibits not only uniform vertical alignment, but also considerably improved stability.

#### 2. Experiments and analysis

A commercial LC mixture with negative dielectric anisotropy (Merck, MJ9612XX) was used in the experiments. OTS+LC mixtures with various OTS concentrations (0.03, 0.1, 1.0 wt%) were prepared. For comparison, a 3 wt% POSS–LC was also prepared. It was reported that 3 wt% is the optimum concentration for the POSS–LC system, which we reconfirmed. Glass substrates partially covered with indium tin oxide (ITO) electrodes were prepared, and the substrates were UV-cleaned in order to remove organic particles from the surface.

In the first experiment, one droplet of pure LC and 0.03 wt% OTS-LC were dropped on each bare

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Figure 1. (a) Chemical structure of OTS; (b)–(g) photographs of the cells with (b) pure LC, (c)–(f) OTS–LC mixtures at various concentrations, and (g)  $3 \text{ wt}^{\circ}$  POSS-LC mixture, under crossed polarisers, respectively. (c) The transition from planar to homeotropic alignment just after covering the upper substrate. (f), (g) The expanded insets show the defects.

substrate and covered by another substrate without an alignment layer. As shown in Figure 1(b), the cell with pure LC shows bright colour under the crossed polarisers, representing a random planar alignment. On the other hand, the cell with 0.03 wt% OTS–LC initially had a planar alignment, then turned dark with propagating boundaries, as shown in Figure 1(c). It took several tens of seconds for all of the areas to become dark, that is, to achieve the vertically aligned state. Interestingly, only 0.03 wt% OTS can induce perfect vertical alignment of the LC.

LC cells were made with all of the OTS-LC mixtures and the POSS-LC mixture, and the cells were soft-baked above the clearing temperature for a moment in order to remove the flow defects, if any, as is usually done in LC cell fabrication. The cells exhibited good vertical alignment as shown in Figure 1(d)–(g), although some defects were observed in the 1 wt% OTS–LC cell and the POSS–LC cell (Figure 1(f) and (g)). It is interesting that while the lowconcentration OTS–LC cells (0.03, 0.1 wt%) exhibited good vertical alignment, the high-concentration cell (1 wt%) had many point defects, as shown in the inset of Figure 1(f). The POSS–LC cell showed line defects after soft baking which had not been seen before soft baking.

It is known that LC alignment on an isotropic surface can be described by a simple rule: if the surface energy of the LC is higher than that of the substrate, the LCs are likely to align normal to the substrate, and if not, the LCs align parallel to the substrate [12]. Hence, the bare glass surface and ITO surface with high surface energy result in planar LC alignment. Since the OTS- and POSS-treated surfaces exhibited vertical LC alignment, we can reasonably deduce that the surface energy of the substrate would be reduced by OTS or POSS treatment, and that the surface would be partially or fully covered with OTS or POSS molecules. The OTS molecule forms a covalent bond with a hydroxyl group on the glass or ITO surface, enabling the formation of a self-assembled monolayer (SAM) by dipping a substrate into OTS solution [13]. Thus, we expect that the OTS in the OTS-LC mixtures would be irreversibly absorbed by the surface and form a monolayer.

In order to investigate the surface variation of each substrate after injecting the dopant-LC mixtures, the cells were disassembled to retrieve the substrates, and the substrates were sonicated in an acetone bath for 10 min to remove the remaining LCs from the surface. We measured the contact angle of a de-ionised water droplet on the collected substrates to verify the surface energy, as shown in Figure 2(a), where the first bar in each data set represents the bare ITO or bare glass substrate. The second bar, labelled 'Ref.', denotes the reference substrates with highly packed OTS or POSS molecules, and the third one, labelled 'Cell', corresponds to the substrates collected from the 0.1 wt% OTS-LC or 3 wt% POSS-LC cells. The reference OTS substrate, which is supposed to have a uniform SAM, was fabricated by dipping a substrate into a 2 mM OTS-toluene solution for 2 h. The reference POSS substrate was made by spin-coating a 3 wt% POSS-acetone solution on a substrate at low rpm and drying it.

As shown Figure 2(a), all of the reference substrates had higher contact angles than those on bare substrates, indicating that the substrates with an OTS or POSS layer had lower surface energy. Meanwhile, the substrates taken from the OTS cells exhibited similar contact angles to the reference, while those taken from the POSS cells exhibited a much lower contact



Figure 2. Surface analysis: (a-i, a-ii) Contact angle of a water droplet on the ITO and glass surfaces, respectively, under various conditions (see text). (b-i, b-ii) atomic force microscopy images of the substrates collected from the cells with 0.1, 1 wt% OTS-LC and 3 wt% POSS-LC.

angle compared with that of the reference. This implies that the POSS molecules on the substrate were largely detached during the ultrasonic cleaning process, while the OTS layer still remained after the process. It was found that by increasing the sonicating time, the contact angle of the POSS-treated substrate decreased further.

The surfaces of the substrates were examined using atomic force microscopy (AFM) (SPA-300HV by SII Nano Technology, Japan), as shown in Figure 2(b). The 0.1 wt% OTS surface had a uniform morphology (Figure 2(b-i)), while the 1 wt% OTS surface had large defect points (b-ii), which were thought to be aggregated OTS bumps. The bumps were large in this sample, such that the largest had a height of 20 nm and a  $0.5 \,\mu\text{m}$  width. The aggregated bumps may have caused defects in the high-concentration OTS-LC cells shown in Figure 1(f). The substrate from the POSS-LC cell also had a few bumps. However, it is not clear whether the defects in the POSS-LC cell shown in Figure 1(g) were related to the bumps in the AFM image because lowering the concentration of POSS did not improve the alignment, unlike the OTS cell.

In the next experiment, we remade cells using the collected substrates, and injected pure LC into the cells, the photographs of which are shown in Figure 3(a). Interestingly, the cells made with the substrates collected from the OTS samples exhibited good vertical alignment, while those from the POSS sample did not, as shown in Figure 3(a). This indicates that the SAM layer, that is, the OTS layer on the surface, was stable, but the POSS layer on the substrate was not. Thus, unlike the strong covalent bonding between the OTS and surface, the POSS–surface interaction is rather weak; hence, it is thought to be a van der Waals interaction. This explains the difference in the concentration required for good LC alignment in the POSS–LC and the OTS–LC. OTS molecules are easily absorbed by the surface due to the strong interaction, while a higher concentration is required for the POSS–LC cell to form a POSS layer between the surface and the bulk LC.

In order to verify the thermal stability of the dopant-induced LC alignment, we carried out a thermal cycling test, where the cells were repeatedly heated to 150°C and kept at this temperature for 10 min each time, and then cooled down to room temperature. The times in the images in Figures 3(b) and (c) represent the cumulative time at 150°C. While the OTS cell maintained good vertical alignment for up to 18 thermal cycles, the POSS cell showed some degradation of alignment at the edge of the cell. Thus, the thermal stability test confirmed that the OTS layer has better thermal stability than the POSS layer.

The general applicability of the technology was examined, wherein the cell exhibited a usual voltage to transmittance response, as shown in Figure 4(a). However, many textures were observed on microscopy



(c) Thermal cycling for POSS cell

Figure 3. Photographs of the LC cells under crossed polarisers: (a) Re-fabricated cells using the pure LC and the substrates taken from the OTS and POSS cells. (b),(c) Thermal cycling test results; the time in each image is the cumulative time at  $150^{\circ}$ C (see text).

due to the lack of a preferred LC tilting direction. The texture may be easily removable by adopting already known multi-domain technologies such as a patterned electrode and protrusion. One of the main advantages of the dopant-induced alignment control technology is that the method is applicable to arbitrarily shaped cavities or curved surfaces, such as a capillary tube, which are not easy to coat uniformly using conventional methods. Figure 4(b) illustrates the difference in LC alignment between capillary tubes injected with pure LC and those injected with OTS–LC. The clear contrast in the two rotated polariser directions in the OTS–LC capillary indicates well-aligned LCs; however, those in the pure LC capillary tube show a random LC alignment.

#### 3. Conclusion

We demonstrated an alignment layer-free LC cell manufacturing method by directly injecting the OTS-added LC mixture into a cell. The optimum



Figure 4. (a) Voltage vs. transmittance curve in the VA cell of the 0.03 wt% OTS-LC cell. (b) Capillary tubes injected with pure LC or OTS LC (diameter  $\sim 100 \,\mu$ m); the arrows indicate the directions of the polarisers.

concentration of OTS was found to be just about 0.03 w%, which is 1/100 of the concentration of POSS in the POSS–LC system. Moreover, the OTS–LC system exhibited very stable LC alignment in the surface cleaning test and the thermal cycling test. By analysing the surface of the substrates retrieved from the cells, it was confirmed that the OTS molecules were absorbed by the substrate, forming a stable monolayer. We also demonstrated that the OTS–LC system can be used in a capillary tube, which may yield a new method for LC alignment in applications with curved surfaces.

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