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Bulk-mediated *in-situ* homogeneous photoalignment induced by reactive mesogen containing diphenylacetylene moiety

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ABSTRACT

We designed and synthesised a reactive mesogen containing diphenylacetylene moiety in the mesogenic core and two polymerisable acrylate groups at both ends. By irradiating linearly polarised UV light on the conventional host LC mixture containing a small amount of the synthesised reactive mesogen in a sandwiched cell without an alignment layer, we demonstrated an in-situ photo-induced homogeneous alignment of liquid crystals without a pre-treated alignment layer, which was achieved by an irreversible polarisation-selective [2 + 2] photodimerization of diphenylacetylene moiety with linearly polarised UV irradiation at above the isotropic temperature of LC mixture. The resulting homogeneous alignment showed a superior initial dark state, negligible pretilt angle and excellent stabilities. Furthermore, the in-plane switching (IPS) LC cell prepared by this method exhibited a better dark state and electro-optic performance compared to that with conventional-rubbed polyimide alignment layer. The single photoirradiation process automatically resulted in a perfect alignment matching of optical axes between the top and bottom substrates in the LC cell, giving rise to an excellent dark state overcoming an intrinsic misalignment issue and complex fabrication process. The proposed in-situ alignment method is a promising candidate for cost-effective, green-manufacturing, and high-quality alignment technique in the manufacturing of high-resolution liquid crystal displays.
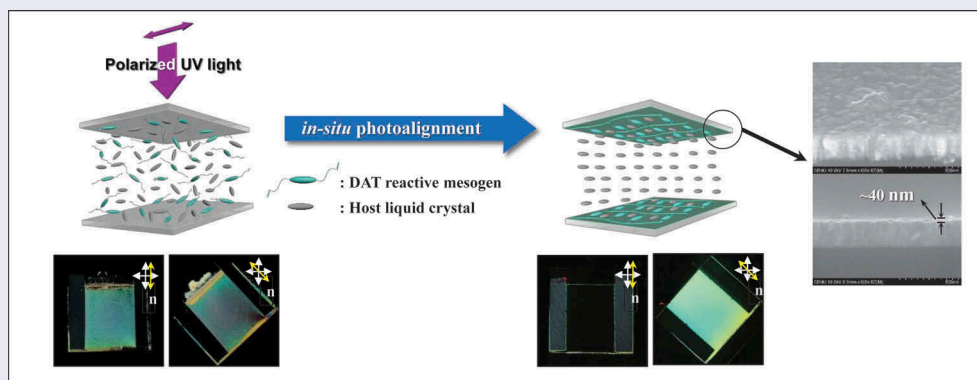
1. Introduction

The first twisted nematic liquid crystal (TN-LC) cell was developed in the 1970s, and after the development of active matrix liquid crystal display (AMLCD) in the 1980s, AMLCD was commercialised for notebook displays in early 1990s [1–3]. Nowadays, the LCDs dominate flat panel display markets owing to various advantages such as lightweight, low price, low power consumption, high resolution and so on [4], though organic light emissive display (OLED) challenges the market especially in the mobile displays. Various types of advanced LCDs have been developed and manufactured such as in plane switching (IPS) [5,6], fringe field switching (FFS) [7–11], multi-domain vertical alignment (MVA) [12,13] and so on. Among these high-performance advanced LCDs, IPS and FFS mode LCDs are known to exhibit intrinsically wide-viewing-angle, superior transmittance, fast response time and low operating voltage. The high electro-optic performance of IPS and FFS LCDs is mainly attributed to the in-plane rotation of homogeneously aligned LC molecules [10].

To achieve the homogeneous alignment, numerous techniques for preparing an alignment layer have been adopted on the substrate so as to give a preferred directional ordering of LCs by mechanical rubbing [14–16], ion beam treatment [17,18] or photoalignment [19–21] techniques. The conventional mechanical rubbing technique employed so far for homogeneous alignment layer involves multi-step processes, i.e. polyimide coating, high-temperature baking and mechanical rubbing, which results in a complicated fabrication process and high consumption of electrical energy and water. Furthermore, some serious drawbacks such as a debris generation, electrostatic charges and contamination problems can be accompanied [22]. Therefore, the photoalignment technique has become an alternative technology for clean and non-contact fabrication process. Numerous efforts have been focused on this photo-alignment technology [23–26]. Generally, irradiation of linearly polarised UV (LPUV) light to the photosensitive alignment layer coated on a substrate results in a homogeneously oriented anisotropic alignment by an axis-selective photoreaction. The LC molecules on the alignment layer surface tend to uniaxially align by the anisotropic molecular interaction between the LC molecules and the alignment surface. However, the photo-alignment method still requires additional fabrication processes such as polymer layer coating, baking, as well as UV irradiation with long processing time, which results in a cost increase and energy consumption. To further improve the photoalignment technique from the industrial viewpoint, it is strongly desired to achieve homogeneous alignment by a simpler, less expensive and energy-saving process. Therefore, a so-called poly-imide-free homogeneously alignment technology has been proposed. So far, few researchers have reported the fabrication of homogeneously aligned IPS/FFS LC cells without conventional alignment layer [27,28]. Mizusaki et al. described the fabrication of homogeneously self-aligned FFS mode LC cell without a conventional alignment layer by exposing LPUV on a mixture of LC host doped with photosensitive monomer, chalcone diacrylate, in a sandwich cell [28]. Recently, we also reported a polyimide-free homogeneous alignment technique by using a liquid crystalline monomer having a cinnamate moiety [29]. The IPS mode LC cell prepared by this method exhibited excellent optical properties at lower irradiation dose. All these methods produced the polymer alignment layer on the surface of substrates by the polymerisation of photo-sensitive liquid crystalline monomer included in the host LC at above the isotropic temperature of the LC

mixture. It should be noted that both the chalcone and cinnamate derivatives can undergo photochemical reaction either via trans/cis isomerisation or [2 + 2] photo-dimerization [21,30,31], that is, either can be responsible for the surface ordering for LCs. Therefore, the generation mechanism of homogeneous alignment from chalcone and cinnamate derivatives has not been fully understood due to the complexity of photochemical reactions.

From the viewpoint of photochemistry, the homogeneous LC alignment generated from the photochemical reactions upon LPUV irradiation can be classified into two categories: reversible and irreversible photoreactions. The reversible photoreaction involves trans/cis isomerisation [32], α-hydrazono/β-ketoesters [33] or spiropyran/merocyanine [34] transfer system, in which the surface anisotropy arises from the reorientation of molecular axis. On the other hand, the irreversible photoreaction comprises photodecomposition reaction [35] and [2 + 2] photodimerization reaction [36,37]. The homogeneous alignment induced by [2 + 2] photo-dimerization has been proposed to refer to an axis-selective photochemical process [3]. Obi et al. illustrated the photocontrol of LC alignment in a thin-coated film of polymethacrylate having a diphenylacetylene side chain. LPUV irradiation on the diphenylacetylene moiety generated a photo-dichroism owing to the depletion of diphenylacetylene moiety with the transition moment parallel to the electric vector of the incident LPUV. As a result, a stable homogeneous alignment of LCs was induced with the molecular axis perpendicular to the electric vector of the incident LPUV [38]. However, there have been no subsequent studies focused on the photoalignment of diphenylacetylene structure.

In this study, we took account of the diphenylacetylene structure, which exhibits an irreversible [2 + 2] photo-dimerization reaction rather than trans/cis photoisomerisation upon UV irradiation. We designed and synthesised a reactive mesogen (abbreviated as DAT) containing a diphenylacetylene moiety in the core and two polymerisable acrylate groups at both ends, which showed a smectic A phase at between 17.9°C and 119.2°C. A small amount of DAT was mixed with conventional host LC, and the resulting mixture was injected into a sandwich cell without an alignment layer. We demonstrated the polyimide-free *in-situ* homogeneous alignment of LCs by irradiating the LPUV on the cell at above T_{NI} of the LC mixture. This gave rise to the photopolymerisation of acrylate groups in the DAT reactive mesogen, and simultaneously, [2 + 2] photodimerization of diphenylacetylene moiety, which generated an

anisotropic polymer layer on the surface of both substrates inducing homogeneous alignment of LCs, as illustrated in Figure 1. The resulting irreversible homogeneous LC alignment layer exhibited excellent thermal and UV stabilities. Furthermore, by this approach, we were able to fabricate an *in-situ* homogeneously aligned IPS cell (DAT-IPS) without using a pretreated alignment layer. In this work, we describe the synthesis and characterisation of DAT, the fabrication processes of DAT-IPS cells, and their electro-optic properties. We believe that this simple *in-situ* fabrication method is one of the potential alternatives to the conventional alignment technique to achieve a low-cost, eco-friendly and effective alignment in LCDs. Additionally, this *in-situ* photoalignment technique possesses a great potential for the fabrication of polarisation-selective-patterned devices or advanced flexible LCDs.

2. Experimental

2.1. Materials

DAT was synthesised according to the procedures described in the Supporting Information. All the chemicals used in the synthetic procedure were purchased from Sigma-Aldrich and used without further purification. The LC material (MLC-6873-100) of positive dielectric anisotropy with T_{NI} = 70.5°C, $\triangle \varepsilon$ = 9.9 and $\triangle n$ = 0.1016 was purchased from Merck. The dichroic black dye (Irgaphor® Black X12) was obtained from BASF and used without further purification.

2.2. Preparation of DAT-doped LC mixture

The LC material (MLC-6873-100, Merck) and DAT were mixed in a weight ratio of 99:1. The DAT/LC mixture was kept in an ultrasonic bath at room temperature for 5 min and stored in an oven at 80°C for 30 min to assure a complete mixing.

2.3. Fabrication of DAT-ITO cell

At first, the cell was fabricated by assembling two cleaned ITO-glass substrates without any alignment layer (DAT-ITO). The cell gap was maintained at approximately 5.0 μm by using the spacers. The DAT-doped LC mixture was injected into the plain ITO-cell by a capillary force at 80°C. Then, DAT-ITO cell was exposed with LPUV at 80°C with an intensity of 5.0 mW/cm^2 (@365 nm) for an appropriate period of time.

2.4. Fabrication of DAT-IPS cell

DAT-IPS cell was fabricated by combining a bottom IPS-substrate and a top bare glass substrate. The IPS-substrate was comprised of one-domain-interdigitated electrodes with a pixel electrode (W = 7.0 μm) and a common electrode (L = 15.0 μm). The cell gap was maintained at approximately 5.0 μm by using the spacers. The DAT-doped LC mixture was injected into the empty DAT-IPS cell by a capillary force at 80°C. Then, the cell was exposed to LPUV for 15 min at 80°C with an intensity of 5 mW/cm^2 (@365 nm). The UV light was incident normal to the substrate, and the polarisation direction was set at 10° with respect to the electrode direction.

2.5. Fabrication of PI-IPS cell

To compare the electro-optic properties of the photo-aligned DAT-IPS cell with those of conventional IPS cell, we also fabricated an IPS cell with rubbed polyimide alignment layers (PI-IPS). For rubbing-induced homogeneous alignment, both the IPS substrate (bottom) and the bare glass substrate (top) were spin-coated with polyimide AL-16470 (JSR Co.), and uniaxially rubbed with a velvet cloth. The rubbing direction was set to 80° with respect to the electrode direction.
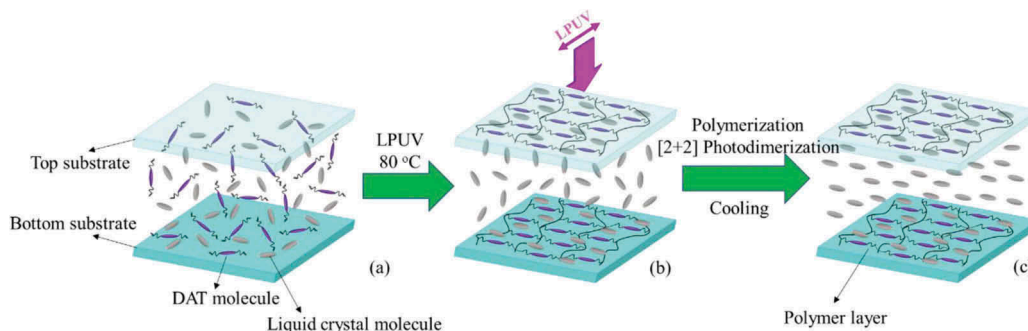

Figure 1. (Colour online) Schematic representation of the fabrication process to achieve in-situ homogeneous alignment of LC.

Subsequently, the top and bottom substrates were assembled antiparallel to the rubbing direction with 5 μm cell gap. The LC material (MLC-6873-100, Merck) with no DAT was injected into the empty PI-IPS cell by a capillary force at 80°C.

2.6 Measurements

The ^{1}H NMR spectrum of the DAT was recorded with JNM-AL400 FT/NMR spectrometers (400 MHz, JEOL Ltd., Japan) in chloroform-d or DMSO-d$_6$ solvent. Thermal decomposition property was investigated with TGA Q50 thermogravimetric analyser (TGA) (TA Instruments Inc., USA) at a heating rate of 10°C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted on DSC 2010 differential scanning calorimeter (TA Instruments Inc., USA) at heating and cooling rates of 5°C/min under nitrogen atmosphere. The phase transition behaviours of DAT were investigated by using a polarised optical microscopy (POM, Nikon ECLIPSE LV100, Japan) equipped with Nikon DS-Ri1 digital camera and a hot-stage. UV-Vis spectra were recorded with S-3100 UV-Vis spectrophotometer (Scinco Co., Korea). Polarised UV-Vis spectra were recorded with the S-3100 UV-Vis spectrophotometer (Scinco Co., Korea) equipped with a calcite Glan-Taylor rotating polariser. The order parameter (S) was calculated from the equation as follows: S = $(A_{||}/A_{\perp} - 1) / A_{||}/A_{\perp} + 2)$, where $A_{||}$ and $A_{\perp}$ are defined as the absorbance of the sample when the polariser is parallel and perpendicular to the average orientation of long axis of dye chromophores, respectively. Inner surface images of the substrates were investigated by the field emission scanning electron microscopy (FE-SEM) (S-4300SE, Hitachi High-Technology Co., Japan). The pretilt angles of DAT-IPS and PI-IPS cells were measured by crystal rotation method with PAMS-200 (Sesim Photonics Technology Inc., Korea) pretilt measurement system. The electro-optic properties and response times of both IPS cells were measured with LCMS-200 (Sesim Photonics Technology Inc., Korea) electro-optic evaluation system.

3. Results and discussions

3.1. Synthesis and characterisation of DAT

The reactive mesogen DAT was synthesised according to the synthetic route in Scheme S1, and the detailed synthetic procedures are described in the Supporting Information. The chemical structure of DAT monomer containing diphenylacetylene moiety is displayed in Figure 2(a), which was characterised by ^{1}H NMR spectroscopic

method (Figure S1). The thermal property of DAT was studied by TGA analysis as described in Supporting Information (Figure S2). The mesogenic phase behaviour of DAT was also investigated by DSC (Figure 2) and a polarised optical microscopy (POM, insets in Figure 2). As shown in the DSC curve, DAT showed a smectic phase between 63.8°C and 121.0^{o}C and a nematic phase between 121.0°C and 128.2^{o}C during the heating process. During the cooling process, a nematic phase appeared between 126.5°C and 119.2^{o}C, followed by a smectic phase in a wide temperature range between 119.2°C and 17.9^{o}C, which indicated an enantiotropic phase transition behaviour. The phase transition behaviour of DAT was also confirmed by the POM images during the cooling process. POM images in Figure 2(d) taken at 121.0^{o}C corresponds to a flow-induced planar orientation of the nematic phase, while that in Figure 2(c) displays a typical fan-shaped texture of smectic A phase at 111.0^{o}C. The results revealed that the DAT is a smectic A liquid crystal with a wide mesomorphic temperature range.

The photochemical property of DAT was investigated by UV-Vis spectral change upon UV irradiation in dichloromethane solution, as shown in Figure 3. Before UV irradiation, DAT in dichloromethane shows absorption peaks at 282, 302, and 318 nm, respectively. Upon UV irradiation, while these absorption peaks decreased gradually with the prolonged UV irradiation, new absorption increases were observed at 238 and 345 nm. Furthermore, two isosbestic points were observed at 263 and 325 nm, respectively. After a UV irradiation of 3.0 J/cm^2, the absorption spectra did not show any significant change for an extended period of time of UV irradiation. The results can be ascribed to the photo-induced formation of dimeric species via an irreversible mechanism from the cleavage of the conjugated π-electron system of diphenylacetylene structure as reported previously [39,40]. Buchi et.al [39] firstly reported the photoreaction of diphenylacetylene structure, in which the photodimerization of phenyl substituted acetylenes occurs under UV irradiation to produce various dimerised products such as tetraphenylcyclobutadiene, 1,2,3-triphenylazulene, 1,2,3-triphenylnaphthale and others. Therefore, it seems reasonable to assume that the DAT can undergo an axis-selective photodimerization by LPUV irradiation.

3.2. In-situ homogeneous photoalignment induced by DAT

The in-situ homogeneous alignment of LCs in a sandwich cell induced by LPUV irradiation is schematically illustrated in Figure 1. The DAT-doped LC mixture was injected at above the isotropic temperature of the LC mixture into a sandwich cell fabricated from two bare
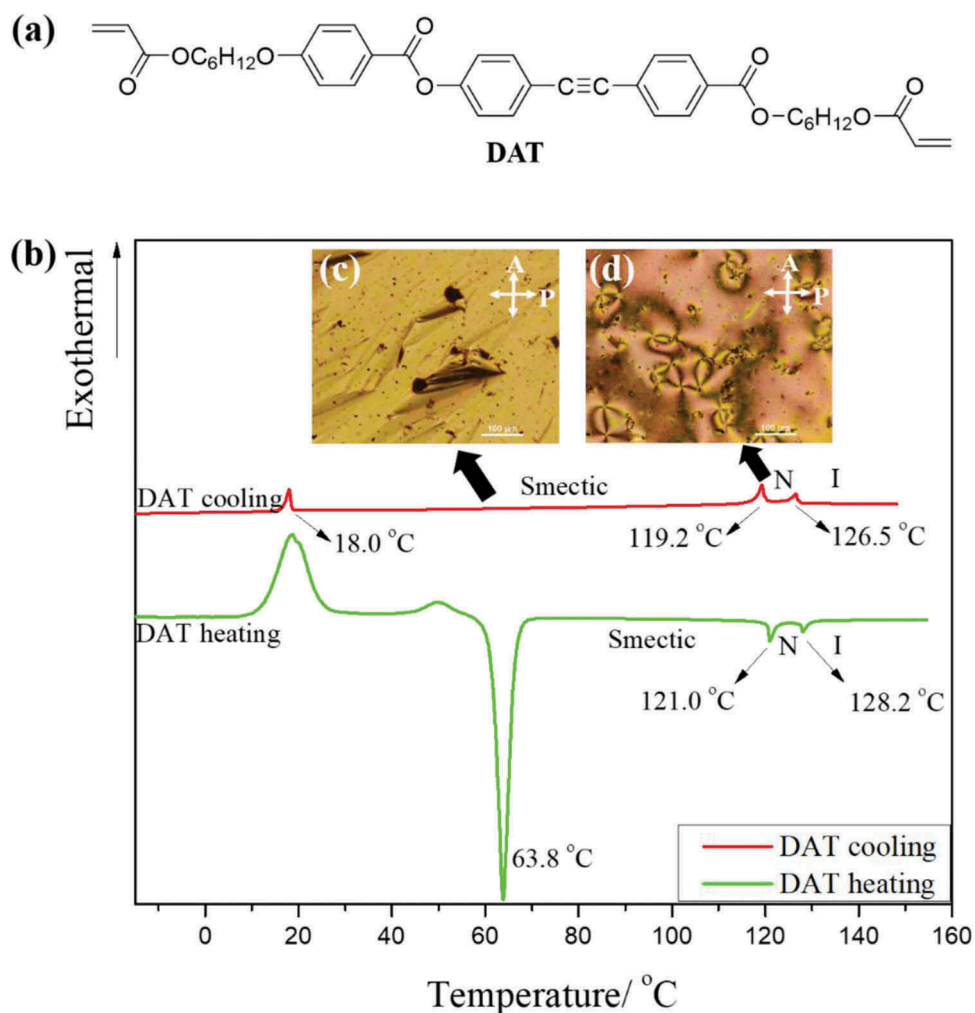
Figure 2. (Colour online) (a) Structure of DAT monomer. (b) DSC thermogram and phase transition behaviour of DAT. Insets are POM images representing (c) fan-shaped smectic A phase at 111°C, (d) Schlieren texture of nematic phase at 121°C.
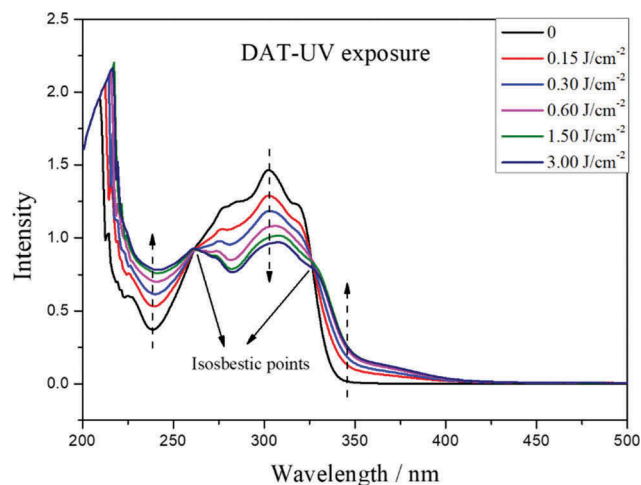

Figure 3. (Colour online) UV-Vis spectra of DAT in dichloromethane under UV irradiation.

ITO glass substrates without any conventional alignment layer (DAT-ITO cell). It should be noted that the DAT showed an excellent compatibility with the host LC material due to its liquid crystalline nature as observed by POM. After sealing the cell opening, LPUV was irradiated on the cell either at room temperature or at 80°C (above T_{NI}), respectively. The DAT-ITO cells treated at room temperature did not show a homogeneous alignment even with a prolonged irradiation time. On the other hand, when the LPUV was irradiated on the DAT-ITO cell at an isotropic temperature (80°C), an uniaxially homogeneous alignment was achieved. This can be ascribed to the depolarisation of incident LPUV caused by birefringence of the host LC molecules at room temperature. Therefore, the LPUV irradiation was carried out at 80°C (above T_{NI}) in the following experiments.

A series of DAT-ITO samples were prepared with various LPUV exposure energy from 0 to 18.0 J/cm^2, of which the photographic images are displayed in Figure 4(a). While the DAT-ITO cell showed a random alignment before LPUV irradiation, the samples with LPUV irradiation for more than 3 min (0.9 J/cm^2) resulted in a uniform homogeneous alignment. The cell exhibited a perfect homogeneous alignment without any defects even after the LPUV irradiation for 60 min (18.0 J/cm^2). POM images of DAT-ITO cell before and after LPUV irradiation are displayed in Figure 4(b-d). As expected, a typical nematic random texture representing a random planar orientation was observed before the LPUV irradiation (Figure 4(b)). On the other hand, after LPUV exposure at 80°C, a completely dark state was observed with the LPUV direction parallel to the analyser direction (Figure (4c)), and a bright state was observed (Figure (4d)) with the LPUV direction 45° to the analyser direction, indicating an uniaxial orientation of LCs in the cell. In our previous study on the polyimide-free homogeneous alignment of LCs induced by a cinnamate-containing reactive mesogen (CRM) [29], uniform homogeneous alignments were
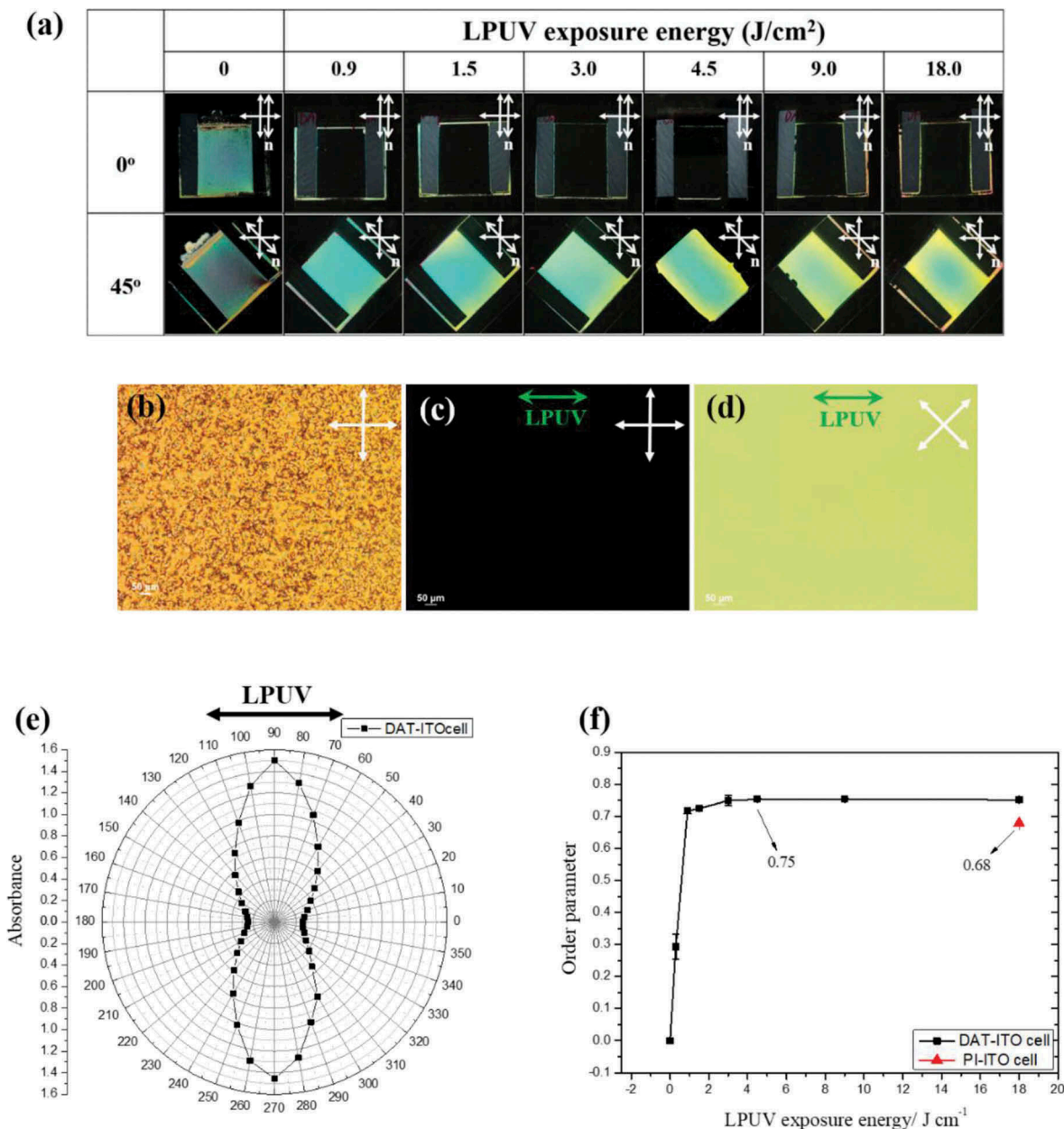

Figure 4. (a) Photographic images of DAT-ITO cells under crossed polariser with various LPUV exposure energy. POM images of DAT-ITO cell (b) before UV irradiation, (c) after UV irradiation (LPUV axis is parallel to the analyser direction) and (d) after UV irradiation (LPUV axis is 45 ° to the analyser direction). (e) Angle-dependent polar diagram of reassembled DAT-ITO cell containing LC mixture doped with 1.0 wt% dichroic dye. (f) Order parameter values of the DAT-ITO cells with respect to the LPUV exposure energy.

achieved by LPUV exposure energy only in the range of 1.2 to 2.4 J/cm^2. When the exposure energy was higher than 2.4 J/cm^2, the sample showed some defects accompanied by partially disordered regions. This was probably due to the [2 +2] photodimerization and/or chemical decomposition of cinnamic moieties under extended LPUV irradiation, which deteriorated the alignment quality of the anisotropic polymer film originally formed by the trans-cis photoisomerisation. In contrast, DAT-ITO cells exhibited excellent alignment properties without any observable degradation or defect generation even after LPUV irradiation for 1 h (18.0 J/cm^2). These results imply a superior stability of the DAT-induced homogeneous alignment compared to that of the previous CRM-based cell.

It has been accepted that LPUV irradiation of a polymer layer based on azobenzene or cinnamic moieties induces a repetition of trans/cis photoisomerisation of the chromophores resulting in the continuous reorientation of molecular axes preferentially perpendicular to the electric vector of incident LPUV. On the other hand, in this study, the mechanism is different from the azobenzene or cinnamate derivatives due to the absence of photoisomerisation transition in the diphenylacetylene moiety. It is a reasonable interpretation that an optically anisotropic surface is generated from the [2 +2] photodimerization reaction between the diphenylacetylene moieties during LPUV irradiation. Though the mechanism of this *in-situ* generation of photoalignment requires more detailed experimental evidences, we speculate it as follows: With the LPUV irradiation, the formation of DAT oligomers via photo-induced polymerisation of acrylate moieties caused a phase separation of the products from the host LC mixture. Once the excluded oligomers deposited on the surface of substrates, an axis-selective photodimerization of diphenylacetylene moieties took place, which resulted in an anisotropic polymer layer on the substrate surfaces. Further polymerisation of the remaining acrylate groups stabilised the anisotropic polymer layer and the LC molecules on the surface are aligned by the molecular interaction with the anisotropic polymer layer surface [27]. As previously mentioned, however, the mechanism should be investigated more extensively in the future study.

The LC alignment direction and order parameter were determined by obtaining an angle-dependent polar diagram of the reassembled DAT-ITO cell containing a mixture of host LC material and 1.0 wt% of black dichroic dye. Firstly, the top and bottom substrates of the LPUV-irradiated DAT-ITO cell were detached carefully and rinsed with hexane to remove the host LC. After drying, the top and bottom substrates were reassembled with 5 μm cell gap, and a mixture of host LC material and 1.0 wt% of

black dichroic dye was injected into the reassembled cell above T$_{NI}$. After cooling to the room temperature, the cell exhibited a uniform homogeneous alignment without any defects, indicating that the *in-situ* produced alignment layer still sustained a decent alignment capability even after the solvent washing process. The dichroic absorption of the reassembled cell was recorded by polarised UV-Vis spectra as a function of azimuthal rotation angles of polariser, as shown in Figure 4(e). The maximum absorption was observed at 90° with respect to the electric vector of incident LPUV direction indicating the LC molecules were oriented perpendicular to the electric vector of incident LPUV direction, as in the case of azobenzene or cinnamate-based polymer alignment layers [29,32]. A series of reassembled cells with various LPUV exposure energy from 0 to 18.0 J/cm^2 was prepared, and the order parameter values of each cell were calculated from the angle-dependent polar diagrams as plotted in Figure 4(f). The order parameter values of DAT-ITO cells increased dramatically in the initial 3 min and showed a slow increase afterwards, reaching to a maximum value in 10 min. It is noteworthy that the DAT-ITO cell prepared in this work showed higher-order parameter value (S = 0.75) than that of the conventional-rubbed PI cell (S = 0.68). The above result also suggests that with LPUV irradiation, an optically anisotropic polymer layer is formed on the inner surface of the substrates, which could align the LC molecules in the bulk layer by molecular interaction even after the solvent washing process.

In order to further confirm the formation of a polymer layer on the inner surface of the substrates, the inner surface of the DAT-ITO cell (exposure energy of 4.5 J/cm^2) was examined by the high magnification scanning electron microscopy (SEM) after detaching and rinsing the cell with hexane as shown in Figure 5. The surface view image in Figure 5(a) and the cross-sectional view image in Figure 5(b) indicate that a thin polymer layer was formed with a thickness of around 40 nm on both substrates. It is noteworthy that the polymer layer formed on the substrate showed a decent solvent resistance with good adhesion on the ITO-surface even after rinsing with hexane overnight.

To compare the optical properties of DAT-ITO cells with those of cells with conventional alignment layer, we also prepared sandwich cells from ITO glass substrates coated with a conventional-rubbed PI alignment layer (PI-ITO cell), into which only the host LC was injected. To evaluate the dark states quantitatively, we captured the dark state images of PI-ITO cell and DAT-ITO cells treated with various LPUV irradiation energy, respectively, and the light leakage values were estimated from the average brightness values by image processing. The light leakage values of DAT-ITO and PI-ITO cells are
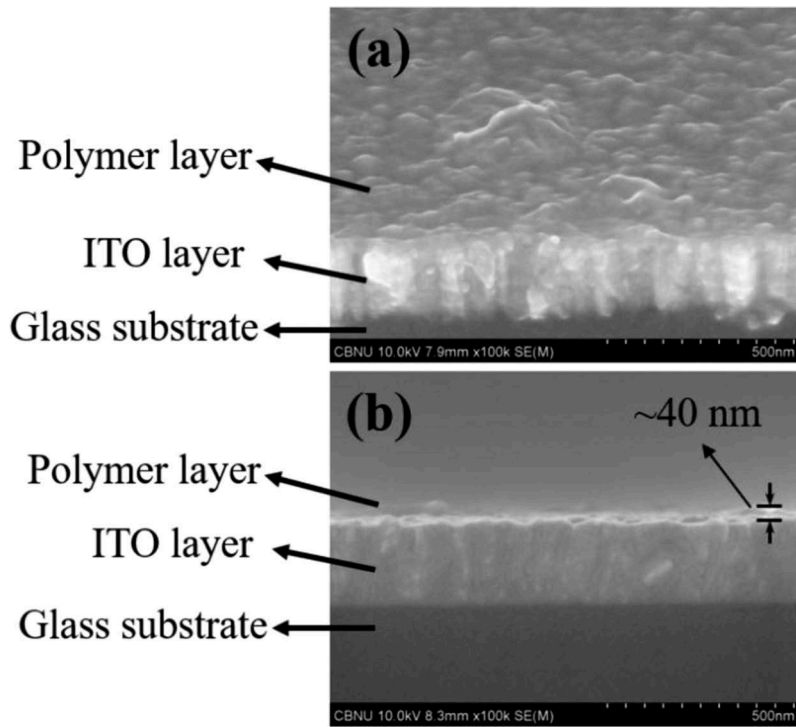
Figure 5. SEM images of substrate inner surface after LPUV exposure, (a) surface view and (b) cross-sectional view.

plotted with respect to the exposure time in Figure S4. As can be seen, the light leakage value of DAT-ITO cell decreased dramatically in the initial 10 min and showed a slow decay afterwards. Finally, the value reached a saturated stage after irradiation for 15 min. The final light leakage value of the DAT-ITO cell and PI-ITO cell are 0.007 and 0.076, respectively. The light leakage of DAT-ITO cell is 10 times lower than that of the conventional PI-ITO cell, indicating a better dark state can be achieved by using this *in-situ* photoalignment technique and LCDs with higher contrast ratio more than 10 times can be fabricated with this approach. The higher light leakage of PI-ITO cell is possibly attributed to the debris and defects generated from the velvet cloth during the rubbing process. In addition, the exceptionally low light leakage of DAT-ITO cell should also be ascribed to the perfect alignment matching of optical axes between the top and bottom substrates. In general, the dark state of LCD with homogenous alignment is proportional to $sin^2\Phi$ where Φ is an angle between LC director and two crossed polarisers. Intrinsically, Φ cannot be zero in the conventional alignment process either by rubbing or photoalignment, since the top and bottom substrates should be assembled together after the surface treatment. However, the single photoirradiation process automatically results in a perfect alignment matching of optical axes between the top and bottom substrates in the DAT-ITO cell, giving rise to an excellent dark state.

3.3. Electro-optic properties of DAT-IPS and PI-IPS cells

To investigate the electro-optic properties of the polyimide-free homogeneous alignment proposed in this study, the IPS cell (DAT-IPS) was fabricated by using the *in-situ* photo-induced alignment process as described in the Experimental Section. Figure 6(a) and (b) show the photographic images of optical switching of DAT-IPS cell at voltage off (0 V) and on states (7.7 V), respectively. The results indicated that an uniaxial homogeneous alignment was successfully achieved in the IPS cell, and the DAT-IPS cell exhibited a reasonable electro-optic switching property. The pretilt angle of the DAT-IPS cell and the conventional-rubbed PI alignment cell (PI-IPS) were measured by crystal rotation method [41] from PAMS-200 pretilt measurement system. The pretilt angles of DAT-IPS cell and PI-IPS cell were 0.08° and 1.3°, respectively. The result confirmed that the DAT-IPS cell showed an extremely low pretilt angle compared to the conventional PI-IPS cell. This suggests that more symmetric
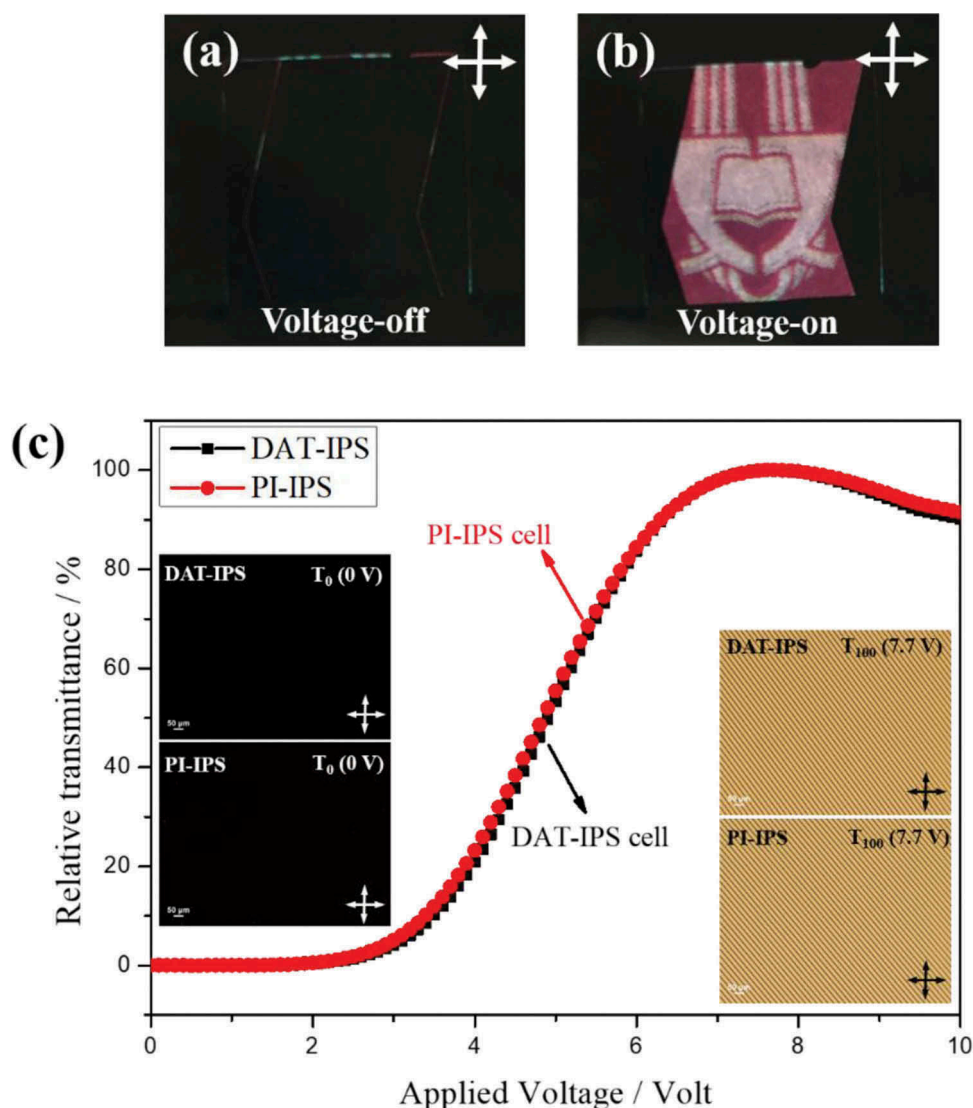
Figure 6. (Colour online) Photographic images of DAT-IPS cell at (a) voltage-off state (0 V) and (b) voltage-on state (7.7 V). (c) Comparison of V-T curves for DAT-IPS and PI-IPS cells. Inset images are POM images observed at voltage-off and voltage-on states, respectively.

viewing angle could be achieved at the off-axis owing to the negligibly low pretilt angle in the proposed method [42].

To compare the electro-optic switching behaviour of the DAT-IPS cell with the conventional PI-IPS cell, the voltage-dependent transmittance (V-T) curves of both cells were measured under the same measurement condition. As shown in Figure 6(c), the DAT-IPS cell exhibits an almost identical V-T curve to the conventional PI-IPS cell, indicating that the electro-optic property of the DAT-IPS cell is comparable to that of the conventional PI-IPS cell. The inset images in Figure 6(c) are the POM images of DAT-IPS and PI-IPS cells at voltage off and on states, respectively. In both cases, the transmittance increases with increasing the applied voltage, and both the cells showed the same level of grey scale images. More

detailed grey scale images at various applied voltages are also displayed in Figure S5. In addition, the voltage-dependent response time of DAT-IPS and PI-IPS cells at various applied voltages were measured and plotted in Figure S6. The rise time (τ_r) of DAT-IPS and PI-IPS cells were 20.9 and 20.5 ms, and the decay time (τ_d) of DAT-IPS and PI-IPS cells were 22.3 and 21.8 ms, respectively. No significant difference was found in the response time between DAT-IPS cell and PI-IPS cell. These results further confirm that the DAT-IPS cell possesses comparable electro-optic switching properties to the conventional PI-IPS cell.

In order to evaluate the anchoring energy of this photo-induced alignment layer, an AC field stress test was performed for 24 h at room temperature to the DAT-IPS cell by applying a voltage of V_{100} (7.7 V)
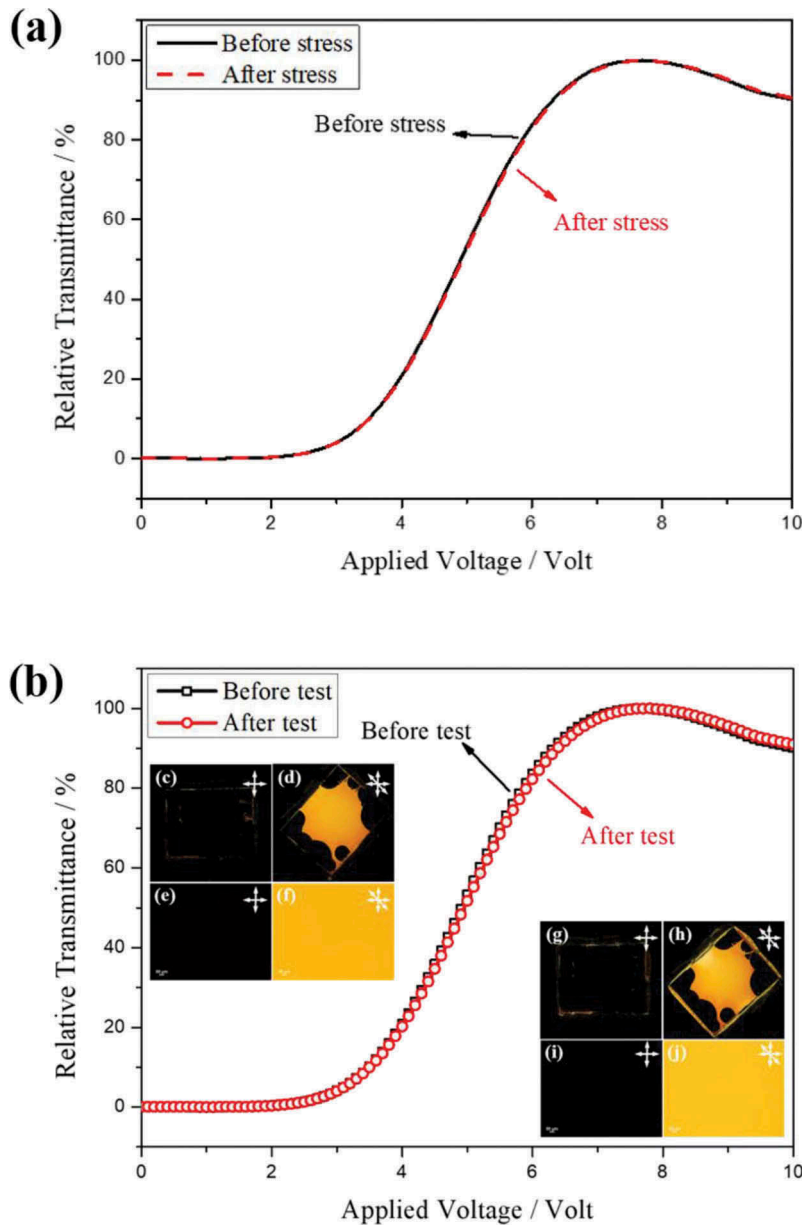
Figure 7. (Colour online) (a) V-T curves of DAT-IPS cell before and after the AC field stress test, (b) V-T curves of DAT-IPS cell before and after the durability test. Inset photographic images (c)(d) and POM images (e)(f) are observed before the test, and inset photographic images (g)(h) and POM images (i)(j) are observed after the test, respectively.

(V_{100} was defined as the voltage which exhibits the maximum transmittance) with 60 Hz square wave frequency. Figure 7(a) displays the V-T curves of the DAT-IPS cell before and after the AC field stress test. No noticeable degradation was observed in the V-T curves before and after the test, indicating a considerable anchoring stability of the photo-induced DAT-IPS cell.

Generally, the image quality and the reliability of LCD depend not only on the electro-optic properties such as the response time and anchoring energy but also on the durability of the cell. For example, thermal stability and UV stability are crucial factors for the practical applications of

photoalignment technology to achieve high image quality and long lifetime. For the durability test, the DAT-IPS cell was firstly kept in an 80°C chamber for 15 days, and subsequently, irradiated with non-polarised UV light of 10 mW/cm^2 (@365 nm) for 2 h. Then, the V-T curves of the cells before and after the treatment were compared in Figure 7(b). It is noteworthy that the V-T curves of the cells are almost identical without any significant degradation before and after the thermal and UV treatment. The photographic images and POM images of the DAT-ITO cell were also examined before and after the durability test as shown in the inset images of Figure 7(c–j). Both the photographic

images and POM images did not show any noticeable defects or degradations. Excellent stability of the proposed alignment layer towards heat and UV light is possibly attributed to the stable dimerised adducts of diphenylacetylene units [38] as well as the crosslinked network structure of the polymer layer. These results indicated that the homogeneously photoaligned cell in this work possesses decent electro-optic properties and excellent stability for the practical applications in high-performance LCDs.

4. Conclusions

In this work, we synthesised a reactive mesogen (DAT) containing a diphenylacetylene moiety in the mesogenic core and two acrylate groups at both ends. We proposed a polyimide-free *in-situ* homogeneous alignment process induced by irradiating linearly polarised UV (LPUV) on the sandwiched cell containing a DAT-doped LC mixture at above T_{NI} temperature. After the irradiation of LPUV, an uniaxially homogeneous alignment of LC was achieved with the LC molecules aligned perpendicular to the electric vector of the incident LPUV. Due to the preferential consumption of diphenylacetylene moieties via a [2 +2] photo-dimerization with the transition moment parallel to the electric vector of the incident LPUV, chemically anisotropic polymer layers were formed on the inner surfaces of the sandwich cell. The IPS cell (DAT-IPS) prepared by the proposed method exhibited an excellent alignment state and electro-optic properties such as low light leakage and zero pretilt angle. Moreover, the resulting alignment layer exhibited outstanding thermal and UV stabilities even after the harsh thermal and UV treatment. In conclusion, we demonstrated that the proposed *in-situ* alignment method can be a promising candidate for cost-effective, eco-friendly, and high-quality fabrication process in the practical applications of high-resolution LCDs.

Disclosure statement

No potential conflict of interest was reported by the authors.

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