

## Electronic Supplementary Information

### Photo-induced guest-host interactions produce grain boundaries between smectic blocks

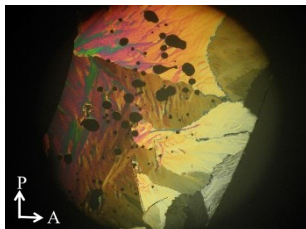
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1. Fig. S1 Effects of repetition of the UV on-off cycle on the photo-induced transition for trimer **I** at  $T - T_{\text{Iso-Cry1}} = -1.5$  K. The sample on a glass slide with a cover glass was irradiated with 365 nm UV irradiation at a power of  $10 \text{ mW cm}^{-2}$ .
2. Fig. S2 UV-vis spectra of trimer **I** in a chloroform solution ( $2.5 \times 10^{-5} \text{ M}$ ) under UV light with a wave length of 365 nm as a function of irradiation intensity. After the sample was exposed to UV light at room temperature for 10 s, UV-vis spectra were recorded.
3. Fig. S3 Optical texture of: (a) a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%) on a glass slide with a cover glass on cooling at a rate of  $5 \text{ }^{\circ}\text{C min}^{-1}$  in the N phase at  $156.5 \text{ }^{\circ}\text{C}$ , (b) in the coexistence of the N and X phases at  $88.8 \text{ }^{\circ}\text{C}$ , (c) in the coexistence of the SmC and Y phases at  $67.3 \text{ }^{\circ}\text{C}$  and (d) in the Cry phase at  $40.2 \text{ }^{\circ}\text{C}$ .
4. Fig. S4 Optical textures of a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%) in a homogeneously aligned cell on the cooling phase transition.
5. Fig. S5 Optical textures during the formation of grain boundaries for a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%). The sample on a glass plate with a cover glass was irradiated with 365 nm UV at a power of  $20 \text{ mW cm}^{-2}$  on cooling at a rate of  $5 \text{ }^{\circ}\text{C min}^{-1}$ . (a) Spherical nuclei of the SmC phase were formed in the N phase. (b) They spread radially to collapse with each other. (c) The N-SmC phase transition was completed. (d) Collision regions became blight.

6. Fig. S6 (a) Optical texture of a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%) in a 5  $\mu\text{m}$  homogeneously aligned cell at 61.9  $^{\circ}\text{C}$ ; (b) expansion of (a). The sample was cooled with 365 nm UV irradiation at a power of 20  $\text{mW cm}^{-2}$  from the isotropic liquid. After the spherical nuclei began to form in the N phase, the UV light was turned off.

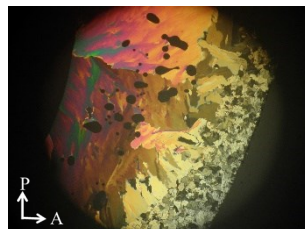
Before UV irradiation



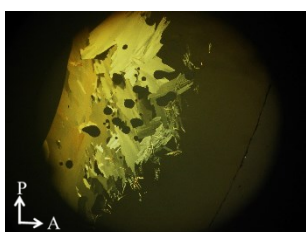
1<sup>st</sup> UV on



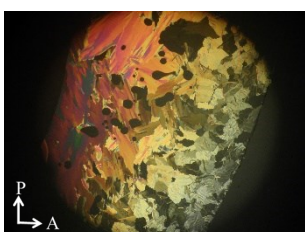
UV off



2<sup>nd</sup> UV on



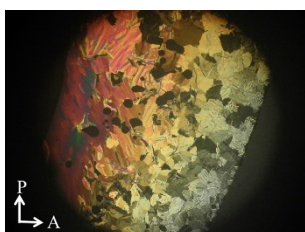
UV off



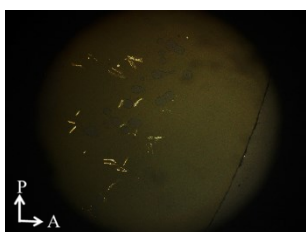
3<sup>rd</sup> UV on



UV off



4<sup>th</sup> UV on



UV off

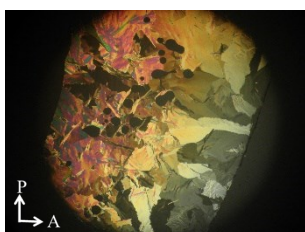


Fig. S1 Effects of repetition of the UV on-off cycle on the photo-induced transition for trimer I at  $T - T_{\text{Iso-Cry1}} = -1.5$  K. The sample on a glass slide with a cover glass was irradiated with 365 nm UV irradiation at a power irradiation  $10 \text{ mW cm}^{-2}$ .

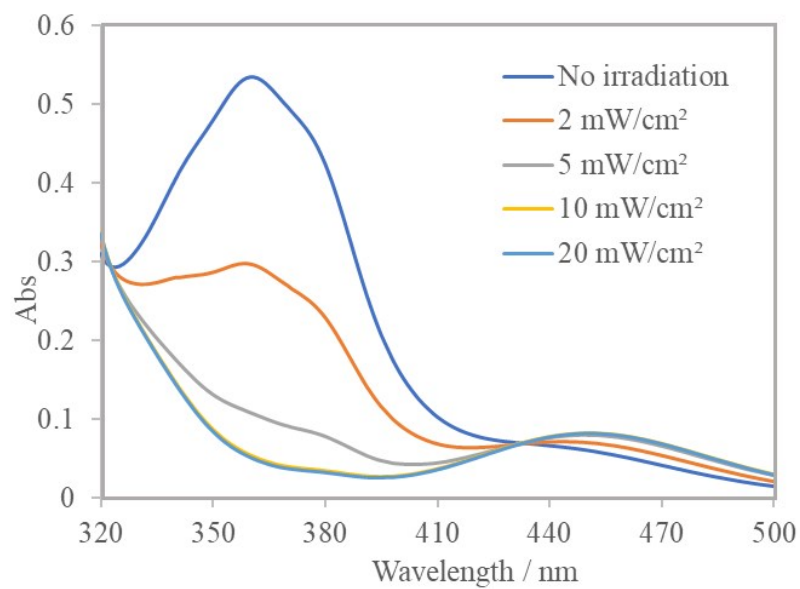
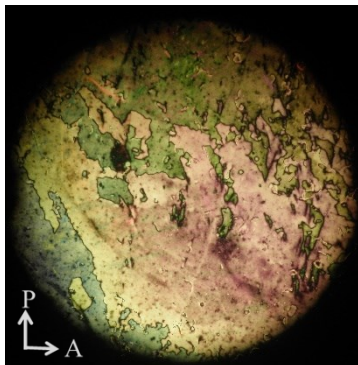


Fig. S2 UV-vis spectra of trimer **I** in a chloroform solution ( $2.5 \times 10^{-5}$  M) under UV light with a wave length of 365 nm as a function of irradiation intensity. After the sample was exposed to UV light at room temperature for 10 s, UV-vis spectra were recorded.

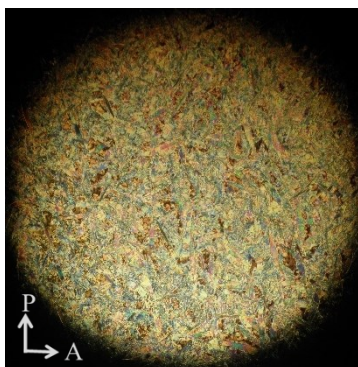
(a) N



(b) N + X



(c) SmC + Y



(d) Cry

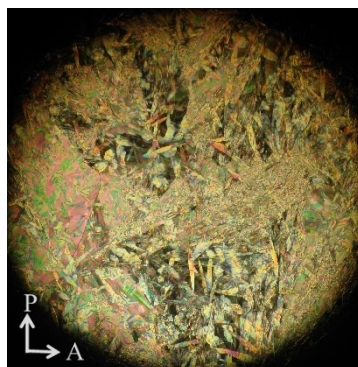


Fig. S3 Optical texture of: (a) a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%) on a glass slide with a cover glass on cooling at a rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  in the N phase at  $156.5\text{ }^{\circ}\text{C}$ , (b) in the coexistence of the N and X phases at  $88.8\text{ }^{\circ}\text{C}$ , (c) in the coexistence of the SmC and Y phases at  $67.3\text{ }^{\circ}\text{C}$  and (d) in the Cry phase at  $40.2\text{ }^{\circ}\text{C}$ .

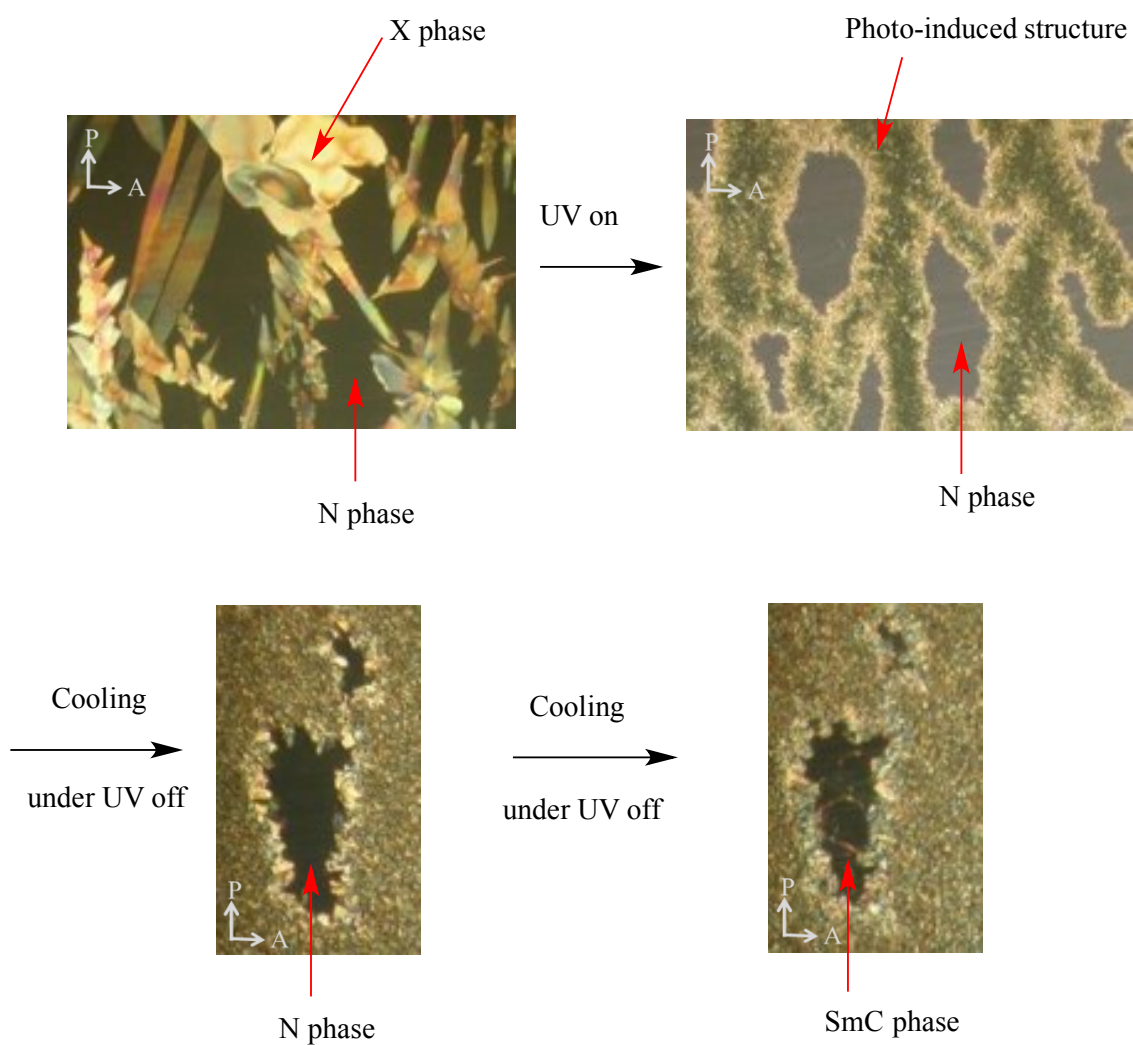


Fig. S4 Optical textures of a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%) in a homogeneously aligned cell on the cooling phase transition.



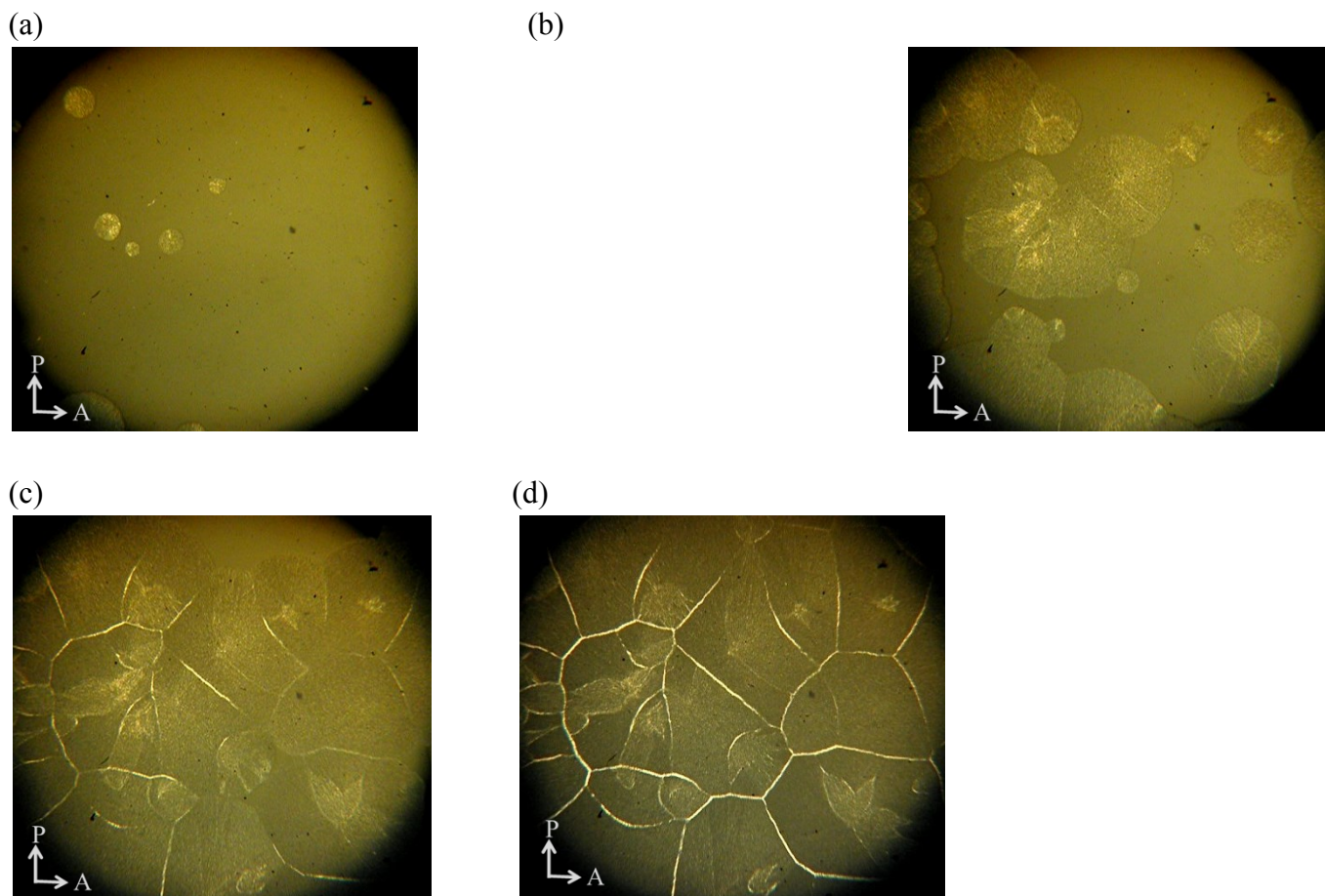


Fig. S5 Optical textures during the formation of grain boundaries for a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%). The sample on a glass plate with a cover glass was irradiated with 365 nm UV at a power of  $20 \text{ mW cm}^{-2}$  on cooling at a rate of  $5 \text{ }^{\circ}\text{C min}^{-1}$ . (a) Spherical nuclei of the SmC phase were formed in the N phase. (b) They spread radially to collapse with each other. (c) The N–SmC phase transition was completed. (d) Collision regions became blight.

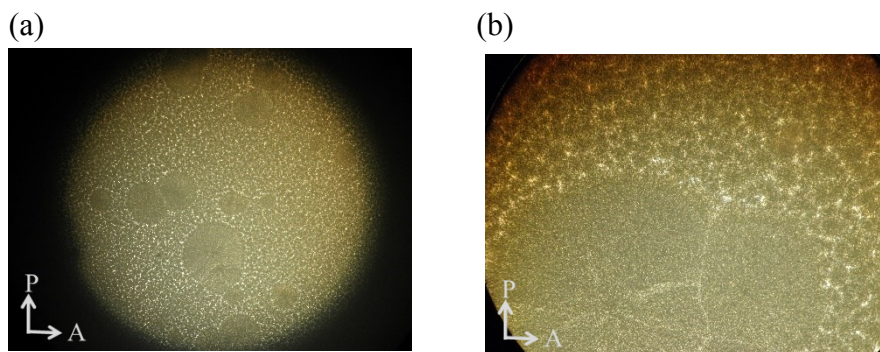


Fig. S6 (a) Optical texture of a mixture of trimer **I** (20 wt%) and compound **II** (80 wt%) in a 5  $\mu\text{m}$  homogeneously aligned cell at 61.9  $^{\circ}\text{C}$ ; (b) expansion of (a). The sample was cooled with 365 nm UV irradiation at a power of 20  $\text{mW cm}^{-2}$  from the isotropic liquid. After the spherical nuclei began to form in the N phase, the UV light was turned off.