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Supporting Information

In Situ Planar Photoalignment of Liquid Crystals: Two-Step Interfacial Modifications through Light-Matter Interactions Actuated by Linearly Polarized UV-Light

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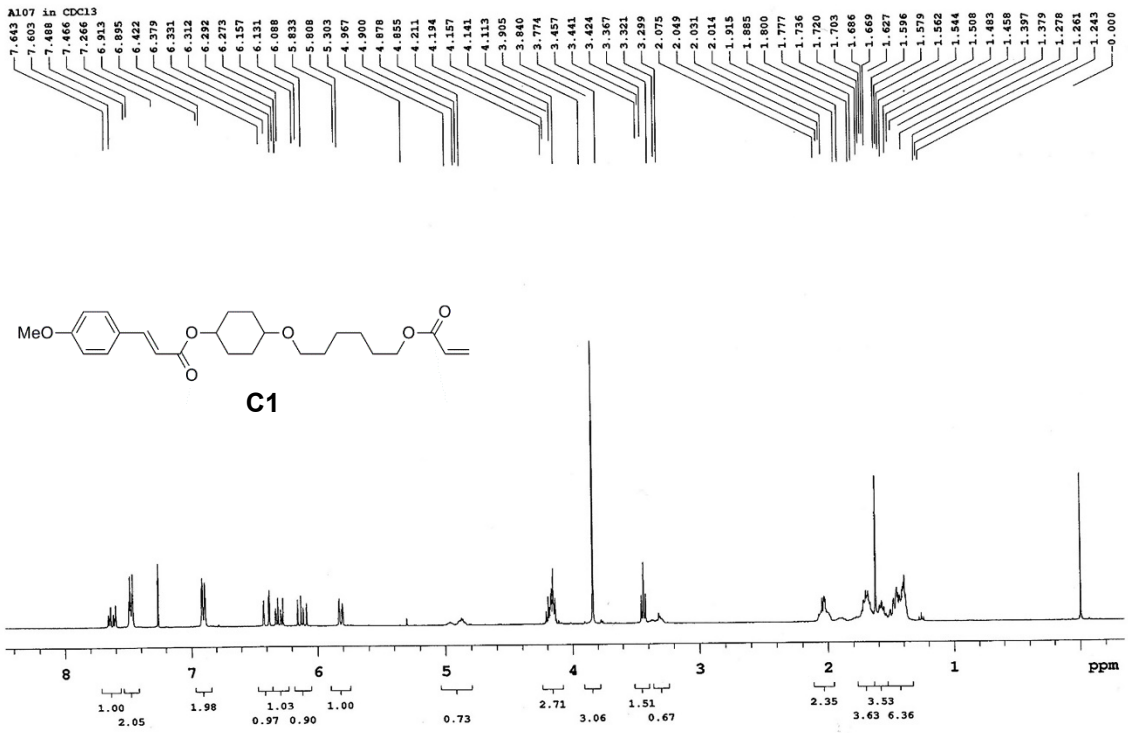
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MeO
C1
8 7 6 5 4 3 2 1 ppm
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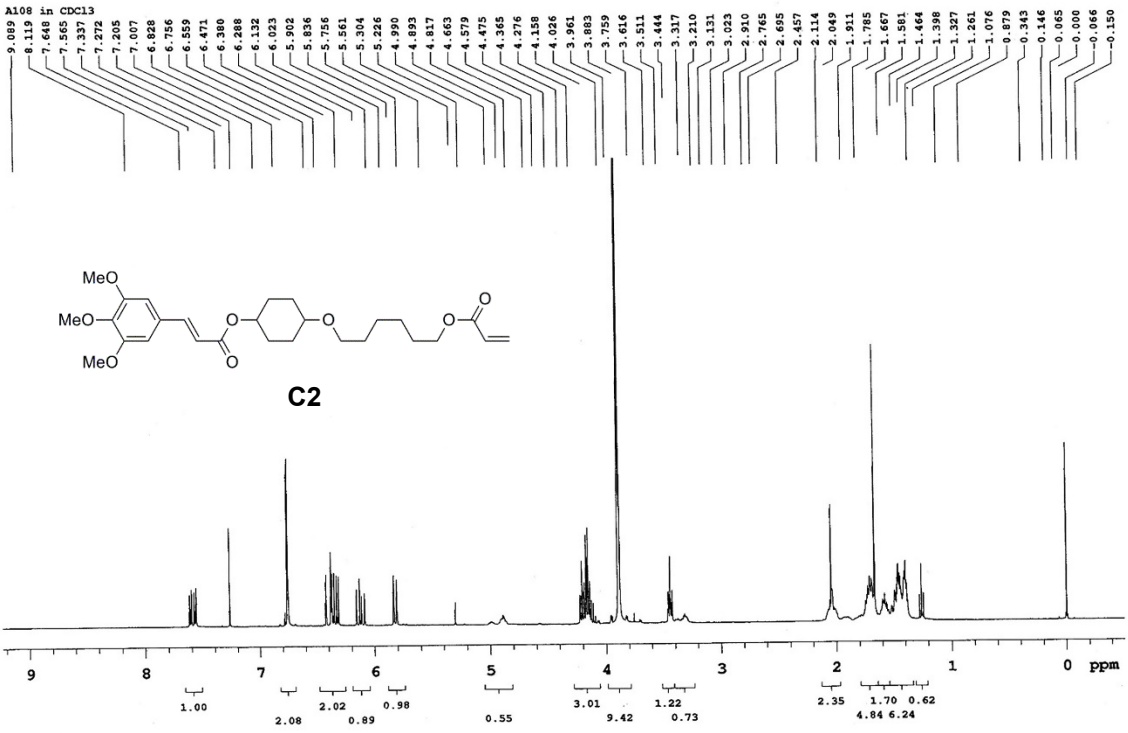
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MeO
MeO
MeO
C2
9 8 7 6 5 4 3 2 1 0 ppm
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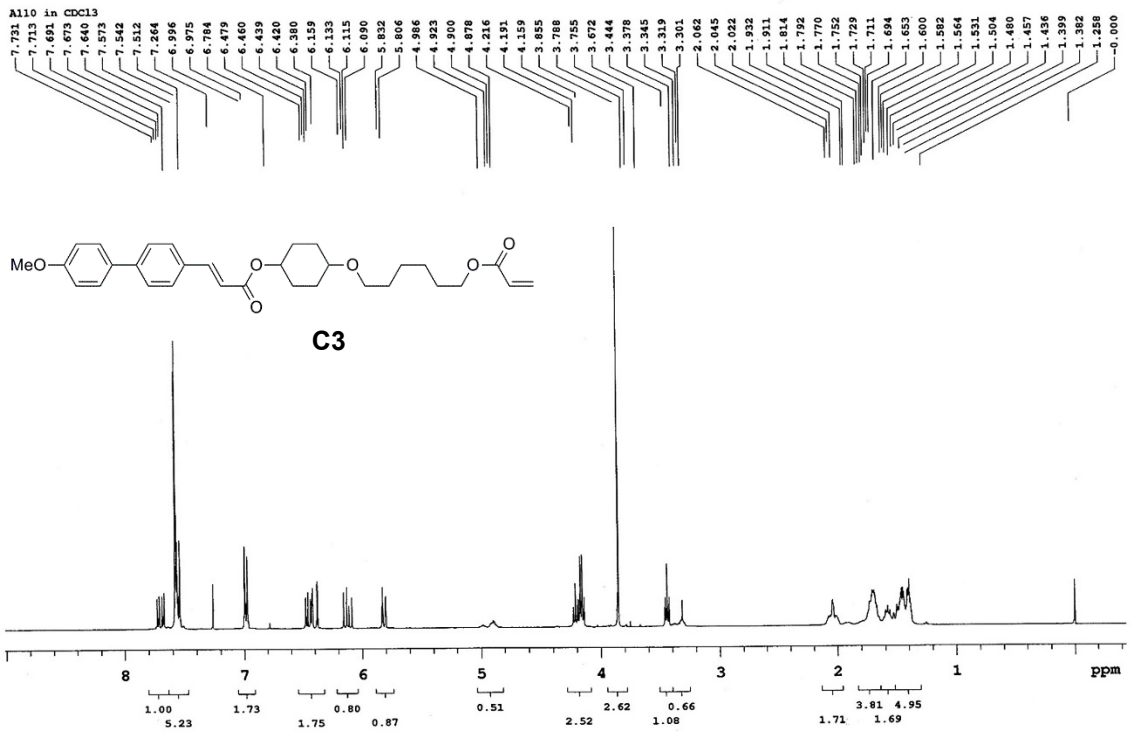

Fig. S1. ^{1}H NMR spectra of the **C1**, **C2**, and **C3** compounds.

C1 compound:

^{1}HNMR(400 MHz, $CDCl_3$, δ): 7.64 (1H, d, J= 15.8 cinnamate ArCH), 7.46 (m, 2H, Ar), 6.91 (m, 2H, Ar), 6.42 (m, 1H, cinnamate =CH), 6.33 (1H, m, acylate =CH), 6.15 (m, 1H, acylate =CH), 5.83 (m,1H, acrylate=CH), 4.90 (m, 1H, Cyclo OCH) 4.15 (m, 3H, acrylate OCH2 + Cyclo OCH), 3.9 (s, 3H, $ArOCH_3$), 3.44 (1H, m, (cyclo OCH)), 3.301 (1H, t, J = 7.1, (cyclo OCH_2)), 2.03 -1.45 (m, 16H, cyclohexane + alkyl chain)

C2 compound:

^{1}HNMR(400 MHz, $CDCl_3$, δ): 7.61 (1H, d, J = 15.7, cinnamate ArCH), 6.75 (2H, m, Ar), 6.55-6.28 (2H, m, =CH, acrylate + cynnamate), 6.15-6.13 (1H, m, acrylate COOCH=), 5.83 (1H, m, =CH(acrylate)), 4.89 (1H, m, (Cyclo OCH)), 4.2 (m, 3H, acrylate OCH_2 + Cyclo OCH), 3.88 (s, 9H, $Ar(OCH_3)_3$), 3.44 (1H, m, (cyclo OCH)), 3.301 (1H, t, J = 7.2, (cyclo OCH_2)) 3.44-3.31 (m, 2H,OCH_2), 2.11-1.2 (m, 16H, cyclohexane + alkyl chain)

C3 compound:

^{1}HNMR(400 MHz, $CDCl_3$, δ): 7.69 (1H, d, J= 16.2 Hz, (cinnamate)ArCH=), 7.57-7.51 (6H, m, Ar), 6.98 (m, Ar, 2H,), 6.48-6.42 (1H, m ArCH=CH (cinnamate)) 6.38 (1H, m, =CH(acrylate)), 6.13 (1H, m, (acrylate)COOCH=), 5.83 (1H, m, =CH(acrylate)), 4.90 (1H, m, (cyclo OCH)) 4.21 (m, 3H, acrylate OCH_2 + Cyclo OCH), 3.85 (s, 3H, $ArOCH_3$), 3.44 (1H, m, (cyclo OCH)), 3.301 (1H, t, J = 7.2, (cyclo OCH_2)), 2.04 -1.4 (m, 16H, cyclohexane + alkyl chain)

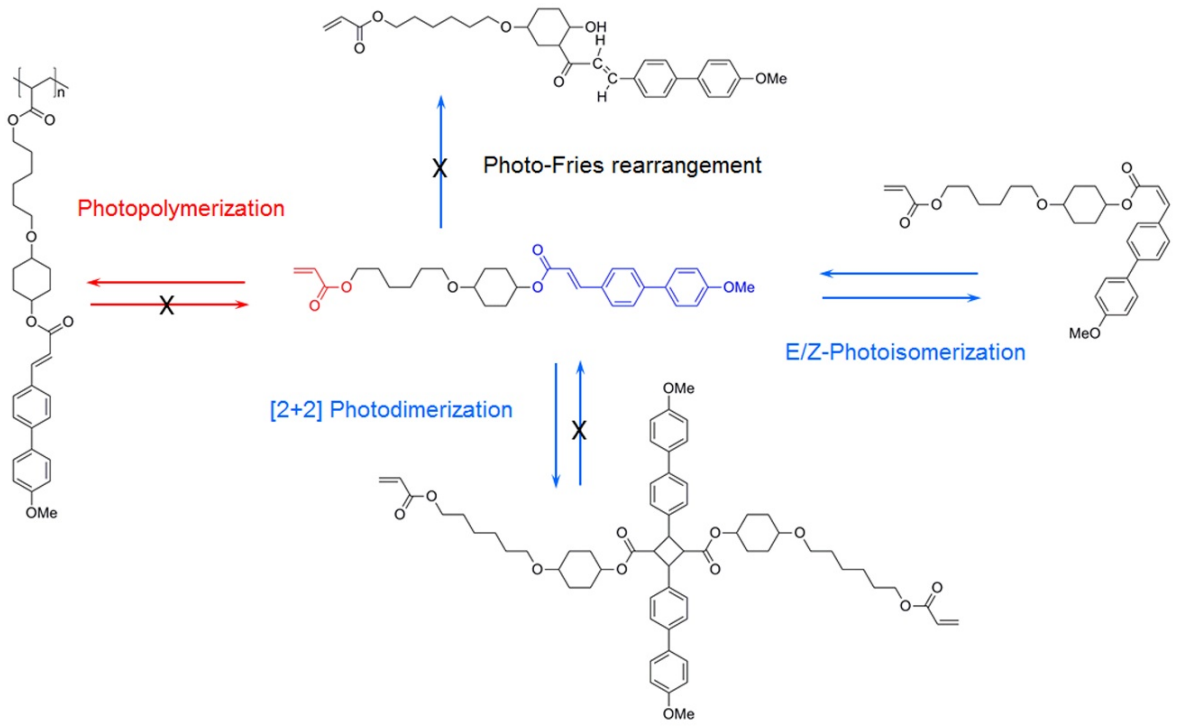

Fig. S2. The different types of photochemical reactions, possible for the **C3** model compound; irreversible photopolymerization of acryl group (in red), reversible E/Z-photoisomerization (in blue), and irreversible [2+2] photodimerization (in blue). The Photo-Fries rearrangement is not expected because of an absence of aromatic group in the hexylene position.

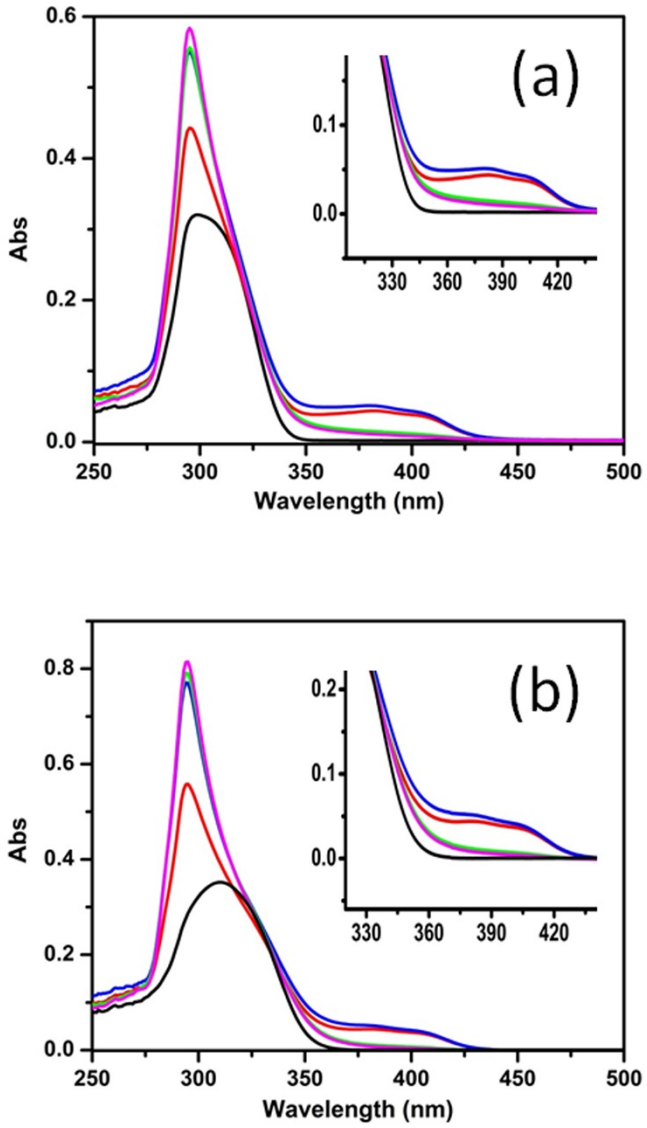

Fig. S3. The spectral changes in UV-vis absorption of the **C1** and **C2** chromophores after varied UV irradiations. The 0.01 mM solutions in toluene, contained in a quartz cuvette, were exposed to UV lights with different wavelength. The **C1** monomer solution: (a) Fresh (black), 3.0 J cm^{-2} (red), 6.0 J cm^{-2} (blue) of unfiltered UV light, and 6.0 J cm^{-2} (green), 18.0 J cm^{-2} (pink) of the additional filtered light with the long-pass filter (λ > 350 nm). The **C2** monomer solution: (a) Fresh (black), 3.0 J cm^{-2} (red), 6.0 J cm^{-2} (blue) of unfiltered UV light, and 6.0 J cm^{-2} (green), 18.0 J cm^{-2} (pink) of the additional filtered light with the long-pass filter (λ > 350 nm).

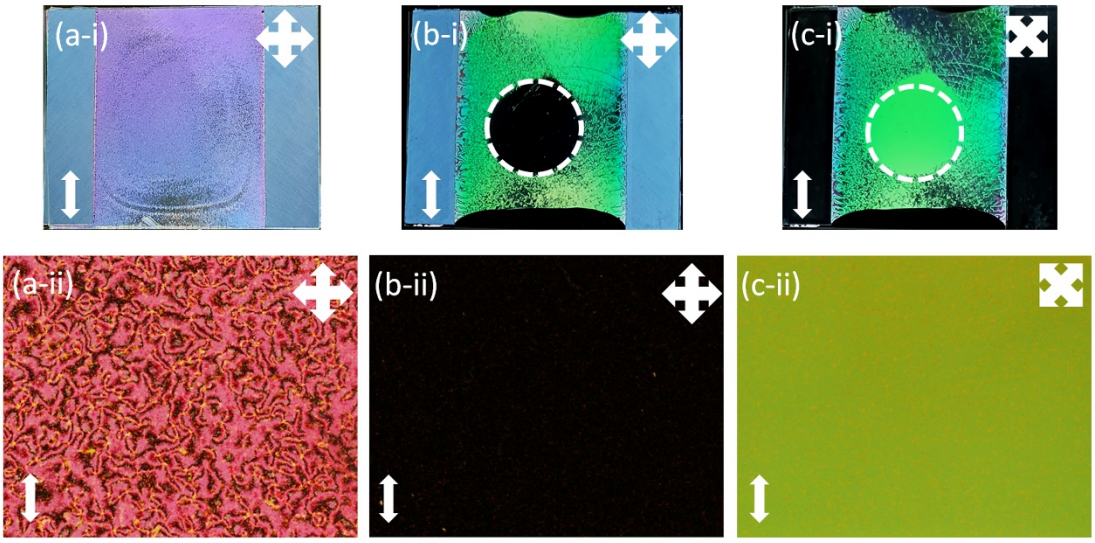

Fig. S4. Macroscopic and microscopic polarized optical images of the LC cells, prepared using the **C1** monomer. (a-i)/(a-ii) before LPUV treatment, (b-i)/(b-ii) and (c-i)/(c-ii) after 3.6 J cm^{-2} LPUV treatment, respectively. The exposed area was marked by the dotted circle.The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections.

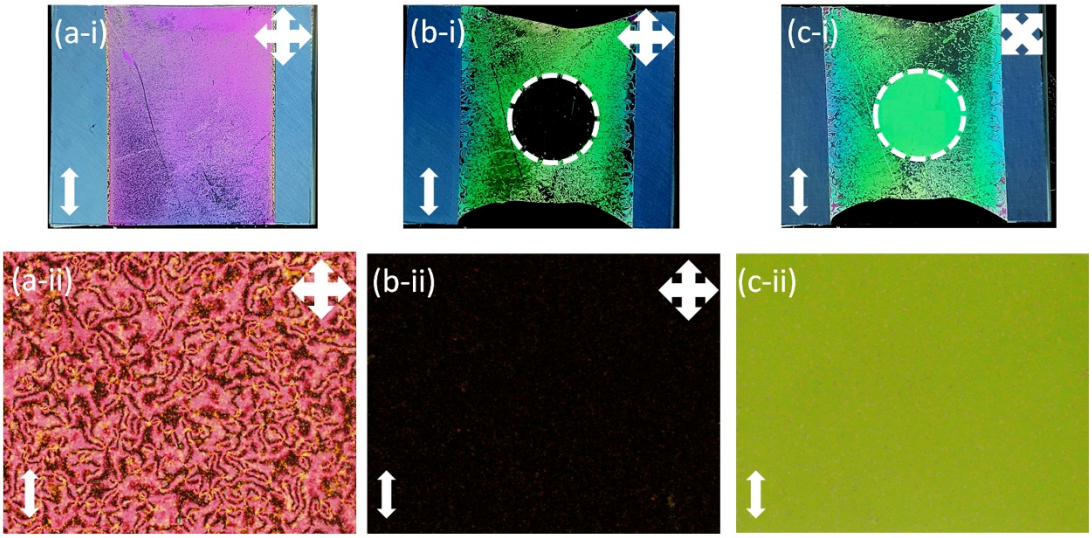

Fig. S5. Macroscopic and microscopic polarized optical images of the LC cells, prepared using the **C2** monomer. (a-i)/(a-ii) before LPUV treatment, (b-i)/(b-ii) and (c-i)/(c-ii) after 3.6 J cm^{-2} LPUV treatment, respectively. The exposed area was marked by the dotted circle. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections.

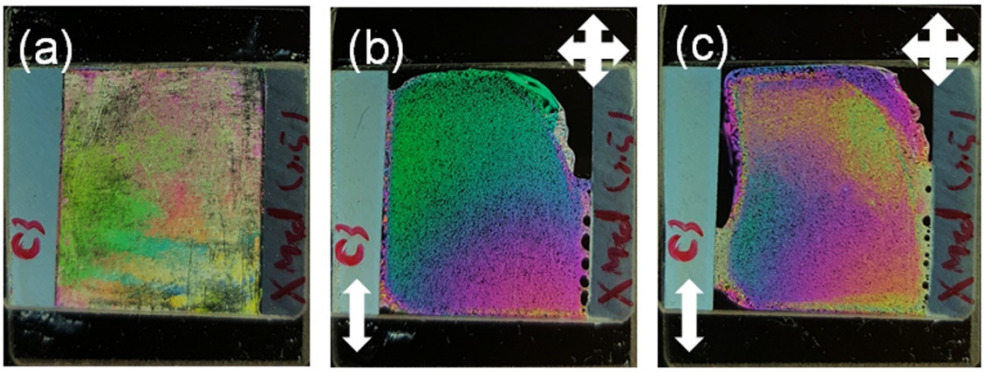

Fig. S6. Macroscopic polarized optical images of the LC cell with quartz substrates, prepared using the **C3** monomer. (a) Before LPUV treatment, (b) after 3.6 J cm^{-2} LPUV with no filter, and (c) after an additional 3.6 J cm^{-2} LPUV treatment with an ITO-glass filter. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections.

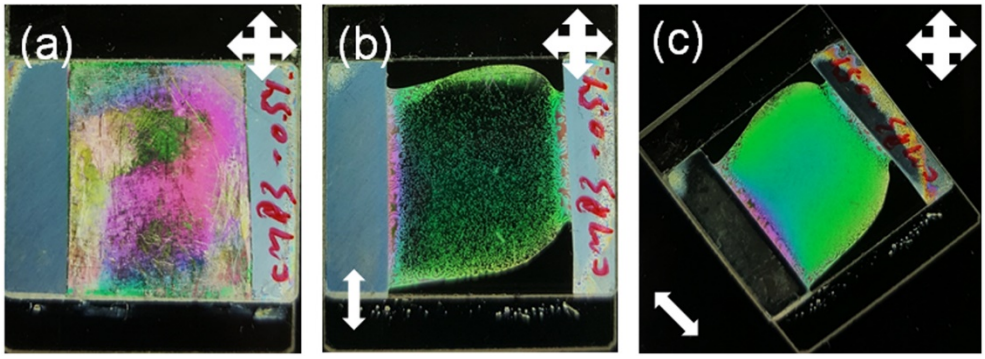

Fig. S7. Macroscopic polarized optical images of the LC cell with quartz substrates, prepared using the **C3** monomer. (a) Before LPUV treatment and (b)/(c) after 3.6 J cm^{-2} LPUV with the 308 nm filter, with different orientation to the crossed polarizers. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections.

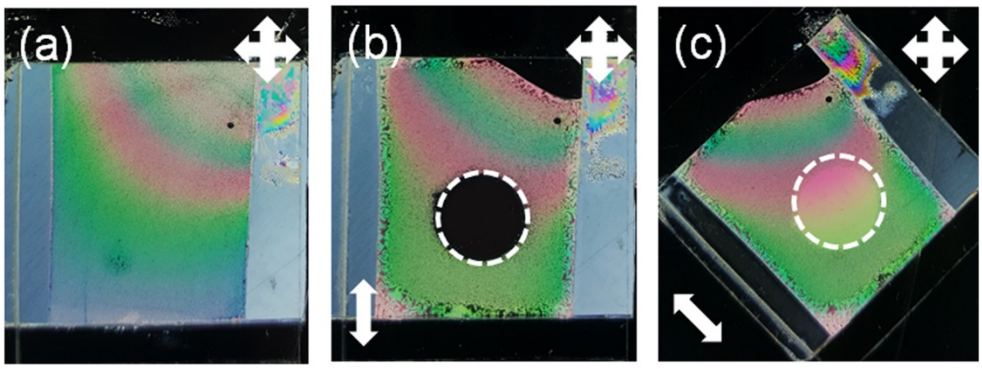

Fig. S8. Macroscopic polarized optical images of the LC cell with quartz substrates, prepared using the **C3** monomer. (a) Before LPUV treatment and (b)/(c) after 3.6 J cm^{-2} LPUV with the ITO-glass filter, with different orientation to the crossed polarizers. The exposed area was marked by the dotted circle. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections.

Fig. S9. Macroscopic polarized optical images of the LC cell with quartz substrates, prepared using the **C3** monomer. (a) Before LPUV treatment and (b)/(c) after 3.6 J cm^{-2} LPUV with the long-pass filter (λ > 350 nm), with different orientation to the crossed polarizers. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections.

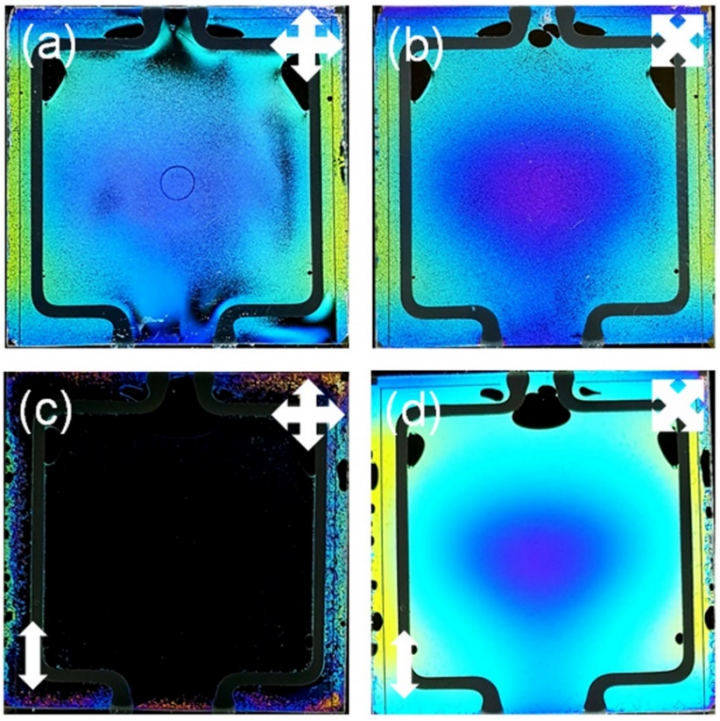

Fig. S10. Macroscopic polarized optical images of the LC cell with glass substrates, prepared using the **C3** monomer and employed for multistep UV treatments. (a)/(b) After UPUV treatment (3.6 J cm^{-2}) and (c)/(d) after the 1st LPUV treatment (3.6 J cm^{-2}). No filter was used for UPUV and LPUV treatments. Each set of images represent maximum dark and light states after the corresponding UV treatments. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The circle near the center area in (a) is an artifact, originated from the substrate. The corresponding microscopic images were shown in Figure 6.

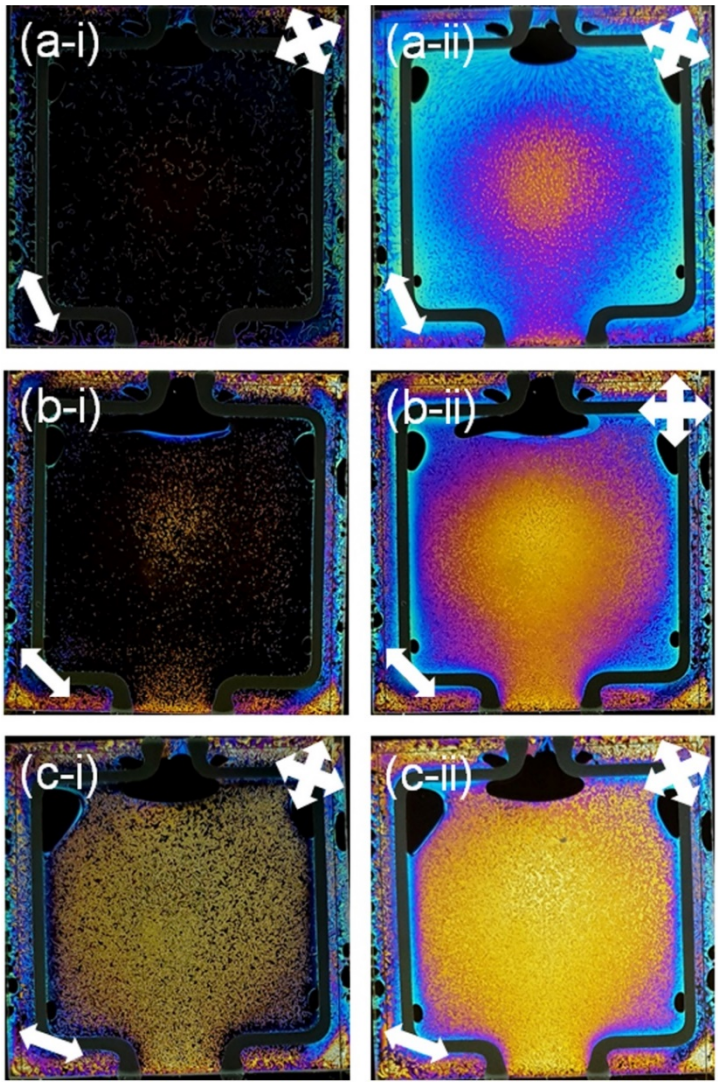

Fig. S11. Macroscopic polarized optical images of the LC cell with glass substrates, fabricated using the **C3** monomer and employed for multistep UV treatments. (a-i)/(a-ii) After the 2nd LPUV treatment (3.6 J cm^{-2}), (b-i)/(b-ii) after the 3rd LPUV treatment (3.6 J cm^{-2}), and after the 4th LPUV treatment (3.6 J cm^{-2}). As indicated by the single arrow, for an accumulative multistep UV irradiation, the polarization direction of an LPUV was rotated by 25°, 45°, and 70° from the first LPUV (Figure S10). Each set of images represent maximum dark and light states after the corresponding LPUV treatments. No filter was used for an LPUV treatment. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The corresponding microscopic images were shown in Figure 6.

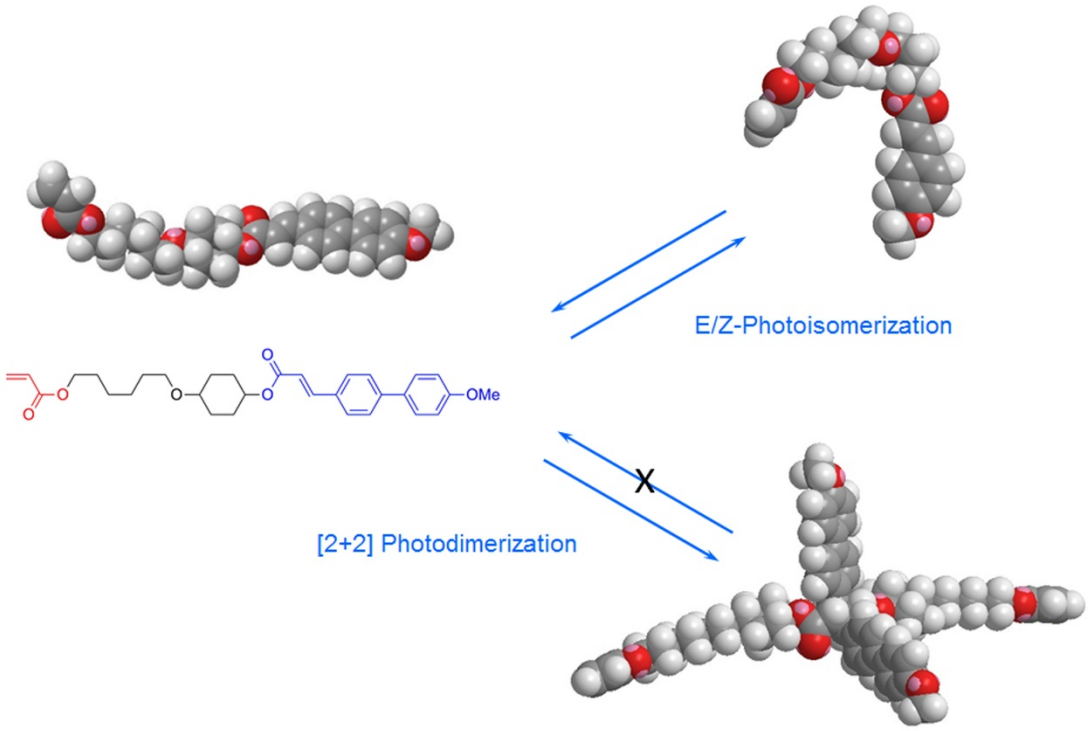

Fig. S12. Molecular models of the *trans*-form monomer, *cis*-form monomer, and dimer of the **C3** chromophore, formed through the reversible E/Z-photoisomerization and the irreversible [2+2] photodimerization.

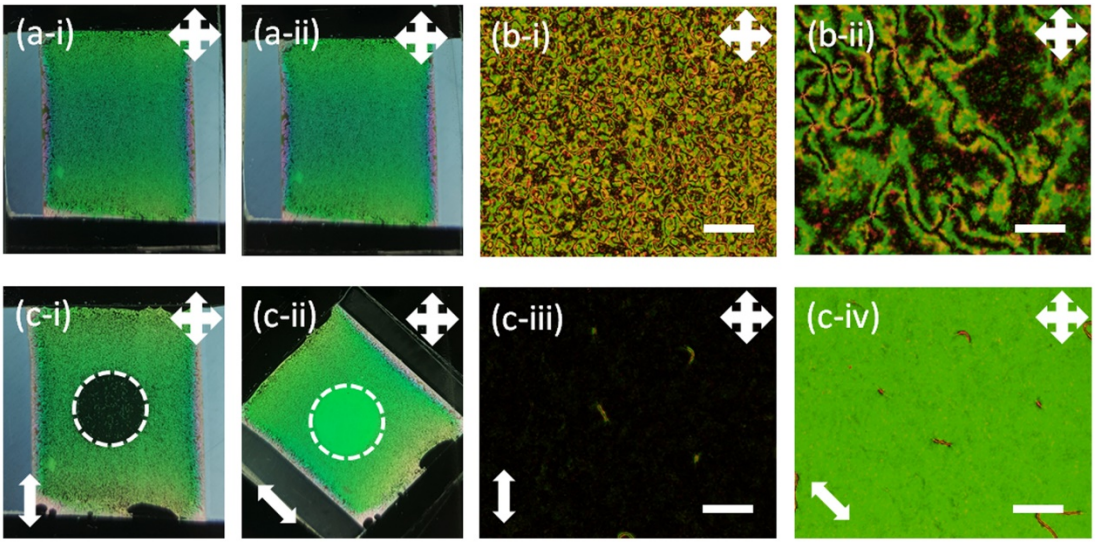

Fig. S13. Polarized optical images of the LC cell with ITO-glass substrates, fabricated using the **C3** monomer and employed for multistep UV treatments. (a-i)/(b-i) Before and (a-ii)/(b-ii) after the UPUV treatment (3.6 J cm^{-2}), (c-i)/(c-iii) dark and (c-ii)/(c-iv) light states after the 1st LPUV treatment (3.6 J cm^{-2}). No filter was used for an LPUV treatment. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The scale bars correspond to 200 μm.

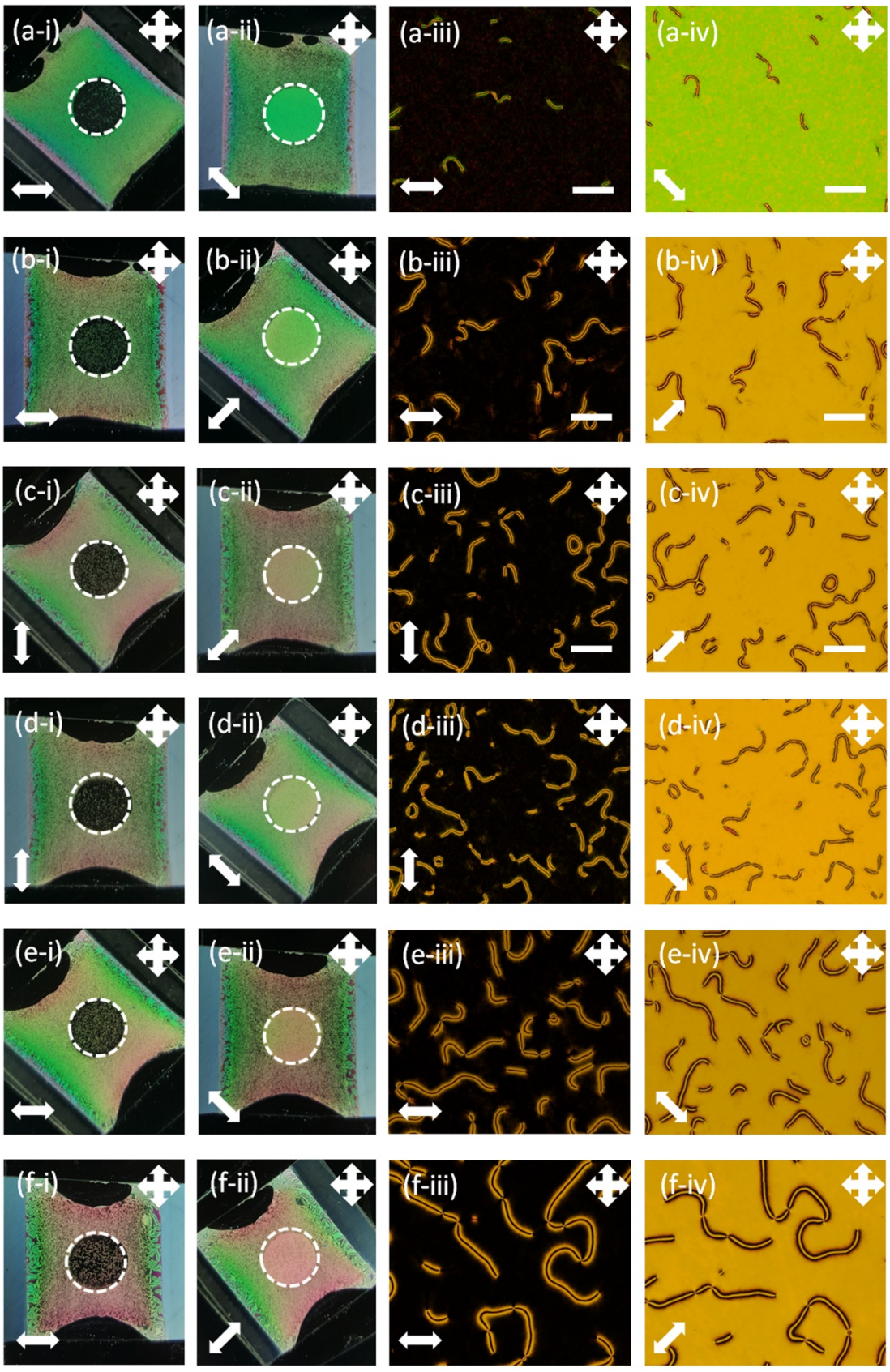
(a-i)
(a-ii)
(a-iii)
(a-iv)
(b-i)
(b-ii)
(b-iii)
(b-iv)
(c-i)
(c-ii)
(c-iii)
(c-iv)
(d-i)
(d-ii)
(d-iii)
(d-iv)
(e-i)
(e-ii)
(e-iii)
(e-iv)
(f-i)
(f-ii)
(f-iii)
(f-iv)

Fig. S14. Polarized optical images of the LC cell with ITO-glass substrates, fabricated using the **C3** monomer and employed for multistep UV treatments. (a-i) − (a-iv) After the 3rd LPUV treatment (3.6 J cm^{-2}), (b-i) − (b-iv) after the 4th LPUV treatment (3.6 J cm^{-2}), (c-i) − (c-iv) after the 5th LPUV treatment (3.6 J cm^{-2}), (d-i) − (d-iv) after the 6th LPUV treatment (3.6 J cm^{-2}), (e-i) − (e-iv) after the 7th LPUV treatment (3.6 J cm^{-2}), and (f-i) − (f-iv) after the 8th LPUV treatment (3.6 J cm^{-2}). The exposed area was marked by the dotted circle.

As indicated by the single arrow, for an accumulative multistep UV irradiation, the polarization direction of an LPUV was rotated by 45°, 90°, 135°, 180°, 225°, and 270° from the first LPUV. Each set of images represent maximum dark and light states after the corresponding LPUV treatments. No filter was used for an LPUV treatment. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The scale bars correspond to 200 μm.

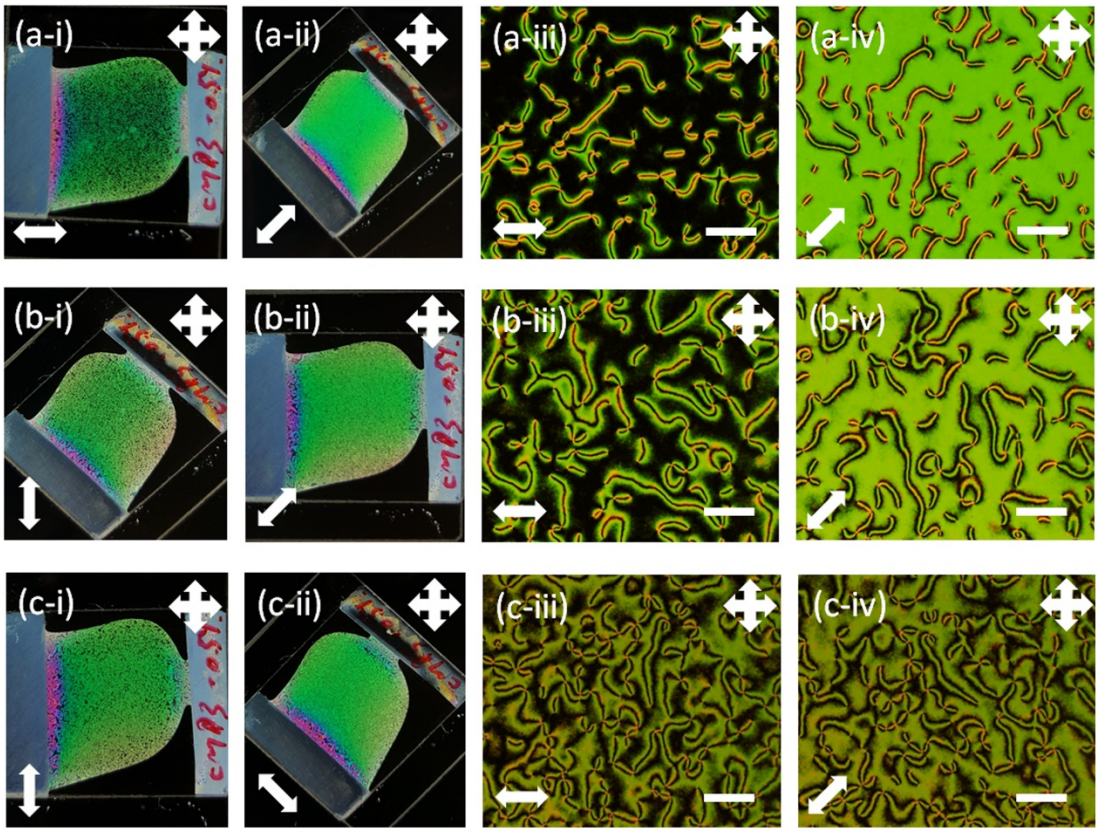

Fig. S15. Polarized optical images of the LC cell with quartz substrates, fabricated using the **C3** monomer and employed for multistep UV treatments with the 308 nm bandpass filter.

(a-i) – (a-iv) After the 3rd LPUV treatment (3.6 J cm^{-2}), (b-i) – (b-iv) after the 4th LPUV treatment (3.6 J cm^{-2}), and (c-i) – (c-iv) after the 5th LPUV treatment (3.6 J cm^{-2}).

As indicated by the single arrow, for an accumulative multistep UV irradiation, the polarization direction of an LPUV was rotated by 90°, 135°, and 180° from the first LPUV. Each set of images represent maximum dark and light states after the corresponding LPUV treatments. The 308 nm filter was used for an LPUV treatment. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The scale bars correspond to 200 μm.

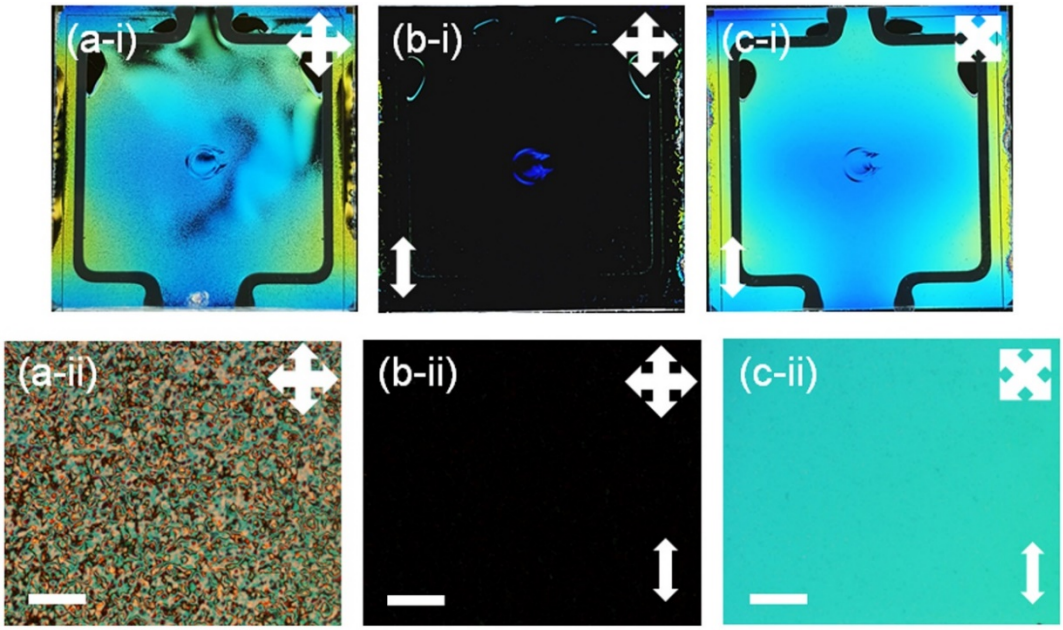

Fig. S16. Polarized optical images of the LC cell with glass substrates, fabricated using the **C3** monomer and employed for multistep UV treatments with the 350 nm long-pass filter. (a-i)/(a-ii) Before UV treatment, (b-i)/(b-ii) dark and (c-i)/(c-ii) light states after the 1st LPUV treatment (3.6 J cm^{-2}). The circular mark near the center area is an artifact, originated from the substrate. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The scale bars correspond to 200 μm.

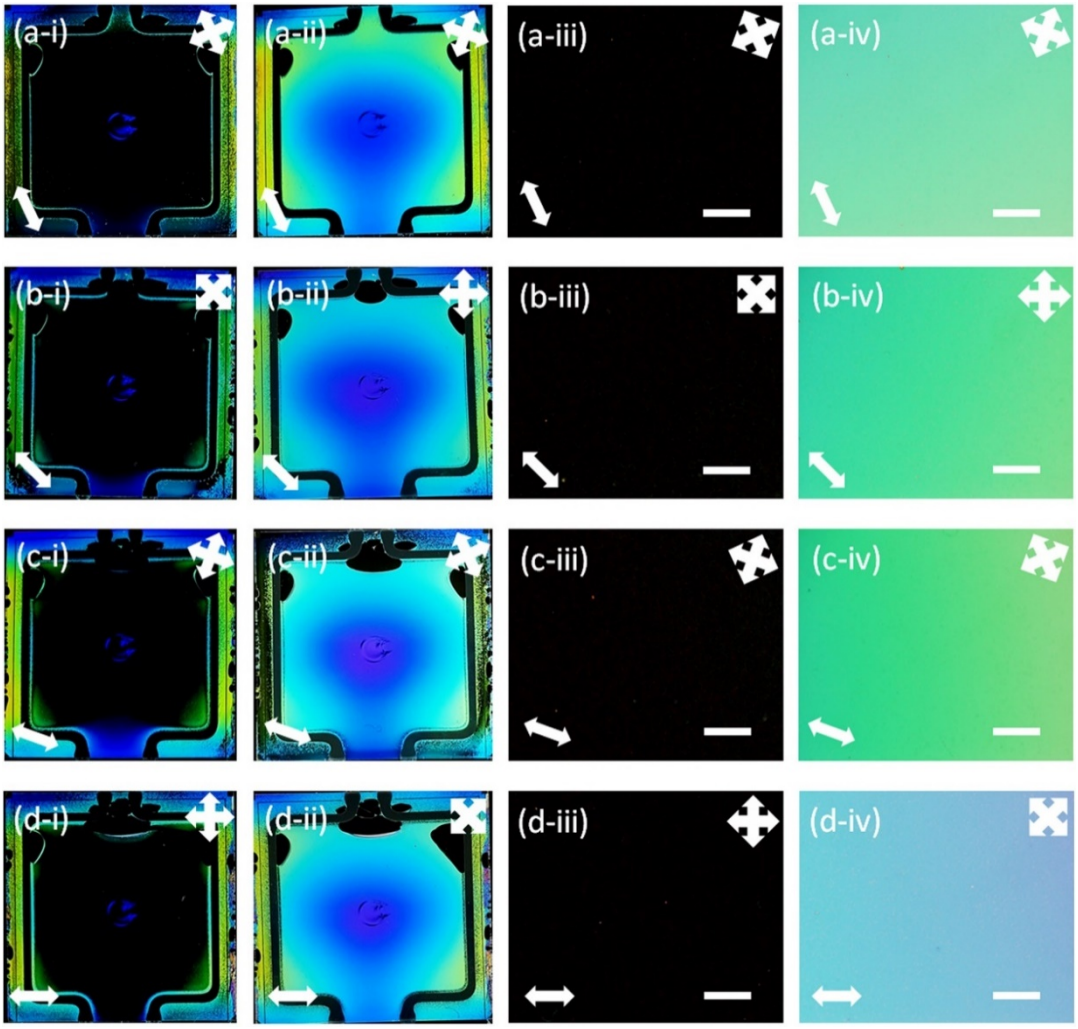

Fig. S17. Polarized optical images of the LC cell with glass substrates, fabricated using the **C3** monomer and employed for multistep UV treatments with the 308 nm bandpass filter.

(a-i) – (a-iv) After the 2nd LPUV treatment (3.6 J cm^{-2}), (b-i) – (b-iv) after the 3rd LPUV treatment (3.6 J cm^{-2}), (c-i) – (c-iv) after the 4th LPUV treatment (3.6 J cm^{-2}), and (d-i) – (d-iv) after the 5th LPUV treatment (3.6 J cm^{-2}).

As indicated by the single arrow, for an accumulative multistep UV irradiation, the polarization direction of an LPUV was rotated by 25°, 45°, 70°, and 90° from the first LPUV. Each set of images represent maximum dark and light states after the corresponding LPUV treatments. The circular mark near the center area is an artifact, originated from the substrate. The 350 nm long-pass filter (λ > 350 nm) was used for an LPUV treatment. The single arrow denotes a polarization direction of the LPUV. The crossed arrows represent crossed polarizers used for inspections. The scale bars correspond to 200 μm.

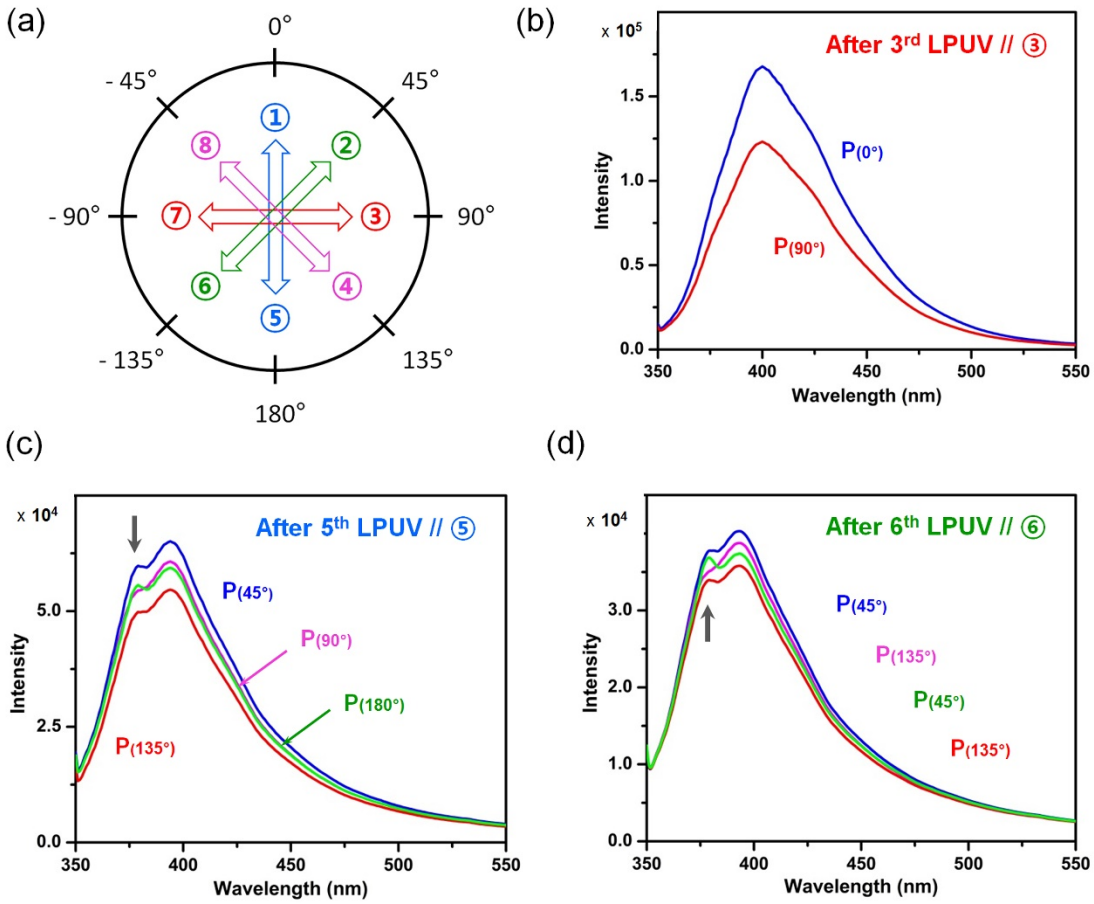

Fig. S18. The polarized fluorescence spectra, measured after a consecutive rewriting process. (a) The schema for consecutive measurements. The colored numbers and arrows designate the order and the polarization direction of LPUV, respectively. (b) The PFS data measured after the 3rd writing (the LPUV along the red arrow in (a)). The long-pass filter was used for UV treatment. The red and blue spectra correspond to the polarizer direction for an inspection at 0° and 90° in (a). The PFS data measured after (c) the 5th and 6th LPUV treatments with the ITO-glass filter (3.6 J cm^{-2}, the LPUV along the blue and green arrows in (a), respectively). The measured polarized fluorescence at different orientations were presented by different colors together with the corresponding orientations.

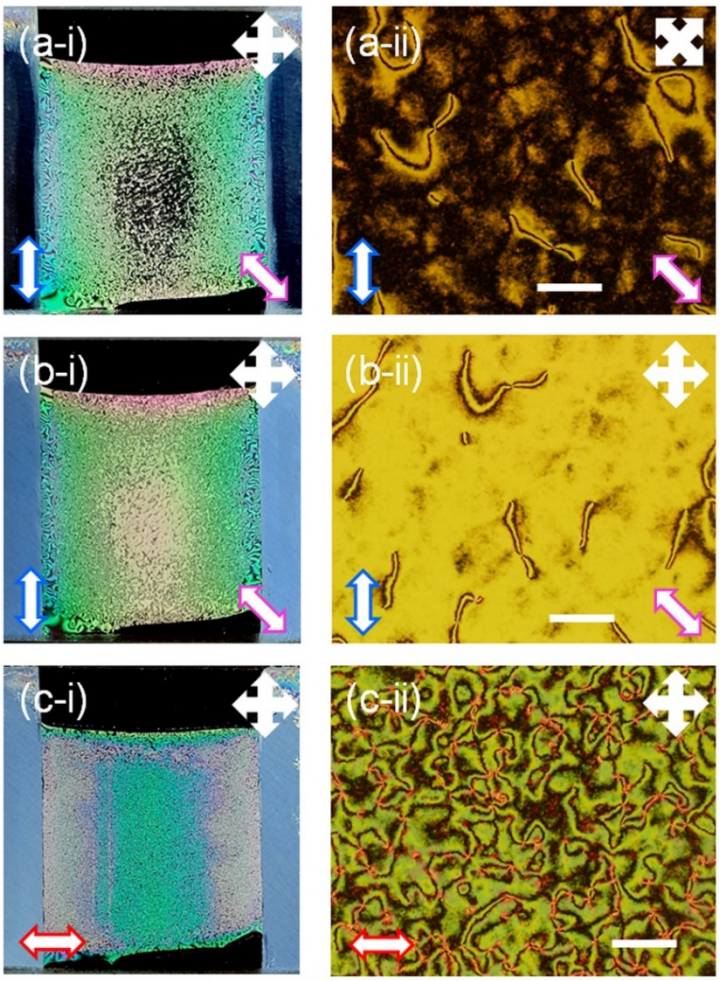

Fig. S19. Polarized optical images of the LC cell with quartz substrates, fabricated using the **C3** monomer and employed for multistep UV treatments. (a-i)/(a-ii) The dark and (b-i)/(b-ii) light states after the 5th LPUV treatment (3.6 J cm^{-2}) with the ITO-glass filter, and (c-i)/(c-ii) after the 7th LPUV treatment (3.6 J cm^{-2}) with no filter. For an accumulative multistep UV irradiation, the polarization directions of an LPUV were represented by the pink (4th LPUV, 135°), blue (5th LPUV, 180°), and red (7th LPUV, -90°) arrows. Each set of images represent maximum dark and light states after the corresponding LPUV treatments. The corresponding LC cell images before and the 1st LPUV treatment were shown in Figure 4d and Figure S8. The 1st ~ 3rd LPUVs (3.6 J cm^{-2}) were treated with the 350 nm long-pass filter (λ > 350 nm) and the 4th ~ 6th LPUVs (3.6 J cm^{-2}) were treated with the ITO-glass filter. The 7th LPUV treatment (3.6 J cm^{-2}) was completed without using any filter. The crossed arrows represent crossed polarizers used for inspections. The scale bars correspond to 200 μm.