

Cinnamate Phosphonic Acid as Monomolecular Alignment Layer

Oleksandr Semenenko^{1,2}, Xinyi Yu^{1,2}, Valerii Vashchenko^{1,2}, Maksym Prodanov^{1,2} and Abhishek Kumar Srivastava^{1,2,3*}

¹State Key Laboratory of Advanced Displays and Optoelectronics Technologies, and Centre for Display Research, Electronics and Computer Engineering Department, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong 999077, China

²Centre for Display Research, Department of Electronics and Computer Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong 999077, China

³IAS Center for Quantum Technologies, The Hong Kong University of Science and Technology, Hong Kong, China

Abstract

This work presents a new monomolecular photo-alignment layer material based on a cinnamate core and a phosphonic anchoring group that offers excellent photo-alignment properties and utilizes a dip-washing deposition process. The significant advantages of such materials include a room-temperature deposition process with no rubbing and baking procedures, which makes the alignment materials suitable for flexible substrates. Irradiation by linearly polarized light for a short time, 30-60 seconds, provides robust and stable planar/vertical alignment with good values of VHR and RDC. Such cinnamate derivatives with vertical and planar alignment capabilities open new opportunities to achieve a monomolecular alignment layer with an intermediate pretilt angle.

Author Keywords

Alignment; phosphonic acid; monomolecular layer; cinnamate derivatives.

1. Introduction

Liquid crystal displays (LCD) play important roles in our life. Improving the properties of such displays requires new materials with better properties, especially for flexible devices.^[1-4] One such material is the alignment layer, which provides macroscopic uniform alignment of liquid crystalline molecules near the surface. Nowadays, commonly used materials are different polyimides (PI). Despite those PIs having good performance and can provide both vertical and planar alignment, they have several disadvantages. First, it is a rubbing procedure to get alignment direction, which leads to static charge and dust contamination, and secondly, a high-temperature backing process of around 200 °C^[5], which makes them unsuitable for flexible substrates. Moreover, with the PIs layer, there is one more problem: the piling of the alignment layer from flexible substrates due to banding.^[6] Another option is using a photoalignment layer such as azo dyes. This approach can solve the issue of static charge and dust contamination due to the non-contact alignment procedure. However, such materials usually have a low value of VHR and are sensitive to humidity.^[7-8] Search for a new “low temperature” alignment layer is still ongoing^[4,9,10]; one potential solution can be the monomolecular photoalignment layer^[11]. Based on [2+2] photochemical reaction of cinnamate derivatives, we propose a new non-contact monomolecular alignment material, eliminating all described drawbacks of PI. Moreover, such materials have an easy synthetic route and require significantly lower power consumption for the deposition procedure.

In general, the cinnamate phosphonic acid (CPA) molecule can be divided into several parts, as shown in Fig. 1(a). The anchoring

group, in our case, is a phosphonic acid unit that makes permanent chemical bond with the ITO electrode; spacer increases the flexibility of molecule attached to the surface; the body is the main part of a molecule that can contain different substitution groups, such as methyl, methoxy, ester, etc. to control the polarity of the molecule; photo dimerizing or polymerizing group is responsible for photoalignment and tail which can limit interaction of liquid crystal (LC) with cinnamate body.

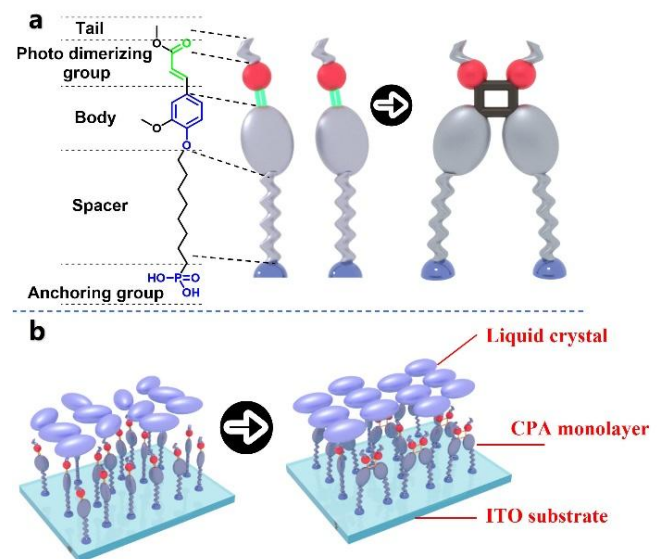


Figure 1. (a) Structure of CPA molecule. Its schematic dimer (b) is the CPA monolayer's conduction on liquid crystal molecules.

Recently, we reported cinnamate phosphonic acid with a long nonpolar tail, which provides vertical alignment with a pretilt 86-88°.^[11] In this work, we show a new material, CPA-032, that is conducting planar alignment and has an electro-optical performance compared to commercial material PI4210.

2. Experiments

To get planar alignment, we change the design of the CPA molecule. Compared to the structure of CPA-086^[11] with vertical alignment, we turn the polar ester group to the “top” and decrease the length of the tail. Synthetic route of CPA-032 is shown in Fig. 2, including alkylation of methyl ferulate by 1,8-dibromooctane, Arbuzov reaction and saponification with trimethylsilyl bromide.

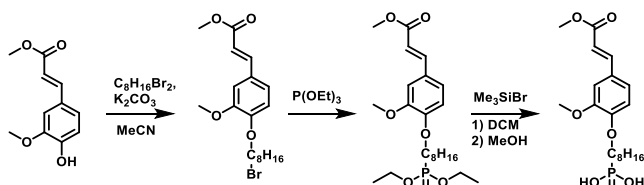


Figure 2. Synthetic route of alignment material with planar alignment direction.

Due to the short tail obtained, phosphonic acid has limited solubility in organic solvents and can be dissolved in DMF, DMSO, NMP, methanol, or ethanol. Since our materials are oriented toward industry applications, we should avoid toxic solvents such as DMF and methanol. Our choice falls to widely used in industry NMP as the main solvent for CPA family materials.

Deposition of CPA-032 has been achieved by dip-washing (DW) procedure at room temperature described in ^[11] see Fig. 3(a). The glass substrates coated with ITO were treated with ozone plasma to make them easily wet by liquids. Subsequently, the substrates were immersed in NMP solution of 0.1 wt% CPA-032. Due to the fast reaction of phosphonic acid with ITO, this process takes only 30 sec.

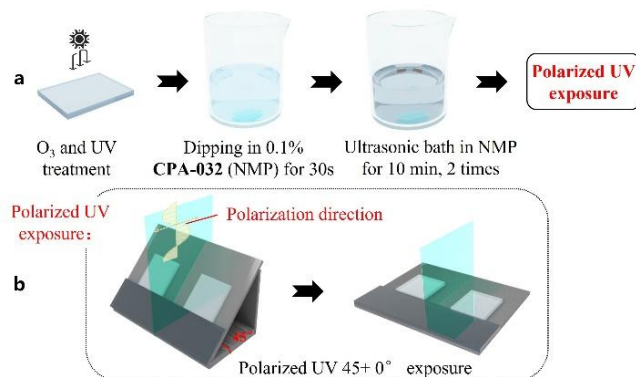


Figure 3. (a) The DW process of CPA-032 deposition, including 2 times of NMP washing cycle. (b) The oblique exposure of UV polarized light pre-exposure and 0° exposure.

After removing residual drops of solution from the substrate surface by airflow, the excess material was washed out by pure NMP and subjected to ultrasonic treatment for 10 min as a cleaning cycle. Before each cycle began, any liquid residue on the substrate was removed. After 2 times of washing cycle, the substrates were obliquely pre-irradiated with UV-polarized light, followed by horizontal irradiation. The spatial relationship between tilt direction and polarization direction is shown in Fig. 3(b).

Since CPA series materials can provide a pre-tilt angle greater than 0°, we tilted the substrates at a certain angle during pre-irradiation to prevent defects such as multi-domain alignment of liquid crystals. ^[12] The pre-irradiation time is generally set to 2 s when the irradiation intensity is 1.13 mW/cm² (@310nm) and 1.9 mW/cm² (@365nm). Subsequently, we conducted horizontal irradiation at different durations to investigate how it would affect LC alignment. It is noted that wavelengths less than 300 nm should be avoided in the irradiation light. Two substrates were assembled into an LC cell in an anti-parallel manner, separated by 5 μm spacers in the middle. We injected E7 into the LC cell to examine its optical performance. We introduce CPA patterning alignment technology. Unlike the reversible photo-induced rewriting process, we need first to cover

the substrate with a mask and illuminate it until the dimerization reaction is complete, then change the polarization aspect and remove the mask to illuminate the entire substrate. Therefore, the two areas conduct planar alignment in different azimuthal directions.

We measured the transmittance versus voltage (TVV) curve using the setup in Fig. 4(a), which is defined as the LC-cell-modulated light intensity's dependence on the voltage applied to the LC cell, which can be used to judge the quality and the stability of the LC alignment. In addition, we placed LC cells between mutually perpendicular polarizers and rotated cells to observe their phase delay towards light, thus obtaining the uniformity of the alignment layer's performance.

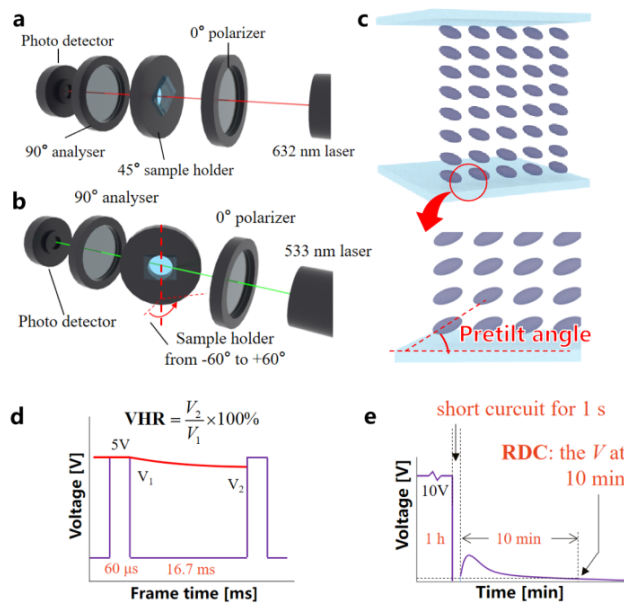


Figure 4. The optical testing setup for (a) TVC and (b) pre-tilt angle measurement. (c) The definition of pre-tilt angle. The calculation regulation of (d) VHR and (e) RDC.

Pre-tilt angle measurement setup (crystal rotation method) ^[13] is shown in Fig. 4(b). The VHR of LC cells is an important parameter in the industry, and it greatly affects the addressing and grayscale maintenance of TFT LCDs. Therefore, we compared the VHR of the cell with the commercial material PI4210. We measured VHR at 60 °C using the LCE-X measuring device (Japan TOYO), and Figure 4(d) illustrates the measurement principle. LCE-X applied a narrow pulse of 60 μs to the LC cell and calculated the voltage ratio between the first pulse (V_1) and the second pulse (V_2). Here, we used the 60 Hz frame rate from classic testing and the 200 Hz frame rate from modern high refresh rate screens. RDC is the main culprit of display image sticking caused by free ions in LC cells, mainly due to the accumulation of ions in the alignment layer. We applied 10 V DC to the cell at 60 °C for one hour, then short-circuited it for 1 s to discharge the capacitor. Afterward, according to the standards specified in ^[4], we read the residual voltage of the cell at 10 min as the RDC value (Fig. 4(e)). The results are listed in Table 1.

Table 1. Electro-optical properties of new CPA compared to commercial material

Material	Deposition	VHR, %	RDC, mV
CPA-032	Dip-washing, 25°C	98.8	6.1
PI4210	Spin-coating, 200-300°C	98.7	5.4

The anchoring energy determines the strength of the interaction between the alignment layer and LC molecules, which can be divided into azimuthal anchoring energy and polar anchoring energy (AAE & PAE) [14]. The AAE was measured using 10 μm twist nematic CPA-032 cells, whose alignment directions differed by 85° between the upper and lower substrates. We utilized the TN testing system (Center for Display Research, HKUST) to measure the actual twist angle of LC and calculated the AAE of CPA-032 based on equation (1). Besides, we validated the PAE of CPA-032 by calculating the boundary conditions of the LC cell, whose relaxation time (τ_0) was used to infer PAE [15], as shown in equation (2).

$$W_A = \frac{2K_{22}\varphi_t}{d \sin 2(\varphi_e - \varphi_t)} \quad (1)$$

Here, K_{22} is the twist elastic constant, d is the cell gap, φ_t is the actual achieved twist angle, while φ_e is the set twist angle 85°.

$$\tau_0 = \frac{\gamma_1}{K_{33}\pi^2} \left(d^2 + \frac{4dK_{33}}{W_{polar}} \right) \quad (2)$$

Among them, γ_1 is rotation viscosity, K_{33} is the bend elastic constant, d is cell gap, and W_{polar} is PAE.

3. Results and discussions

A fabricated LC cell with a new alignment monolayer had 8 exposure windows with different illumination times, as shown in Fig. 5(a), where the cross-white arrows mean the direction of cross polarizers. Starting from 30 s of exposure time, we found that CPA-032 can guide a uniform planar alignment, forming a sharp contrast with covered areas filled with flow effects, which partially proves its high anchoring energy. The AAE of CPA-032 saturates at $9.22 \times 10^{-5} \text{ J}\cdot\text{m}^{-2}$ when the exposure time reaches 600 s (at irradiating energy $0.68 \text{ J}\cdot\text{m}^{-2}$ @ 310 nm). It is close to the average range of general PA materials (such as PI is $1 \times 10^{-4} \sim 10^{-3} \text{ J}\cdot\text{m}^{-2}$ range [14], sulfonic bis-azo dye 1 (SD1) is $7.2 \times 10^{-5} \text{ J}\cdot\text{m}^{-2}$) [16]. Its PAE value is as high as $1.5 \times 10^{-3} \text{ J}\cdot\text{m}^{-2}$, reaching the same level as rubbed PI film at the $10^{-3} \text{ J}\cdot\text{m}^{-2}$ range. [17]

The variation of the pre-tilt angle of CPA-032 guided LC with different exposures does not change a lot, as shown in Fig. 5(b). After ~ 60 sec and up to 600 sec, pretilt is stable, which can be explained by fast and permanent directed dimerization of cinnamate units.

Fig. 5(c) shows that CPA-032 is able to conduct high-resolution graphical LC alignment. The pitch of the checkerboard mask is as small as ten μm , but CPA can still fully replicate the pattern, ensuring its application prospects in various LC optical devices. With the increase in CPA anchoring energy and the application of interferometric graphical illumination, the minimum pitch and alignment quality of the CPA family can be further optimized.

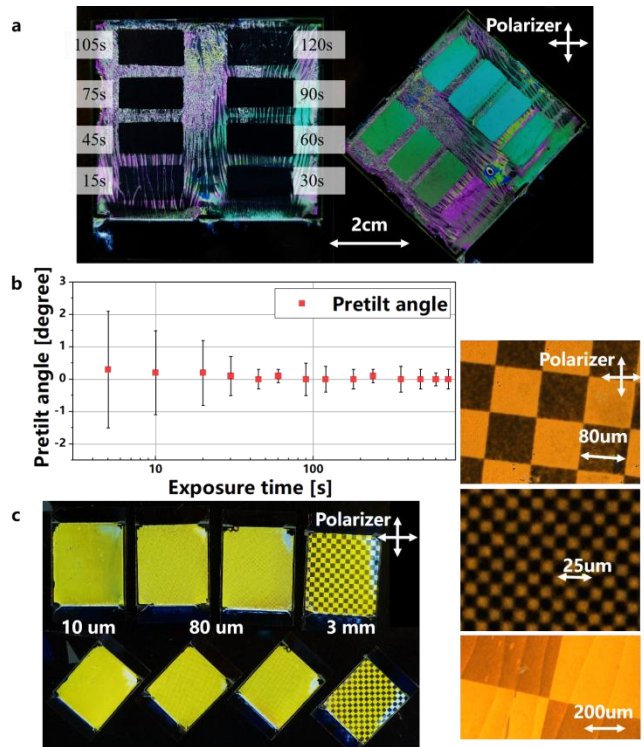


Figure 5. (a) The optical observation of multi-dose CPA-032 cell between cross polarizers. (b) The pre-tilt angle versus exposure duration. (c) The results of patterning exposure.

4. Conclusion

This work demonstrated a cinnamate phosphonic acid that makes a self-assembled monomolecular layer with good electro-optical properties. CPA-032 cells provide great planar alignment with a measured pretilt angle of ~0°. DW procedure at room temperature allows to achieve of VHR value up to 98.9% and RDC as small as 6.1 mV. Those advantages make such materials competitive to PI. In addition, due to the removal of hard baking, such CPA series are more energy-saving, which can decrease carbon footprint around the globe. Besides, its PAE reaches $\sim 1.5 \times 10^{-3} \text{ J}\cdot\text{m}^{-2}$, but AAE is $9 \times 10^{-5} \text{ J}\cdot\text{m}^{-2}$ level that needs to increase further. We are now searching for the possibility of combining vertical and planar alignment CPA to achieve a controllable pre-tilt angle to create an even better future for the CPA family.

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O. Semenenko and X. Yu contributed equally to this work.

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