

SUPPORTING INFORMATION

Photo-induced reversible topographical changes of photochromic dithienylethene microcrystalline surfaces

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Coating Film Preparations.

The chloroform solution containing diarylethene **2** (100 mg/ml) was dropped on the glass substrate (10 x 10 mm). The substrate was stored at room temperature to be evaporated the solvent, followed by placed in a desiccator, and the residual solvent was removed under 58 mmHg for 30 min. The last procedure was necessary for SEM observation. The residual chloroform was not observed in ¹H-NMR in C₆D₆.

Contact Angle Measurements.

Contact angle (CA) measurement was carried out on an optical contact angle meter (Kyowa Interface Science Co., Ltd., Drop Master 500) by $\theta/2$ method at 25 °C. Deionized water (1.5 μ l) was dropped carefully onto the surface. An average CA value was obtained by measuring the same sample at ten different positions for surface of e, g, and h and at five different points for surface f to determine reproducibility. The detailed procedures are explained as follows.

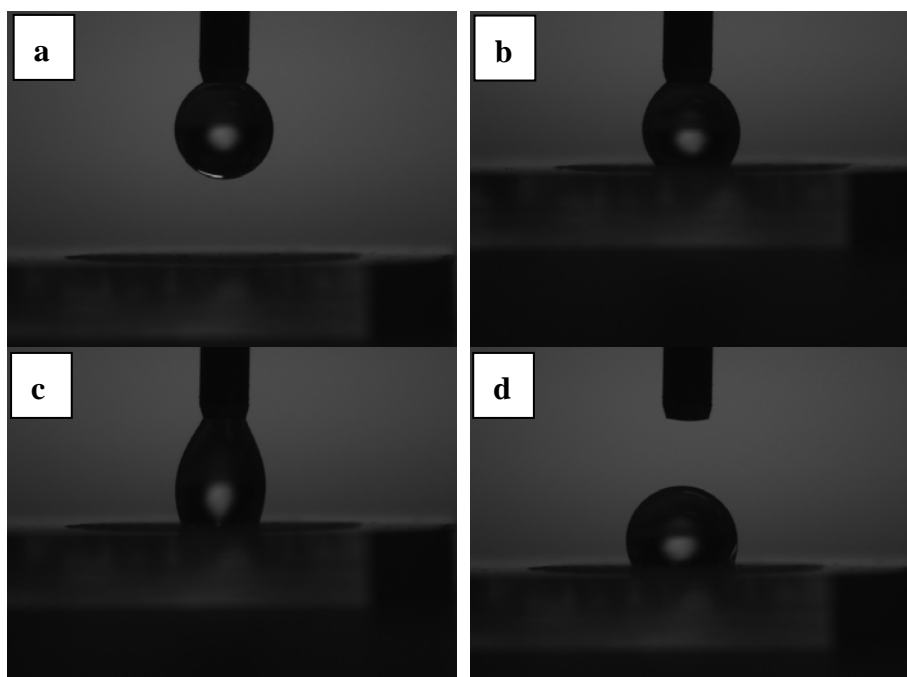


Figure S1. Preparation of a water droplet on the sample surface by Drop Master 500

- (a) A water droplet with 1.5 μl was prepared on the top of the pipette over the sample film.
(b) The stage was lifted up to touch the droplet on the surface. (c) Then the stage was shifted down in order to leave the droplet on the surface. (d) The droplet on the surface for the measurement.

Table S1. Contact angles of a water droplet on each surface.

	surface e	surface f	surface g	surface h
1	119.6	95.7	131.5	116.1
2	119.9	95.9	134.2	116.4
3	120.1	95.9	135.3	117.0
4	120.3	96.0	135.5	117.2
5	120.4	96.4	136.1	117.6
6	120.4	-	136.3	117.8
7	120.5	-	136.5	118.6
8	120.7	-	136.6	119.1
9	120.8	-	137.0	119.3
10	121.3	-	137.7	120.1
average	120.4	96.0	135.7	117.9
standard deviation (σ)	0.42	0.23	1.67	1.25

Crystal data for **2o** and **2c**

Crystal data for **2o**. ($\text{C}_{27}\text{H}_{18}\text{F}_6\text{S}_2$) Crystal system: Monoclinic, Space group: $P2_1/c$, $a = 18.786(2) \text{ \AA}$, $b = 11.762(1) \text{ \AA}$, $c = 21.675(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 96.323(2)^\circ$, $\gamma = 90^\circ$, $V = 4759.9(10) \text{ \AA}^3$, $Z = 8$, $T = 296(2) \text{ K}$

Crystal data for **2c**. ($\text{C}_{27}\text{H}_{18}\text{F}_6\text{S}_2$) Crystal system: Triclinic, Space group: $P-1$, $a = 11.770(4) \text{ \AA}$, $b = 12.023(5) \text{ \AA}$, $c = 9.626(3) \text{ \AA}$, $\alpha = 94.45(3)^\circ$, $\beta = 95.89(3)^\circ$, $\gamma = 60.07(3)^\circ$, $V = 1173.7(7) \text{ \AA}^3$, $Z = 2$, $T = 296(2) \text{ K}$

The reversible morphology changes of the surface of diarylethene **2** are shown in Fig. S2.

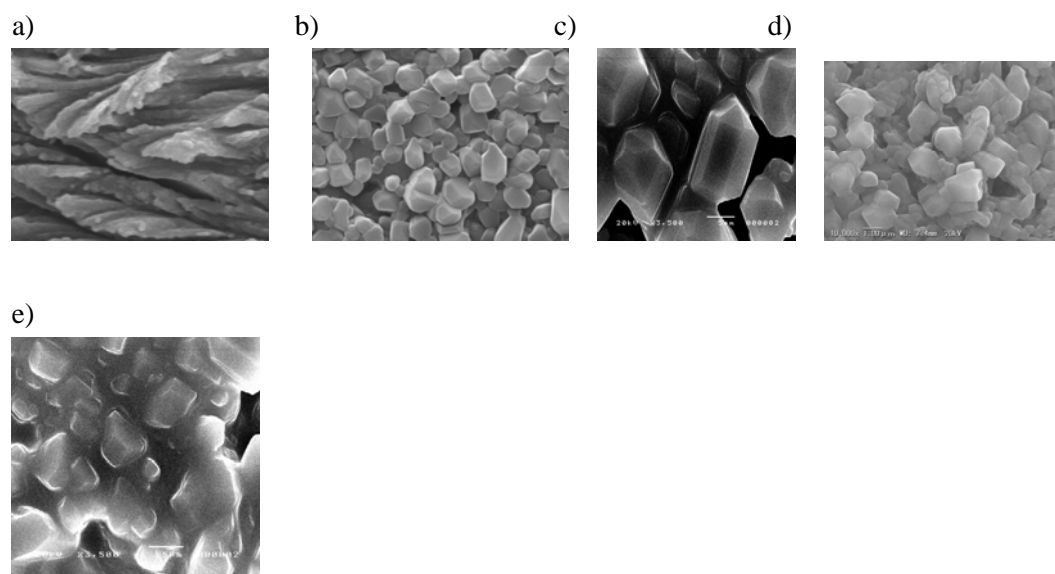


Figure S2. Reversible topographical changes on the surface of diarylethene **2**

(a) Before UV irradiation, (b) after UV irradiation (1st cycle), (c) after Vis. irradiation (1st cycle), (d) after UV irradiation (2nd cycle), (e) after Vis. irradiation (2nd cycle)
 (a, b, d: x 10000, c, e: x 3500)

The contact angle changes are considered to be attributable for the surface topographical changes instead of chemical structure changes. The CA changes of spiropyrane derivatives are reported. (see ref.1) Upon UV irradiation, spiropyrane derivative undergo ring-opening reaction and form merocyanine form with betaine structure.

The dipolar moment changes of diarylethenes accompanied with the photochromism are much smaller than those of azobenzenes and spiropyranes. The dipole moment of **2o** and **2c** were calculated by B3LYP/6-31G(d) method and found to be 3.8768 D and 4.3181 D, respectively. (For computational detail, see ref.2.)

Reference

- 1) R. Rosario, D. Gust, M. Hayes, F. Jahnke, J. Springer, A. A. Garcia, *Langmuir*, **2002**, 18, 8062-8069.
- 2) A. Takata, S. Yokojima, H. Nakagawa, Y. Matsuzawa, A. Murakami, S. Nakamura, M. Irie, and K. Uchida, *J. Phys. Org. Chem.*, 2007, **20**, 998-1006.