## **Supplementary Information:**

## Photoinduced micropatterning by polymorphic crystallization of a photochromic diarylethene in a polymer film

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**Fig. S1.** Photographs during the thermodynamic phase transition between  $\alpha$ -crystal and  $\gamma$ -crystal. a, At room temperature. b, After heated for 1 min at 190 °C. c, After heated for 3 min at 190 °C. d, After heated for 5 min at 190 °C.

**Fig. S2.** ORTEP drawings of  $1a-\gamma$  showing 50% probability displacement ellipsoids. a, Top view. b, Side view. Two molecules are crystallographically independent. The fluorine atoms are disordered.

Fig. S3. Powder X-ray diffraction patterns. a, Microcrystal 1a- $\alpha$ . b, Microcrystal 1a- $\gamma$ . c, 1a/PMMA film heated for 2 min at 130 °C.

**Fig. S4.** Cross-sectional view of a part on photomicropatterning. The left and right sides in the sectional view are the amorphous and microcrystalline states, respectively.

**Fig. S5.** Optical microphotographs of photopatterning prepared under the various conditions. The white and black parts are the amorphous and micro-crystalline states, respectively. b and e are under the same condition.

Table S1. X-ray crystallographic data of 1a-γ.

**Video S1.** The movie shows the crystal growth of  $1a-\gamma$  from the transparent film of the mixture containing PMMA/1a (1:5 wt ratio). The stage was heated at 130 °C. The movie is fast-forwarded as much as 8 times.



Fig. S1. Photographs during the thermodynamic phase transition between  $\alpha$ -crystal and  $\gamma$ -crystal. a, At room temperature. b, After heated for 1 min at 190 °C. c, After heated for 3 min at 190 °C. d, After heated for 5 min at 190 °C.



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Fig. S3. Powder X-ray diffraction patterns. a, Microcrystal 1a- $\alpha$ . b, Microcrystal 1a- $\gamma$ . c, 1a/PMMA film heated for 2 min at 130 °C.



**Fig. S4.** Cross-sectional view of a part on photomicropatterning. The left and right sides in the sectional view are the amorphous and microcrystalline states, respectively.



Heated for 5 min at 130 °C after UV irradiation for 20 s.



Heated for 30 min at 110 °C after UV irradiation for 30 s.



Heated for 5 min at 130 °C after UV irradiation for 30 s.



Heated for 5 min at 130 °C after UV irradiation for 30 s.

![](_page_6_Picture_9.jpeg)

Heated for 5 min at 130 °C after UV irradiation for 1 min.

![](_page_6_Picture_11.jpeg)

Heated for 1 min at 150 °C after UV irradiation for 30 s.

**Fig. S5.** Optical microphotographs of photopatterning prepared under the various conditions. The white and black parts are the amorphous and micro-crystalline states, respectively. b and e are under the same condition.

	1a-γ
Formula	$C_{23}H_{12}F_6N_2O_4S_2$
Formula wight	558.7
Temperature	190.(2) K
Crystal system	trigonal
Space group	R3(h)
Unit cell dimensions	<i>a</i> = 32.1473(15) Å
	b = 32.1473(15) Å
	c = 11.6175(8) Å
	$\alpha = 90^{\circ}$
	$\beta = 90^{\circ}$
	$\gamma = 120^{\circ}$
Volume	10397.6(10) Å <sup>3</sup>
Ζ	18
Density	$1.605 \text{ g/cm}^3$
Goodness-of-fit on $F^2$	1.104
$R(I > 2\sigma(I))$	R1 = 0.0692
R(all date)	wR2 = 0.1208
χ	0.12(7)

**Table S1.** X-ray crystallographic data of **1a-**γ.