Supporting Information

Mechanical Behavior of Molecular Crystals Induced by Combination of Photochromic Reaction and Reversible Single-Crystal-to-Single-Crystal Phase Transition

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Figure S1. Typical photomechanical behavior of a diarylethene crystal of 1,2-bis(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene.[S1]

Figure S2. Photomechanical behavior of crystal **1a** upon visible light irradiation after UV light irradiation.
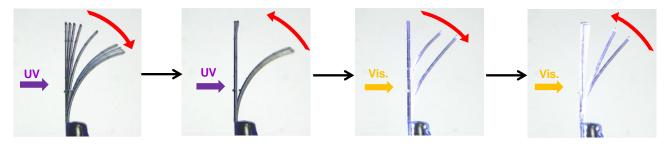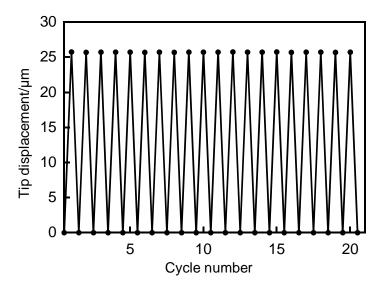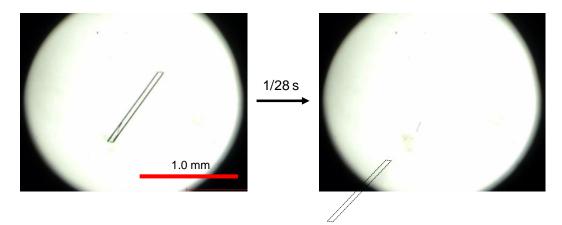

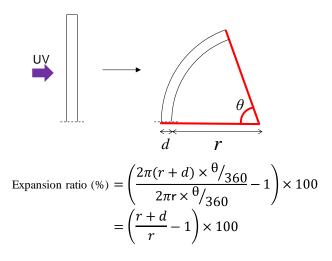**Figure S3.** Reversibility test of initial bending behavior.

Figure S4. Thermosalient effect of crystal **1a.** The crystal suddenly jumped at 36.5 °C. The crystal jumped more than 1.25 mm distance in 1/28 s. The speed of jumping was estimated to be more than 35 mm s^{-1}.

Table S1. Crystallographic data for crystal **1a** at various temperatures.

Formula	C$_{43}$H$_{50}$F$_6$O$_2$S$_2$				
Formula weight	776.95				
Temperature/K	213.15	233.15	253.15	273.15	313.15
Crystal system	triclinic				
Space group	$P\bar{1}$				
a / Å	6.1128	6.1364	6.1709	6.193 (5)	6.389 (5)
b / Å	17.7692	17.7267	17.6559	17.569 (14)	17.125 (16)
c / Å	19.6327	19.6221	19.6053	19.605 (15)	20.105 (18)
α / °	108.0207	107.9132	107.8828	107.797 (5)	108.813 (4)
β / °	89.4390	89.7827	90.0253	90.469 (11)	90.502 (14)
γ / °	99.3331	99.5297	99.7012	100.043 (10)	102.091 (12)
Volume / Å^3	1998.810	1999.813	2000.679	1996 (3)	2029 (3)
Z	–	–	–	2	2
Density / g cm^{-3}	–	–	–	1.293	1.272
Goodness-of-fit on F^2	–	–	–	1.064	1.130
$R(I > 2\sigma(I))$	–	–	–	$R_1 = 0.0763$	$R_1 = 0.0898$
R(all data)	–	–	–	$wR_2 = 0.2223$	$wR_2 = 0.2453$
CCDC No.	–	–	–	1540686	1540687

Estimation of the conversion in the crystal surface when the phase transition takes place at room temperature

In previous work, the change of unit cell parameter along to long axis of crystal by the photoisomerization of diarylethene molecules was determined to be 0.24% when the conversion of diarylethene molecules from the open-ring isomer to the closed-ring isomer is 7%.[S2] From this relationship, in the present work, we estimated the conversion in the crystal surface when the phase transition takes place at room temperature. The crystal shape just before the phase transition takes place at room temperature upon UV irradiation is depicted below.

$$\text{Expansion ratio (\%)} = \left(\frac{2\pi(r+d) \times \theta/360}{2\pi r \times \theta/360} - 1 \right) \times 100$$

$$= \left(\frac{r+d}{r} - 1 \right) \times 100$$

Experimental data

Sample No.	d/μm	r/μm	Expansion ratio (%)
1	6	618	0.97
2	8	470	1.7
3	9	600	1.5
Average	7.7	563	1.4

The expansion ratio in length of crystal surface can be calculated by the above equation. As a result, the expansion ratio in length of crystal surface when the phase transition takes place was estimated to be 1.4%. From this value, the conversion in the crystal surface when the phase transition takes place at room temperature was estimated to be 40%.

Reference

S1. Kitagawa, D.; Kobatake, S. Crystal Thickness Dependence of Photoinduced Crystal Bending of 1,2-Bis(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene. *J. Phys. Chem. C* **2013**, *117*, 20887-20892.

S2. Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. Rapid and Reversible Shape Changes of Molecular Crystals on Photoirradiation. *Nature* **2007**, *446*, 778-781.