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Photochemistry

Dual Photo-functionalized Amphiphile for Photo-reversible Liquid Crystal Alignments

Dae-Yoon Kim, Sang-A Lee, Minwook Park, and Kwang-Un Jeong*[a]

Abstract: Without the conventional polymer-based liquid crystal (LC) alignment process, a newly synthesized dual photo-functionalized amphiphile (abbreviated as $ADMA_1$) was successfully applied as a robust photo-reversible LC alignment layer by self-assembly and photo-polymerization. The LC alignment layer constructed by directly adding dual photo-functionalized amphiphiles into LC media significantly cuts the manufacturing cost as well as opens new doors for the fabrication of novel electro-optical devices.

The control of liquid crystal (LC) alignment has attracted considerable interest in the fundamental scientific aspects of partially ordered soft materials as well as from the engineering application point-of-view of LC electro-optical devices.[1] LC alignment strongly depends on the surface environments and LC properties.[2] For the LC alignment layer, mechanical rubbing on the polymer-coated surface has been most widely used. However, polymer-based rubbing alignment has some limitations, such as long processing times, low yield, and high cost due to the direct contact process.[3] Recently, photo-alignment has become a technologically important and attractive method for controlling LC orientation because of its contact-free and photo-patternable characteristics.[4] There are several reports for the modification of LC-anchoring conditions on the surface of substrates by introducing photochromic materials exhibiting photo-isomerization, photo-polymerization, photo-dimerization and photo-decomposition.[5] In this context, our objective is to obtain reversible homeotropic (LC director is parallel to the surface normal) and homogeneous (LC director is perpendicular to the surface normal) LC orientation by transforming azobenzene chromophores by tuning the wavelength of light. However, since there is no covalent bonding or cross-linking, conventional azobenzene-based compounds for the photo-alignment layer lack thermal and long-term stability.[6] To overcome this barrier, as shown in Figure 1, we newly designed and synthesized the dual photo-functionalized amphiphilic supramolecule containing both azobenzene and diacetylene groups (abbreviated as $ADMA_1$). Here, the carboxylic acid function is specifically placed at the end of $ADMA_1$ to induce automatic two-dimensional $ADMA_1$ monolayer formation on substrates by the sequential processes of phase-separation from the LC medium, diffusion to the substrate and self-assembly on the surface.

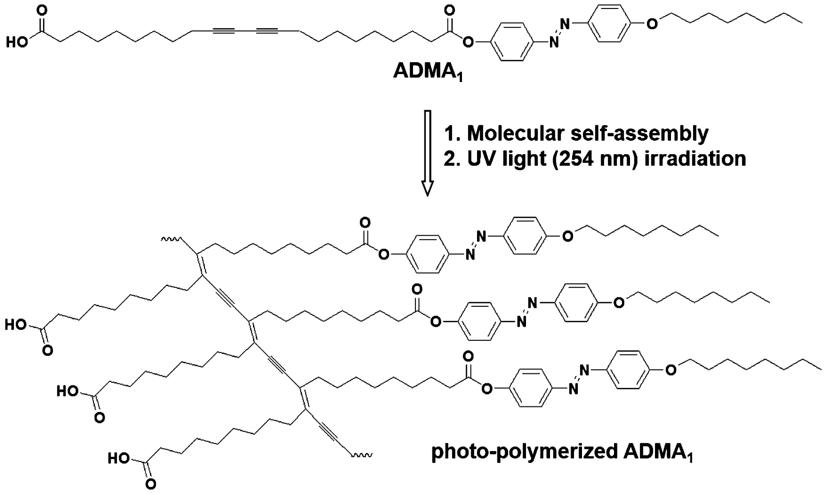

Figure 1. Schematic presentation of $ADMA_1$ and its photo-polymerization of self-assembled diacetylenes by irradiation with 254 nm UV light.

The detailed synthetic procedures of $ADMA_1$ are illustrated in Figure S1 in the Supporting Information. Chemical structures and purities of $ADMA_1$ and its intermediates were confirmed by ^1H NMR spectroscopy (Figures S2–S5 in the Supporting Information), ^{13}C NMR spectroscopy (Figure S6 in the Supporting Information), MALDI-ToF (Figure S7 in the Supporting Information), and elemental analysis (Figure S8 in the Supporting Information). The flexible alkyl chains chemically attached to the azobenzene mesogen and diacetylene moiety not only increase the solubility but also induce favorable LC alignment. It

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[a] *D.-Y. Kim, S.-A. Lee, M. Park, Dr. K.-U. Jeong*
Department of Polymer-Nano Science and Technology
Polymer Materials Fusion Research Center, Chonbuk National University
Jeonju, Jeonbuk, 561–756 (Korea)
E-mail: kujeong@jbnu.ac.kr

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is well known that azobenzene and its derivatives are photo-isomerizable and undergo a reversible transformation between *trans* and *cis* isomers in the presence of light.[7] Therefore, the cooperative conformational changes of azobenzene depending on the wavelength of light is a most effective method for application in photo-modulated LC devices. Furthermore, since the cross-linked structure of polydiacetylene is simply formed by irradiating 254 nm ultraviolet (UV) light to the diacetylene moiety without chemical initiator and catalysts, the stability of LC alignment can be significantly increased by introducing a diacetylene moiety. Therefore, the diacetylene photo-polymerizable function is selectively chosen for programming the targeted smart amphiphile molecule.[8]

The dual photochemical behavior of ADMA$_1$ was first investigated by ultraviolet–visible (UV/Vis) spectroscopy. As shown in Figure 2a, by irradiating UV light with a maximum intensity at 365 nm, the thermodynamically stable *trans* conformer of azobenzene transforms to its metastable *cis* conformer and reaches a new photostationary state in 60 s. The absorption band between 300 and 410 nm resulting in the π-to-π^* transition originates from the *trans* conformer of azobenzene, whereas the ground state (n) of the *cis* conformer of azobenzene is excited to the π^* state by absorbing UV light in the range 410–530 nm. The transition between the two photostationary equilibrium states is a fully reversible process by alternating UV- and Vis-light irradiation (Figure S9 in the Supporting Information). It is worth mentioning that not only the cycle is reversible, but also the amplitude of the change remained without deterioration. When 254 nm UV is irradiated, the absorption band at 630 nm gradually increases with irradiation time, as shown in Figure 2b. This result clearly reflects the formation of polydiacetylenes as the consequence of photo-polymerization of the diyne groups in the self-assembled diacetylenes. The 30 min irradiation was sufficient for the saturated polymerization state. This peculiar dual photochemical property of ADMA$_1$ can be very useful for stabilizing the photo-alignment layer and allowed us to fabricate a reversible photo-modulating device.

The homeotropic alignment of nematic LC (NLC) was examined by both orthoscopic and conoscopic polarized optical microscopy (POM). As shown in Figure S10 in the Supporting Information, four different LC cells with 10 μm cell gap were prepared by varying the ADMA$_1$/NLC weight ratio from 0.4:99.6, 0.3:99.7, 0.2:99.8 to 0.1:99.9. Here, the ADMA$_1$/NLC mixtures were filled into the LC cells on a 100 °C hot plate utilizing the one drop filling (ODF) process and slowly cooled to room temperature; this method can prevent the flow effect.[9] When the content of ADMA$_1$ in the LC mixture was reduced from 0.4 to 0.1 wt %, the dark-state area in the magnified POM image was significantly increased and the Maltese cross in the conoscopic image became obvious (Figure S10). Note that the orientation of homeotropic LC should exhibit a dark state under the cross-polarized POM because the molecular orientations of LC are aligned normal to the surface of test LC cells and do not exhibit any birefringence (zero birefringence effect).[10]

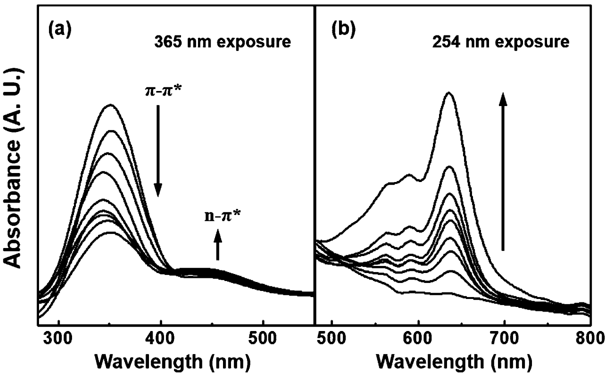

Figure 2. UV/Vis absorption spectra of ADMA$_1$: a) after irradiation with 365 nm UV light for *trans–cis* photo-isomerization of the azobenzene moiety, and b) after irradiation with 254 nm UV light for photo-polymerization of diacetylene groups.

Since the alignment of LC is closely related, not only optimizing the concentration of ADMA$_1$ in the LC mixture but also controlling the rates of phase separation from the NLC medium and diffusion of ADMA$_1$ onto the substrates, the compatibility and interaction of ADMA$_1$ with NLC should be finely tuned by attaching the hydrophilic carboxylic acid and hydrophobic alkyl chains (Figure 3a). To confirm this proposal, the alignment behaviors of 0.1 wt % ADMA$_1$ LC cell were investigated by a specifically designed experiment. When the LC cell with 0.1 wt % ADMA$_1$ was fabricated by a rapid cooling rate (40.0 °C min^{-1}) from 100 to 25 °C, a homogeneously orientated LC was obtained (Figure S11 in the Supporting Information). This means that, due to the insufficient times of the phase-separation from the NLC medium and diffusion to the substrate, the ADMA$_1$ amphiphiles dimerize in the NLC medium by intermolecular hydrogen boding between carboxylic acid groups and do not form the monolayer on the substrate. On the other hand, when the LC cell is slowly cooled at 1.0 °C min^{-1}, a perfect dark state without any light leakage is obtained. This result shows that the initially dissolved ADMA$_1$ in the NLC gradually phase-separated from the NLC medium and diffused onto the substrate for the construction of self-assembled ADMA$_1$ monolayer which is an ideal surface structure for the homeotropic LC alignment layer (Figure 3b). Since the interaction of the polar heads with the substrate is much higher than that of hydrophobic tails, ADMA$_1$ amphiphile can diffuse and be deposited on the surface with molecular orientation perpendicular to the surface.

For enhancing the stability of LC cell, photo-polymerization of the self-assembled ADMA$_1$ monolayer was conducted by irradiating with 254 nm UV light (Figure 3c). Polymer-stabilized ADMA$_1$ LC cell securely maintains the homeotropic state. This result indicates that the photo-polymerization of the self-assembled ADMA$_1$ monolayer does not disturb the LC orientation. By switching the wavelength of light from 365 nm (*trans* isomer) to 450 nm (*cis* isomer), the NLC alignment can be reversibly controlled from homeotropic to homogenous states, as demonstrated in Figure 3c and d, respectively.

To investigate the surface morphological changes of the ADMA$_1$ layer according to light irradiation, the self-assembled ADMA$_1$ monolayer was analyzed by atomic force microscopy (AFM). The surface of bare ITO glass substrate is relatively

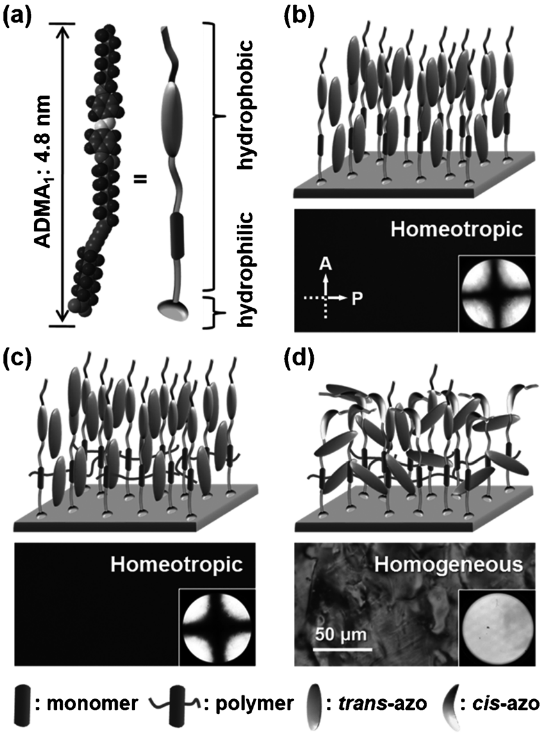

Figure 3. a) Geometric dimensions of ADMA$_1$. Schematic illustration of 0.1 wt% ADMA$_1$ monolayer with NLC and their corresponding POM images of test LC cell: b) before, and c) after photo-polymerization by irradiating with 254 nm UV light. d) POM image of the LC cell with photo-polymerized alignment layer after irradiating with 365 nm UV light. The inset images of orthoscopic POM are their corresponding conoscopic POM images.

smooth and shows 76.0° water contact angles (Figure S12 in the Supporting Information). However, as shown in Figure 4a, the 0.1 wt% ADMA$_1$-coated surface exhibits many protrusions. Its water contact angle is 107.6° (Figure 4b, inset). As presented in Figure 4b, the average height of protrusions of the ADMA$_1$ layers is in the range of 4.63 nm. Note that the calculated geometric length of ADMA$_1$ along the long axis is about 4.8 nm (Figure 3a). Therefore, it can be concluded that the monolayered ADMA$_1$ protrusions are formed by the lateral self-assembly of ADMA$_1$ amphiphiles on the ITO glass substrate. It is believed that the tethered *trans*-azobenzene with alkyl chains make the physical interactions with NLC molecules near to the substrate and provide enough empty spaces for NLC molecules to partially crawl into the empty zones, which results in the creation of homeotropic LC alignment. Figure 4c shows the AFM images of the photo-polymerized ADMA$_1$ monolayer film after 254 nm UV irradiation. The height profile and hydrophobicity of the polymerized surface (Figure 4d) are almost identical with those of the unpolymerized ADMA$_1$ monolayer (Figure 4b). The homeotropic LC alignment is also maintained, as shown in Figure 3c. This result shows that there is no significant surface topographical change during the photo-polymerization of the self-assembled ADMA$_1$ monolayer. When the photo-polymerized ADMA$_1$ is isomerized from the *trans* to *cis* conformer upon irradiation with 365 nm UV light (Figure 3d), the average height profile and hydrophobicity decreases. The photo-polymerized ADMA$_1$ monolayer apparently becomes smooth (Figure 4e), with 3.84 nm average height (Figure 4f) when irradiated with 365 nm UV light. This behavior can be directly correlated with the homogeneous LC orientation (Figure 3d). Subsequent irradiation with visible light reversibly switches azobenzene back to the *trans* stable state (Figure S13 in the Supporting Information).

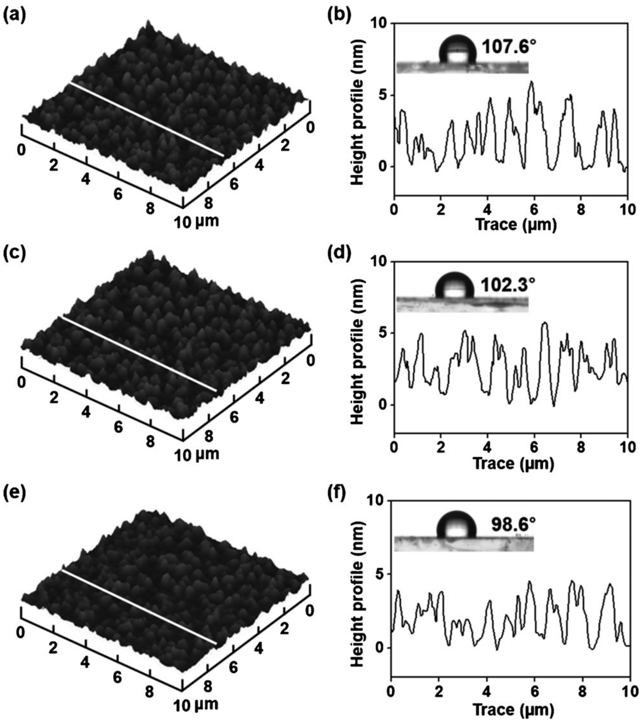

Figure 4. 3D topographic AFM images and their corresponding height profiles with inset contact angle images of the 0.1 wt% ADMA$_1$ monolayer film on ITO glass substrate: a,b) before, and c,d) after photo-polymerization by irradiating with 254 nm UV light, and e,f) *trans*-to-*cis* photo-isomerized film after irradiation with 365 nm UV light.

To confirm the long-term and thermal stability of the photo-polymerized ADMA$_1$ alignment layer, the temperature of the homeotropic LC cell was increased above 85 °C (the T_{NI} transition temperature of NLC medium) and maintained for 12 h, and then decreased to 30 °C. Without the photo-polymerization of diacetylene groups, the homeotropic alignment is only achieved again by a slow cooling rate (1.0 °C min^{-1}), as demonstrated in Figure S11 in the Supporting Information. However, the formation of homeotropic alignment layer in the photo-polymerized ADMA$_1$ LC cell is independent of the cooling rate (Figure S14 in the Supporting Information). As shown in Figure 5, the photo-polymerized ADMA$_1$ alignment layer is robustly retained without any destruction of LC orientation. The combined results indicate that the once-formed cross-linked structure of photo-polymerized ADMA$_1$ film is stable enough to overcome strong thermal fluctuations.

In summary, a dual photo-functionalized amphiphilic supramolecule (ADMA$_1$) containing both azobenzene and diacetylene moieties was specifically designed and synthesized for a reversible liquid crystal (LC) alignment layer without the use

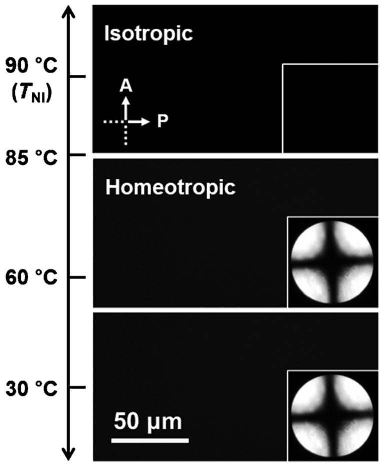

Figure 5. POM images of the 0.1 wt% $ADMA_1$ homeotropic LC cell at various temperatures from 30 to 90 °C during both heating and cooling cycles. The inset images of orthoscopic POM are their corresponding conoscopic POM images.

of the conventional polymer-based LC alignment process. In the LC cell with 0.1 wt% $ADMA_1$, $ADMA_1$ gradually diffused onto the substrate of LC cell and formed monolayered $ADMA_1$ protrusions by lateral self-assembly. The subsequent photopolymerization of the self-assembled $ADMA_1$ monolayer allowed us to fabricate a robust photo-reversible LC alignment layer.

Acknowledgements

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Keywords: amphiphiles · azobenzene · diacetylene · liquid crystal alignment · photochemistry

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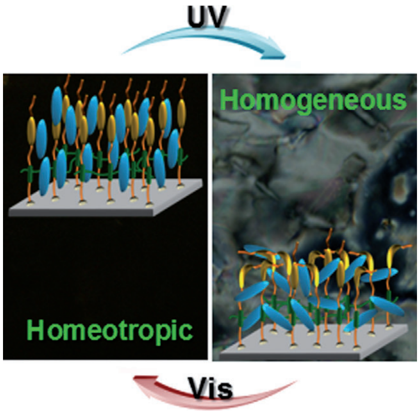
Photo-opportunity: Without the conventional polymer-based liquid crystal (LC) alignment process, a newly synthesized dual photo-functionalized amphiphile was successfully applied as a robust photo-reversible LC alignment layer by self-assembly and photo-polymerization (see figure).



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