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Supporting Information

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Photoinduced Reversible Microfibril Formation on a Photochromic Diarylethene Microcrystalline Surface

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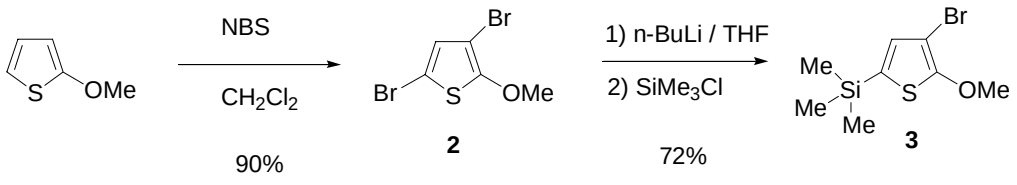
1. Materials

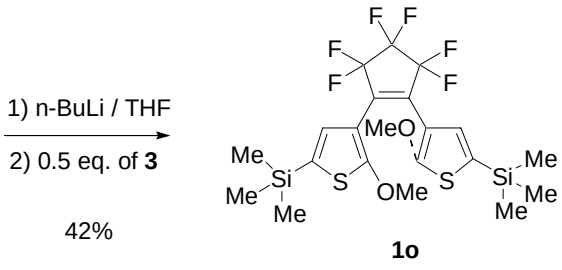
Dehydrated tetrahydrofuran (THF; stabilizer-free) was purchased from Kanto Kagaku, and 1.6 N *n*-butyl lithium ether solution was purchased from Kishida Kagaku. *N*-bromosuccinimide, 2-methoxythiophene and chlorotrimethylsilane were purchased from Tokyo Chemical Industry Co., Ltd. Octafluorocyclopentene was gifted from Nihon Zeon Co. Ltd. Ether, hexane, chloroform, and ethanol were used as received. For column chromatography, Silica gel 60 N (spherical neutral, Kanto Kagaku) and separable TLC (Merck: 1.11798) were used.

2. Methods

3. Synthesis

3.1 Synthesis of compound 1o





3, 5-Dibromo-2-methoxythiophene (2)

To a dichloromethane solution (125 ml) containing 31.0 g of 2-methoxythiophene (0.27 mol), 96 g (0.54 mol) of *N*-bromosuccinimide was added at 10 °C under argon gas atmosphere, and stirred for 1 h at the temperature. The reaction mixture was poured into the chloroform and washed with water. The organic phase was separated and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on silica gel with hexane as an eluent to obtain **2** as colorless oil in 90% yield (66.3 g).

^{1}H-NMR (400 MHz; $CDCl_3$; 25 °C) δ = 3.99 (s, 3H), 6.76 ppm (s, 1H)

3-Bromo-2-methoxy-5-trimethylsilylthiophene (3)

To an anhydrous THF solution (150 ml) containing 19.0 g (70 mmol) of 3,5-dibromo-2-methoxythiophene (**2**), 48 ml of 1.6 N *n*-butyl lithium ether solution (80 mmol, 1.1 eq.) was gradually added at -72 °C under argon gas atmosphere, and stirred for 1h at the temperature. Then 10.7 ml (80 mmol, 1.1 eq.) of chlorotrimethylsilane was added and stirred for 1h at the same temperature. The reaction mixture was allowed to warm to room temperature and poured into the water (300 ml) and extracted with ether (150 ml x 3). The combined ether solution was dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on silica gel with hexane as an eluent to obtain **3** as colorless oil in 72% yield (13.4 g). ^{1}H-NMR (400 MHz; $CDCl_3$; 25 °C) 0.27 (9H, s), 3.98 (3H, s), 6.88 (1H, s) ppm; FAB-MS m/z : 266(M^+)

Anal. Calcd. for $C_8H_{13}BrOSSi$: C, 36.23; H, 4.94; Found: C, 36.07; H, 4.88.

1, 2-Bis(2-methoxy-5-trimethylsilylthien-3-yl)perfluorocyclopentene (1o)

To an anhydrous THF solution containing 13.0 g (50 mmol) of 3-bromo-2-methoxy-5-trimethylsilylthiophene, 45 ml of 1.6 N *n*-butyl lithium ether solution (60 mmol) was gradually added at -60 °C under argon atmosphere. After one hour stirring at the temperature, 3.33 ml (25 mmol) of octafluorocyclopentene was added to the mixture, followed one more hour stirring at the temperature. Then the reaction mixture was warmed to room temperature, and water was added. The mixture was extracted with ether (50 ml x 3 times), and the combined extract was dried on $MgSO_4$. The solvent was evaporated in vacuo, and the mixture was separated by silica gel chromatography by using hexane as the eluent yielding 5.63 g of **1o** (42%).

Mp. 99.8-100.3 °C

^{1}H-NMR (400 MHz; $CDCl_3$; 25 °C) 0.26(18H, s), 3.61(6H, s), 6.92(2H, s) ppm; FAB-MS m/z : 544(M^+)

Anal. Calcd. for $C_{21}H_{26}F_6O_2S_2Si_2$: C, 46.30; H, 4.81; Found: C, 46.32; H, 4.85.

IR (KBr) 3021, 2956, 2896, 2869, 1625, 1552, 1475, 1428, 1394, 1324, 1295, 1251, 1186, 1122, 1099, 1041, 985, 952, 939, 838, 757, 736 cm^{-1}

3.2 Preparation and purification of the closed-ring isomer (1c)

The hexane solution (500 ml) containing 10 mg of **1o** was placed in a quartz vessel, and irradiated with 254 nm light. Then the blue colored solution was evaporated in vacuo in dark, and **1c** was separated from the photostationary state mixture containing **1o** and **1c** by using separable TLC with a solvent mixture (hexane / chloroform = 20/1 v/v) as the eluent. The blue colored powder was purified by crystallization from ethanol to obtain **1c**.

Mp. 143.2~144.1 °C

^{1}H-NMR (400 MHz; $CDCl_3$; 25 °C) 0.23(18H, s), 3.70(6H, s), 6.10(2H, s) ppm; FAB-MS m/z: 544(M^+)

Anal. Calcd. for $C_{21}H_{26}F_6O_2S_2Si_2$: C, 46.30; H, 4.81; Found: C, 46.42; H, 4.81.

IR (KBr) 2958, 2933, 2898, 1734, 1701, 1637, 1560, 1540, 1458, 1400, 1340, 1270, 1192, 1128, 1070, 1016, 937, 839, 758 cm^{-1}

4. Absorption spectral changes of the diarylethene 1 (Fig. S1)

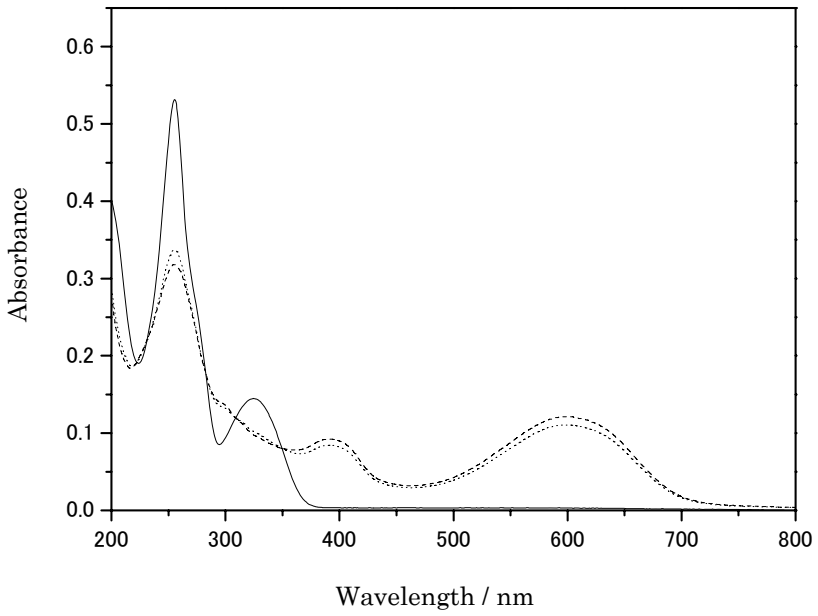


Fig. S1. Absorption spectral changes of diarylethene **1** in hexane solution (1.9×10^{-5} mol / L). Open-ring isomer **1o** (solid line), closed-ring isomer **1c** (broken line), and the photostationary state (dotted line).

Preparation of the casting film of diarylethene 1

The thin films of diarylethene **1** were prepared by a solution casting by using a chloroform solution (120 mg/ml) on a brass plate, and stored in the dark at room temperature.

Single Crystal Analysis:

X-ray Diffraction Data Collection of 1o and 1c.

Suitable colourless prism-shaped crystals (**1o**) and dark blue needle crystals (**1c**) were obtained by recrystallisation from ethanol. A crystal with the dimensions of 0.5 x 0.4 x 0.15 mm (**1o**) and a crystal with the dimensions of 0.5 x 0.1 x 0.05 mm (**1c**) were mounted on top of a glass fibre, and aligned on a Bruker SMART 1000 CCD diffractometer (Platform with full three-circle goniometer) at room temperature. The diffractometer was equipped with a 1K CCD detector set 50.0 mm from the each crystal. Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). Generator settings were 50 KV/ 40 mA. SMART was used for preliminary determination of the unit cell constants and data collection control. The intensities of reflections of a hemisphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. Totals of 1800 frames for each crystal were collected with an exposure time of 5.0 seconds per frame for **1o** and 10.0 seconds per frame for **1c**. Data integration and global cell refinement was performed with the program *SAINT*. The final unit cells were obtained from the xyz centroids of 2912 reflections for **1o** and 1352 reflections for **1c** after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of

symmetry-related reflections measured at different angular settings (*SADABS*), and reduced to Fo^2.

Structure determination and refinement of 1o.

The unit cell was identified as triclinic. Reduced cell calculations did not indicate any higher metric lattice symmetry. Space group, *P-1*, was determined from considerations of the unit cell parameters, statistical analyses of intensity distributions: the *E*-statistics were indicative of a centrosymmetric space group.

The structure was solved by direct methods using the program *SHELXS97* and refined by full-matrix least squares against F^2 of the observed reflections with *SHELXL97*. All non-hydrogen atoms were refined anisotropically except disordered Fluorine atoms (F24A and F24B). Hydrogen atoms were located at ideal positions and refined in isotropic approximation.

Crystal data and structure refinement details are given in Table S1. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table S2. Bond lengths and angles are collected in Table S3.

Structure determination and refinement of 1c.

The unit cell was identified as triclinic. Reduced cell calculations did not indicate any higher metric lattice symmetry. Space group, *P-1*, was determined from considerations of the unit

cell parameters, statistical analyses of intensity distributions: the *E*-statistics were indicative of a centrosymmetric space group.

The structure was solved by direct methods using the program *SHELXS97* and refined by full-matrix least squares against F^2 of the observed reflections with *SHELXL97*. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions and refined in isotropic approximation.

Crystal data and structure refinement details are given in Table S4. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table S5. Bond lengths and angles are collected in Table S6.

Table S1. Crystal data and structure refinement details for 1o.

Empirical formula	C21 H26 F6 O2 S2 Si2
Formula weight	544.72
Temperature	298(2) K
Wavelength	0.71073 Å

Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.122(6) Å alpha=103.355(11) deg.
	b = 11.268(6) Å beta= 94.298(13) deg.
	c = 12.814(7) Å gamma=74.981(12) deg.
Volume	1373.3(13)A^3
Z, Calculated density	2, 1.317 Mg/m^3
Absorption coefficient	0.337 mm^{-1}
F(000)	564
Crystal size	0.5 x 0.4 x 0.15 mm
Theta range for data collection	2.08 to 28.13 deg.
Index ranges	-9<=h<=12, -14<=k<=14, -16<=l<=14
Reflections collected / unique	7913 / 5717 [R(int) = 0.0172]
Completeness to 2theta = 28.13	85.1%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5717 / 4 / 342
Goodness-of-fit on F^2	0.927
Final R indices [I>2sigma(I)]	R1 = 0.0685, wR2 = 0.2056
R indices (all data)	R1 = 0.0988, wR2 = 0.2436
Largest diff. peak and hole	0.742 and -0.706 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non-hydrogen atoms of 1o.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	6456(1)	8634(1)	1413(1)	68(1)
C(2)	7778(4)	7655(4)	593(3)	59(1)
C(3)	8994(4)	7857(4)	1015(3)	57(1)
C(4)	8897(4)	8791(3)	1987(3)	51(1)
C(5)	7579(4)	9296(4)	2299(3)	56(1)
C(6)	10054(4)	9208(3)	2570(3)	48(1)
C(7)	11290(4)	8276(3)	2859(3)	59(1)
C(8)	12204(5)	9036(5)	3467(5)	90(2)
C(9)	11451(4)	10395(4)	3588(3)	64(1)
C(10)	10168(3)	10389(3)	2949(3)	48(1)
C(11)	9262(4)	11569(3)	2768(3)	50(1)

C(12)	8910(4)	12728(3)	3551(3)	55(1)
C(13)	8038(4)	13706(4)	3207(3)	59(1)
S(14)	7629(1)	13218(1)	1869(1)	67(1)
C(15)	8651(4)	11709(3)	1808(3)	56(1)
Si(16)	7413(1)	6587(1)	-672(1)	64(1)
C(17)	6234(8)	7551(7)	-1524(5)	115(2)
C(18)	6594(10)	5432(8)	-348(6)	125(3)
C(19)	9050(7)	5797(7)	-1393(5)	106(2)
O(20)	7181(3)	10182(3)	3191(2)	78(1)
C(21)	5815(6)	10567(9)	3469(5)	121(3)
F(22)	11917(3)	7444(3)	2002(3)	111(1)
F(23)	11010(4)	7554(4)	3452(3)	125(1)
F(24A)	13147(6)	8687(4)	4062(5)	111(2)
F(24B)	11992(11)	8848(9)	4557(7)	110(3)
F(25)	13260(5)	8874(5)	2733(8)	259(5)
F(26)	11213(4)	10874(4)	4641(2)	126(2)
F(27)	12191(4)	11078(4)	3326(4)	139(2)
Si(28)	7321(1)	15355(1)	3942(1)	72(1)
C(29)	7770(9)	15454(6)	5391(5)	109(2)

C(30)	8123(12)	16419(6)	3447(7)	127(3)
C(31)	5444(7)	15740(9)	3699(10)	156(4)
O(32)	8867(4)	10803(3)	908(2)	78(1)
C(33)	7958(6)	10950(6)	35(4)	90(2)

Table S3. Bond lengths [Å] and angles [deg] for 1o.

S(1)-C(5)	1.729(4)
S(1)-C(2)	1.739(4)
C(2)-C(3)	1.359(5)
C(2)-Si(16)	1.858(4)
C(3)-C(4)	1.424(5)
C(4)-C(5)	1.358(5)

C(4)-C(6)	1.464(5)
C(5)-O(20)	1.342(5)
C(6)-C(10)	1.339(5)
C(6)-C(7)	1.495(5)
C(7)-F(23)	1.325(5)
C(7)-F(22)	1.345(5)
C(7)-C(8)	1.480(6)
C(8)-F(24A)	1.218(5)
C(8)-F(25)	1.424(9)
C(8)-C(9)	1.501(6)
C(8)-F(24B)	1.499(8)
C(9)-F(27)	1.313(5)
C(9)-F(26)	1.347(5)
C(9)-C(10)	1.483(5)
C(10)-C(11)	1.464(5)
C(11)-C(15)	1.359(5)
C(11)-C(12)	1.430(5)
C(12)-C(13)	1.361(5)
C(13)-S(14)	1.728(4)

C(13)-Si(28)	1.861(4)
S(14)-C(15)	1.734(4)
C(15)-O(32)	1.341(5)
Si(16)-C(17)	1.864(6)
Si(16)-C(18)	1.847(6)
Si(16)-C(19)	1.864(6)
O(20)-C(21)	1.385(6)
F(24A)-F(24B)	1.323(10)
Si(28)-C(31)	1.855(8)
Si(28)-C(30)	1.852(7)
Si(28)-C(29)	1.863(7)
O(32)-C(33)	1.406(6)

C(5)-S(1)-C(2)	92.18(19)
C(3)-C(2)-S(1)	109.5(3)
C(3)-C(2)-Si(16)	129.6(3)
S(1)-C(2)-Si(16)	120.8(2)
C(2)-C(3)-C(4)	114.9(4)
C(5)-C(4)-C(3)	111.7(3)

C(5)-C(4)-C(6)	123.2(3)
C(3)-C(4)-C(6)	125.0(3)
O(20)-C(5)-C(4)	124.8(3)
O(20)-C(5)-S(1)	123.5(3)
C(4)-C(5)-S(1)	111.7(3)
C(10)-C(6)-C(4)	128.1(3)
C(10)-C(6)-C(7)	111.0(3)
C(4)-C(6)-C(7)	120.8(3)
F(23)-C(7)-F(22)	103.6(4)
F(23)-C(7)-C(8)	109.8(4)
F(22)-C(7)-C(8)	111.5(4)
F(23)-C(7)-C(6)	113.4(4)
F(22)-C(7)-C(6)	113.3(3)
C(8)-C(7)-C(6)	105.4(3)
F(24A)-C(8)-F(25)	84.2(6)
F(24A)-C(8)-C(7)	126.4(5)
F(25)-C(8)-C(7)	104.2(4)
F(24A)-C(8)-C(9)	122.3(4)
F(25)-C(8)-C(9)	103.8(5)

C(7)-C(8)-C(9)	107.1(3)
F(24A)-C(8)-F(24B)	57.1(5)
F(25)-C(8)-F(24B)	141.2(6)
C(7)-C(8)-F(24B)	97.4(5)
C(9)-C(8)-F(24B)	100.0(5)
F(27)-C(9)-F(26)	104.4(4)
F(27)-C(9)-C(10)	114.4(4)
F(26)-C(9)-C(10)	112.3(4)
F(27)-C(9)-C(8)	112.8(4)
F(26)-C(9)-C(8)	107.3(4)
C(10)-C(9)-C(8)	105.5(3)
C(6)-C(10)-C(9)	110.6(3)
C(6)-C(10)-C(11)	129.0(3)
C(9)-C(10)-C(11)	120.4(3)
C(15)-C(11)-C(12)	110.6(3)
C(15)-C(11)-C(10)	123.6(3)
C(12)-C(11)-C(10)	125.8(3)
C(13)-C(12)-C(11)	115.7(4)
C(12)-C(13)-S(14)	109.3(3)

C(12)-C(13)-Si(28)	130.0(3)
S(14)-C(13)-Si(28)	120.7(2)
C(13)-S(14)-C(15)	92.38(19)
O(32)-C(15)-C(11)	123.8(3)
O(32)-C(15)-S(14)	124.0(3)
C(11)-C(15)-S(14)	112.1(3)
C(17)-Si(16)-C(2)	108.5(3)
C(17)-Si(16)-C(18)	109.9(5)
C(2)-Si(16)-C(18)	109.0(3)
C(17)-Si(16)-C(19)	109.0(4)
C(2)-Si(16)-C(19)	108.7(2)
C(18)-Si(16)-C(19)	111.6(4)
C(5)-O(20)-C(21)	119.9(4)
C(8)-F(24A)-F(24B)	72.2(5)
F(24A)-F(24B)-C(8)	50.7(3)
C(31)-Si(28)-C(30)	111.3(6)
C(31)-Si(28)-C(13)	107.7(3)
C(30)-Si(28)-C(13)	109.0(3)
C(31)-Si(28)-C(29)	112.1(5)

C(30)-Si(28)-C(29)	108.6(4)
C(13)-Si(28)-C(29)	108.0(2)
C(15)-O(32)-C(33)	118.2(4)

Table S4. Crystal data and structure refinement details for 1c.

Empirical formula	C21 H26 F6 O2 S2 Si2	
Formula weight	544.72	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 6.697(2) Å	alpha = 96.899(6) deg.
	b = 11.777(4) Å	beta= 96.993(6) deg.
	c = 17.470(6) Å	gamma=98.472(6) deg.

Volume	1339.2(8) A^3
Z, Calculated density	2, 1.351 Mg/m^3
Absorption coefficient	0.346 mm^{-1}
F(000)	564
Crystal size	0.5 x 0.1 x 0.05 mm
Theta range for data collection	2.26 to 24.71 deg.
Index ranges	-7<=h<=7, -13<=k<=13, -20<=l<=13
Reflections collected / unique	6723 / 4496 [R(int) = 0.0359]
Completeness to 2theta = 24.71	98.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4496 / 2 / 338
Goodness-of-fit on F^2	0.883
Final R indices [I>2sigma(I)]	R1 = 0.0791, wR2 = 0.1898
R indices (all data)	R1 = 0.1351, wR2 = 0.2232
Largest diff. peak and hole	0.458 and -0.332 e.$Å^{-3}$

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for non-hydrogen atoms of 1c.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	804(3)	7986(1)	2059(1)	39(1)
C(2)	595(9)	7631(5)	2994(3)	33(1)
C(3)	1194(8)	8536(5)	3560(3)	27(1)
C(4)	1917(8)	9605(4)	3300(3)	25(1)
C(5)	2196(8)	9447(4)	2445(3)	24(1)
C(6)	2389(8)	10693(5)	3664(3)	28(1)
C(7)	2512(11)	11164(5)	4509(4)	43(2)
C(8)	4144(13)	12248(6)	4610(4)	55(2)
C(9)	3940(11)	12704(5)	3823(4)	48(2)
C(10)	2978(8)	11673(4)	3259(3)	30(1)
C(11)	2660(8)	11574(4)	2481(3)	25(1)
C(12)	3297(9)	12345(5)	1948(3)	32(1)
C(13)	2988(9)	11882(5)	1199(3)	33(1)

S(14)	1886(3)	10423(1)	1035(1)	40(1)
C(15)	1432(8)	10420(4)	2056(3)	26(1)
Si(16)	-443(3)	6093(1)	3098(1)	37(1)
C(17)	-3235(11)	5885(7)	2846(6)	67(2)
C(18)	626(13)	5124(6)	2399(5)	62(2)
C(19)	310(15)	5846(6)	4105(5)	67(2)
O(20)	4266(6)	9540(3)	2347(2)	36(1)
C(21)	5439(11)	8854(7)	2769(5)	61(2)
F(22)	2950(8)	10436(3)	5003(2)	76(1)
F(23)	737(7)	11498(4)	4664(3)	77(1)
F(24)	4006(9)	13019(4)	5211(2)	92(2)
F(25)	5986(8)	11900(4)	4731(3)	81(2)
F(26)	2811(9)	13544(4)	3855(3)	95(2)
F(27)	5754(8)	13200(4)	3682(3)	87(2)
Si(28)	3539(3)	12665(2)	350(1)	42(1)
C(29)	5711(16)	13830(8)	700(5)	87(3)
C(30)	1236(14)	13258(9)	22(5)	77(3)
C(31)	4104(17)	11641(9)	-435(5)	84(3)
O(32)	-629(6)	10314(3)	2114(2)	39(1)

C(33)	-1650(11)	11235(7)	1913(6)	63(2)

Table S6. Bond lengths [Å] and angles [deg] for 1c.

S(1)-C(2)	1.750(6)
S(1)-C(5)	1.838(5)
C(2)-C(3)	1.342(8)
C(2)-Si(16)	1.881(6)
C(3)-C(4)	1.427(7)
C(4)-C(6)	1.336(7)
C(4)-C(5)	1.519(7)
C(5)-O(20)	1.407(6)
C(5)-C(15)	1.521(7)
C(6)-C(10)	1.455(7)

C(6)-C(7)	1.501(8)
C(7)-F(22)	1.325(7)
C(7)-F(23)	1.353(8)
C(7)-C(8)	1.530(9)
C(8)-F(24)	1.324(7)
C(8)-F(25)	1.357(9)
C(8)-C(9)	1.533(9)
C(9)-F(26)	1.331(8)
C(9)-F(27)	1.333(8)
C(9)-C(10)	1.479(8)
C(10)-C(11)	1.339(8)
C(11)-C(12)	1.435(7)
C(11)-C(15)	1.534(7)
C(12)-C(13)	1.333(8)
C(13)-S(14)	1.742(6)
C(13)-Si(28)	1.884(6)
S(14)-C(15)	1.846(6)
C(15)-O(32)	1.385(6)
Si(16)-C(18)	1.851(7)

Si(16)-C(17)	1.841(7)
Si(16)-C(19)	1.839(8)
O(20)-C(21)	1.416(7)
Si(28)-C(29)	1.835(9)
Si(28)-C(31)	1.829(8)
Si(28)-C(30)	1.842(8)
O(32)-C(33)	1.422(7)

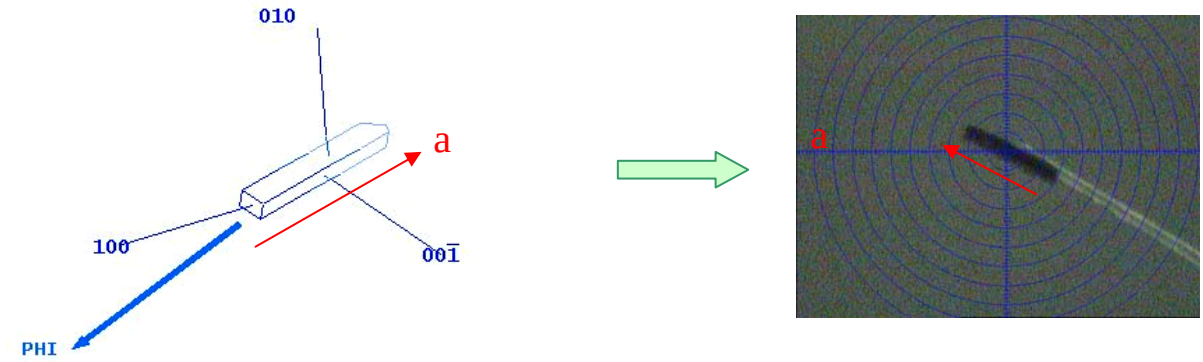
C(2)-S(1)-C(5)	92.4(3)
C(3)-C(2)-S(1)	113.5(4)
C(3)-C(2)-Si(16)	127.8(4)
S(1)-C(2)-Si(16)	118.7(3)
C(2)-C(3)-C(4)	115.0(5)
C(6)-C(4)-C(3)	132.2(5)
C(6)-C(4)-C(5)	115.4(5)
C(3)-C(4)-C(5)	112.4(4)
O(20)-C(5)-C(15)	105.0(4)
O(20)-C(5)-C(4)	112.1(4)
C(15)-C(5)-C(4)	109.5(4)

O(20)-C(5)-S(1)	111.1(3)
C(15)-C(5)-S(1)	114.9(4)
C(4)-C(5)-S(1)	104.4(3)
C(4)-C(6)-C(10)	122.4(5)
C(4)-C(6)-C(7)	130.5(5)
C(10)-C(6)-C(7)	107.0(5)
F(22)-C(7)-F(23)	106.8(5)
F(22)-C(7)-C(6)	115.0(5)
F(23)-C(7)-C(6)	111.2(5)
F(22)-C(7)-C(8)	112.4(6)
F(23)-C(7)-C(8)	108.3(5)
C(6)-C(7)-C(8)	103.0(5)
F(24)-C(8)-F(25)	108.2(6)
F(24)-C(8)-C(9)	114.2(6)
F(25)-C(8)-C(9)	108.4(6)
F(24)-C(8)-C(7)	113.2(6)
F(25)-C(8)-C(7)	107.3(6)
C(9)-C(8)-C(7)	105.3(5)
F(26)-C(9)-F(27)	105.4(5)

F(26)-C(9)-C(10)	113.1(6)
F(27)-C(9)-C(10)	114.5(6)
F(26)-C(9)-C(8)	109.2(6)
F(27)-C(9)-C(8)	110.5(6)
C(10)-C(9)-C(8)	104.2(5)
C(11)-C(10)-C(6)	121.3(5)
C(11)-C(10)-C(9)	128.2(5)
C(6)-C(10)-C(9)	110.4(5)
C(10)-C(11)-C(12)	132.1(5)
C(10)-C(11)-C(15)	115.9(5)
C(12)-C(11)-C(15)	112.0(5)
C(13)-C(12)-C(11)	115.5(5)
C(12)-C(13)-S(14)	113.9(4)
C(12)-C(13)-Si(28)	126.3(4)
S(14)-C(13)-Si(28)	119.8(3)
C(13)-S(14)-C(15)	92.8(3)
O(32)-C(15)-C(5)	106.1(4)
O(32)-C(15)-C(11)	113.0(4)
C(5)-C(15)-C(11)	108.0(4)

O(32)-C(15)-S(14)	111.2(4)
C(5)-C(15)-S(14)	114.7(4)
C(11)-C(15)-S(14)	104.1(3)
C(18)-Si(16)-C(17)	109.6(4)
C(18)-Si(16)-C(19)	111.1(4)
C(17)-Si(16)-C(19)	111.6(4)
C(18)-Si(16)-C(2)	107.7(3)
C(17)-Si(16)-C(2)	107.7(3)
C(19)-Si(16)-C(2)	109.0(3)
C(5)-O(20)-C(21)	116.5(4)
C(29)-Si(28)-C(31)	111.5(5)
C(29)-Si(28)-C(30)	111.0(5)
C(31)-Si(28)-C(30)	110.0(5)
C(29)-Si(28)-C(13)	107.4(3)
C(31)-Si(28)-C(13)	109.4(3)
C(30)-Si(28)-C(13)	107.3(3)
C(15)-O(32)-C(33)	117.6(5)

7. Crystal Growth of 1c

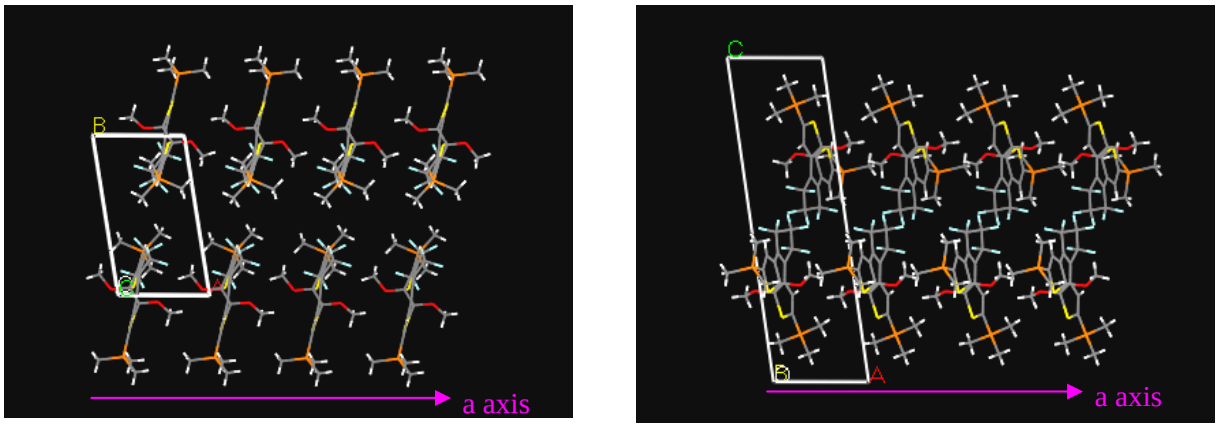


Rotating axis at the

Single crystal of

0.5 x 0.1 x 0.05 mm

Figure S2-1. Crystal shape of **1c**



View along the c axis

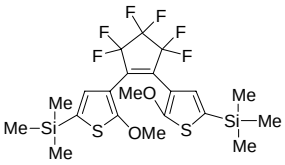
View along the b axis

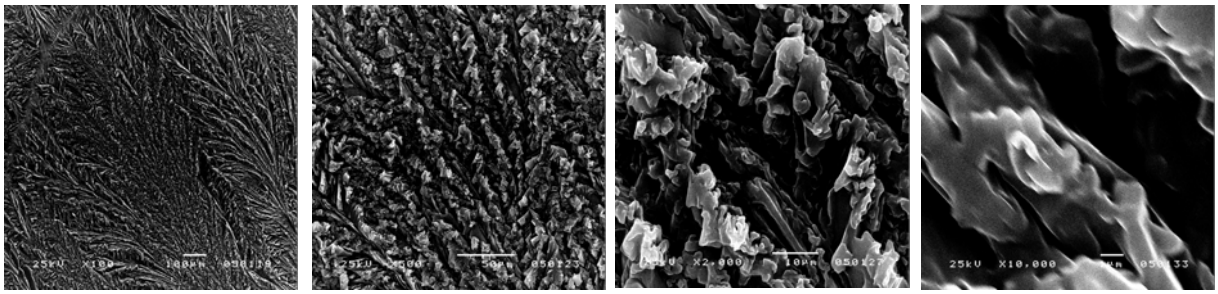
Closed-ring isomer molecules **1c** are apt to stack along the a axis

Fibrils (needle crystals) grow along the a axis.

Fig. S2-2 Crystal structure of **1c** and the crystal growth

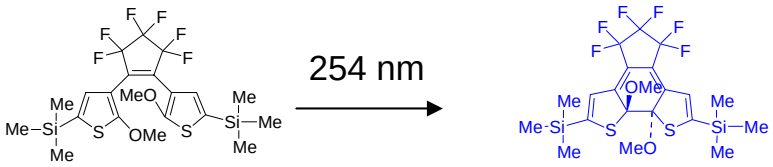
8. SEM images of the casting film before and after UV irradiations and the recovered SEM image after visible light irradiation

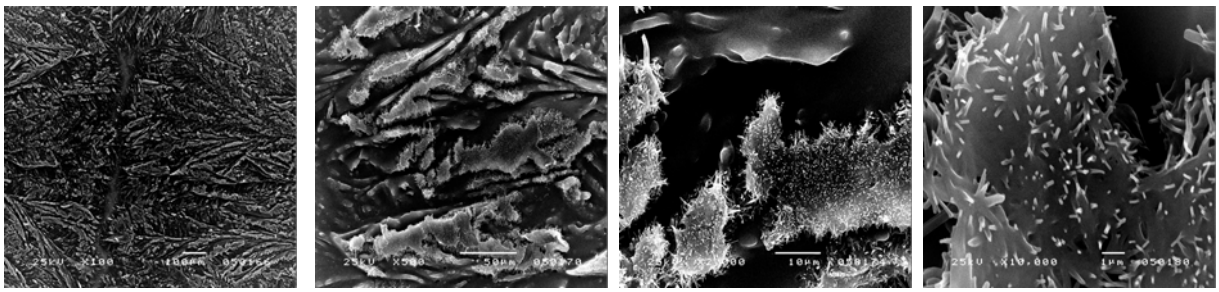




X 100 X 500 X 2000 X 10000

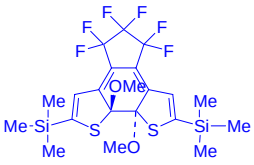
Fig. S3-1. The SEM images on the surface of diarylethene thin film on glass substrate. Without exposure of UV light, NO morphology changes were observed after leaving for 9 days at room temperature

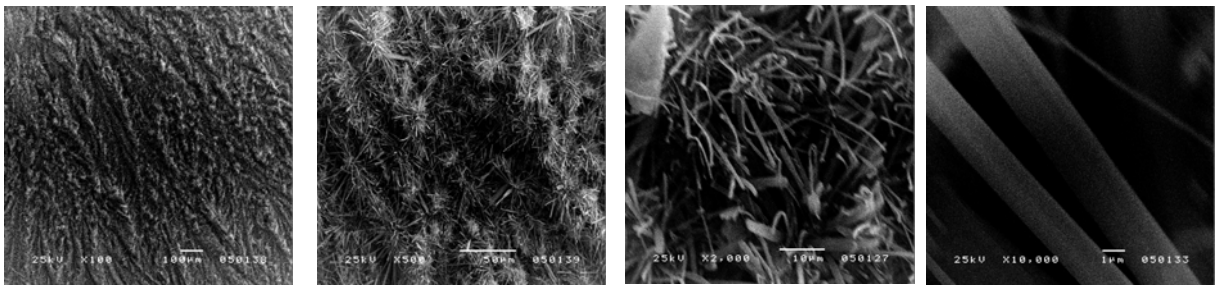




X 100 X 500 X 2000 X 10000

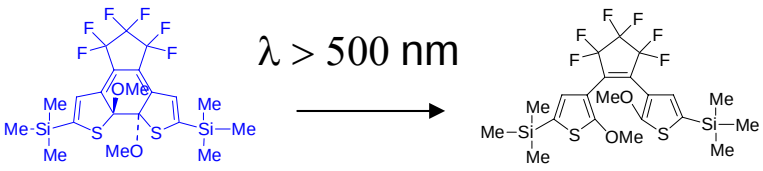
Fig. S3-2. The SEM image of the film after 5 min later of 10 min irradiation with UV light. Small fibrils began to grow on the surface.



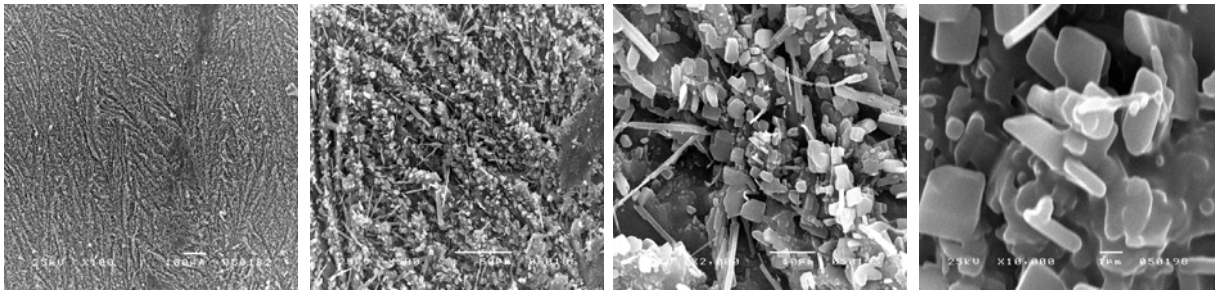


X 100 X 500 X 2000 X 10000

Fig. S3-3. The SEM image of the film after 2 days storing in the dark at 30 ^{o}C. The diameters are 1-2 μm, and the lengths are 10-15 μm.



1c **1o**



X 100 X 500 X 2000 X 10000

Fig. S3-4. The SEM image of the film after visible light irradiation and stored for 2 days in the dark at 30 ^{o}C.

9. SEM images of the coating film on other substrates.

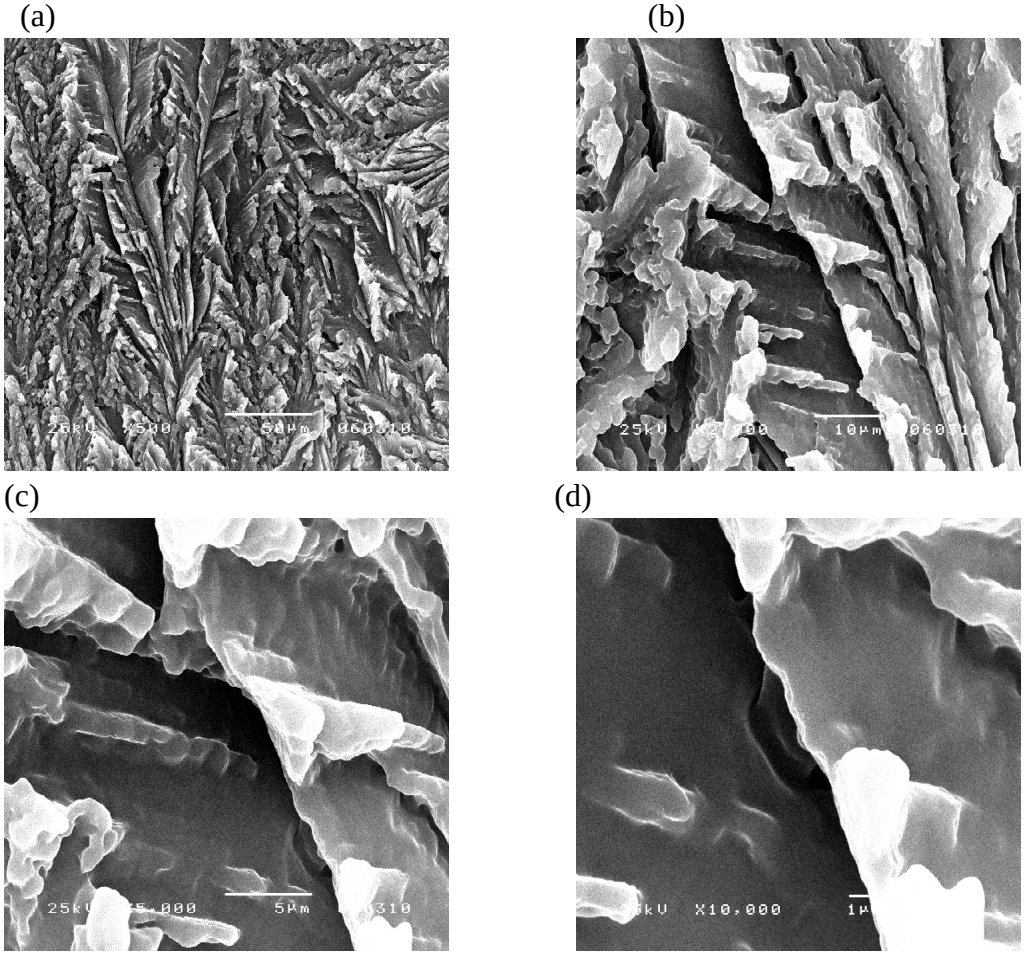
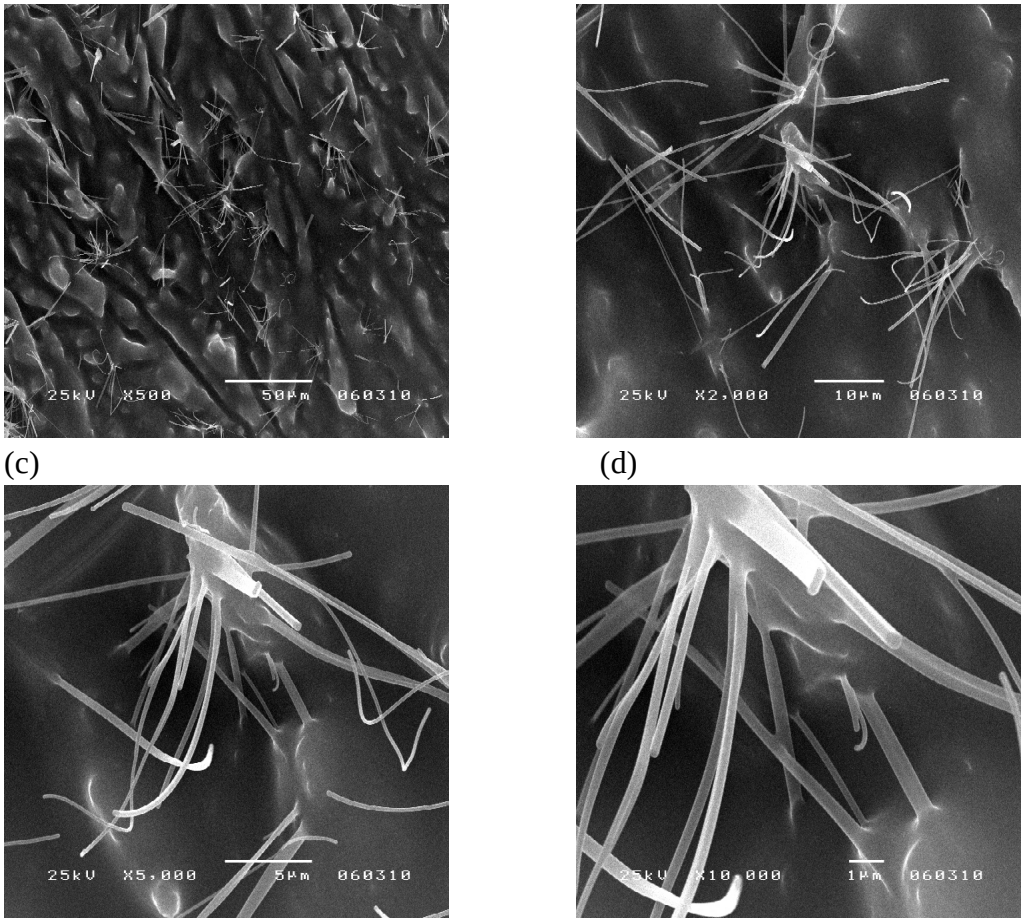


Fig. S4-1. SEM images of a coated film on a polypropylene before UV irradiation (a) x 500, (b) x 2000, (c) x 5000 (d) x 10000

(No significant difference was observed compared with those on the glass substrates.)

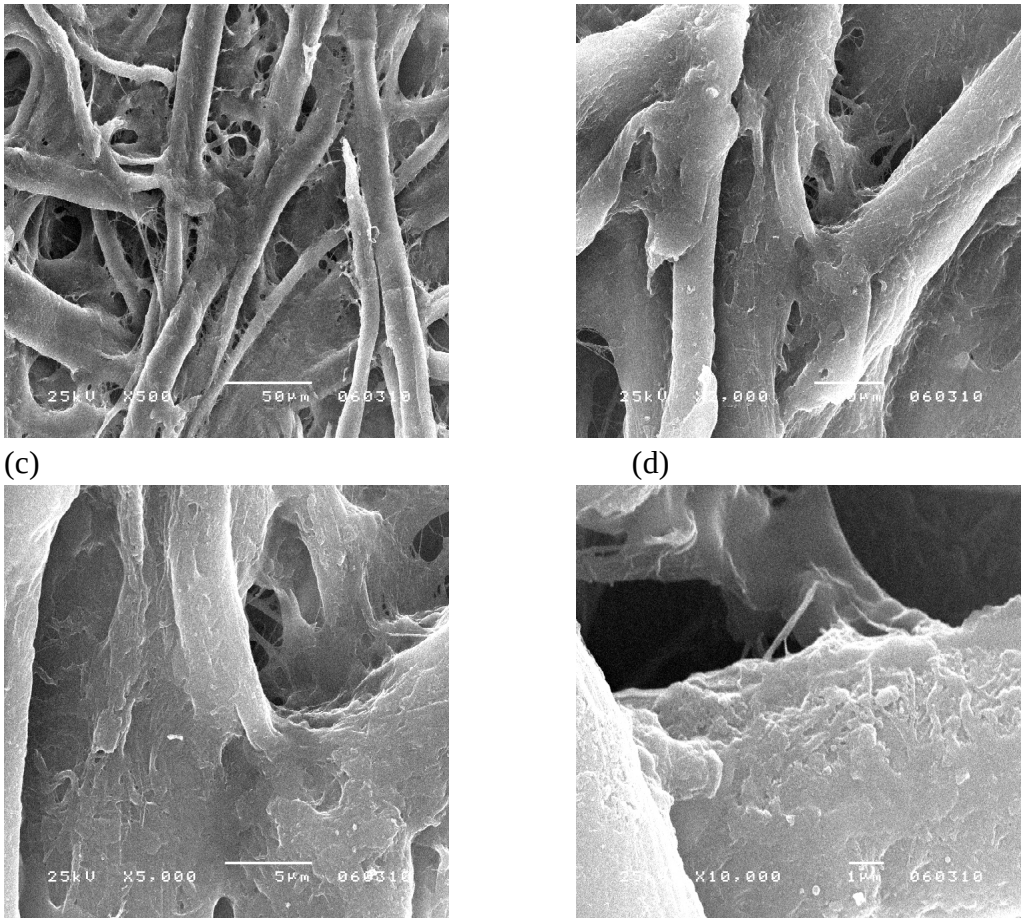
(a) (b)



(c) (d)

Fig. S4-2. SEM images of a coated film on a polypropylene stored in the dark at 30 ^{o}C after 10min UV irradiation (a) x 500, (b) x 2000, (c) x 5000 (d) x 10000
(Fibrils are observed)

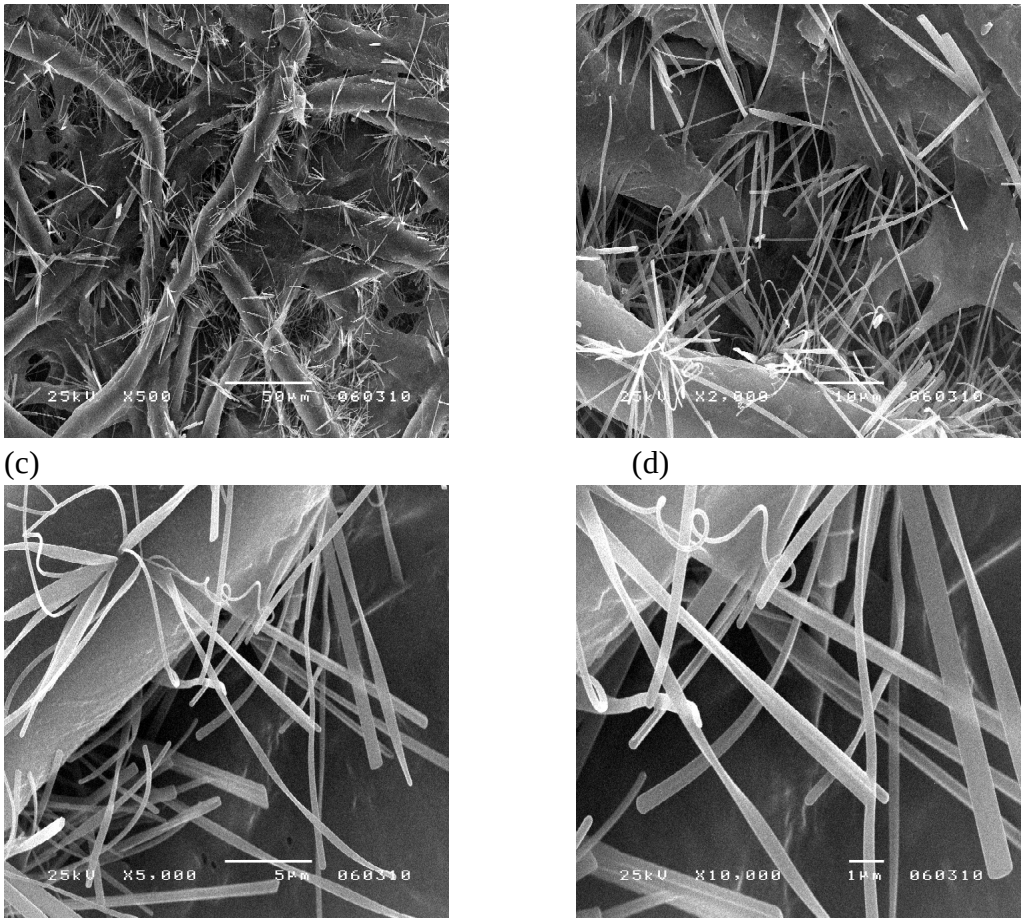
(a) (b)



(c) (d)

Fig. S4-3. SEM images of a coated film on a filter paper before UV irradiation (a) x 500, (b) x 2000, (c) x 5000 (d) x 10000
(The fibers of the filter paper were observed.)

(a) (b)



(c) (d)

Fig. S4-4. SEM images of a coated film on a filter paper stored in the dark at 30 ^{o}C after 10min UV irradiation (a) x 500, (b) x 2000, (c) x 5000 (d) x 10000
(Fibrils of the diarylethene grew up on the paper fibers.)

10. Surface morphology changes of a crystal depending on the temperature.

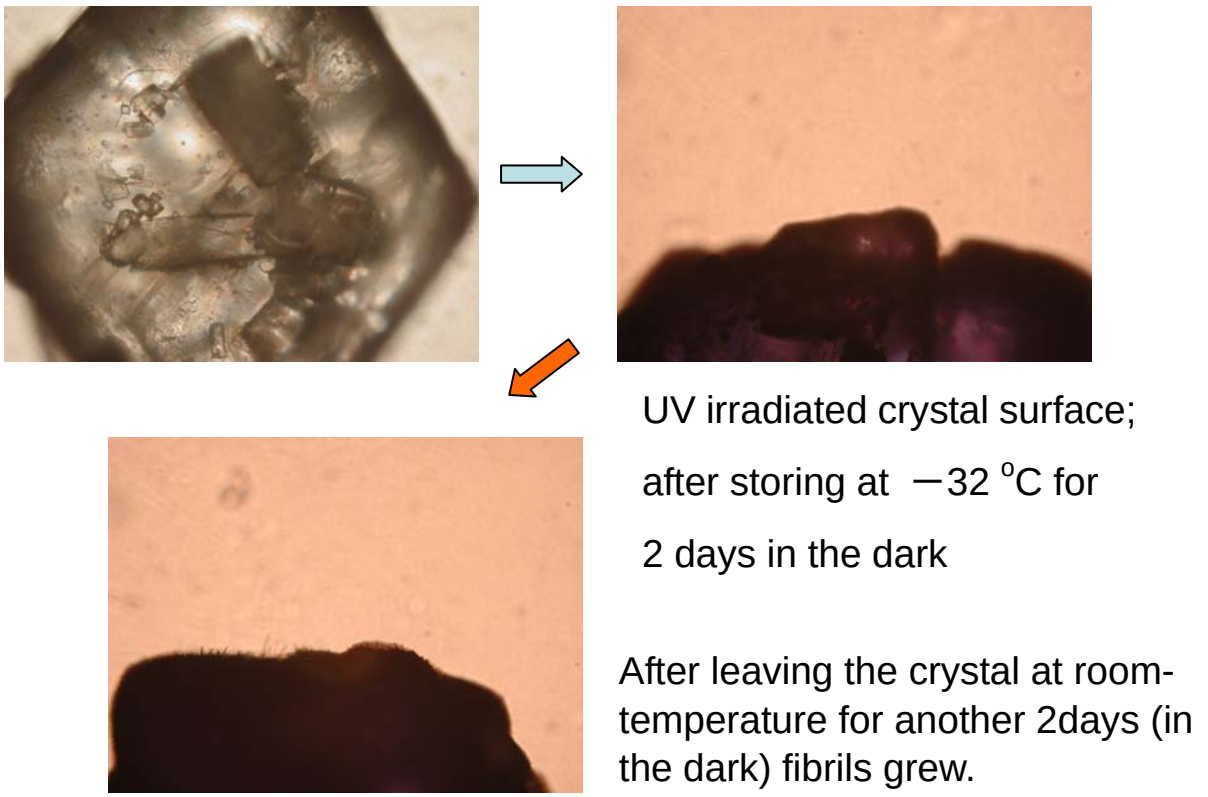


Fig. S5-1. Surface observation of a single crystal of **1o** after UV irradiation. On storing the crystal in the dark at -32 °C for 2 days, NO fibril growth was observed, while the crystal was taken out to room temperature and storing at 30 °C for 1 day fibrils grew up.

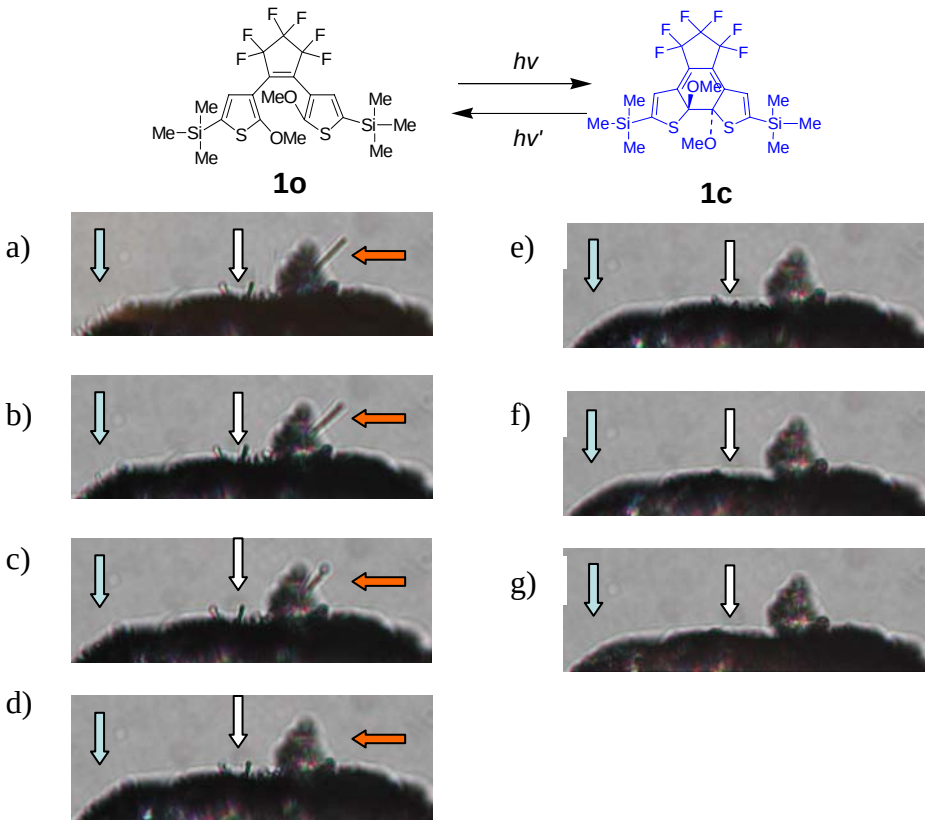


Fig. S5-2. Optical microscopic observation of the fibril disappearing procedure on a crystal at 30 ^{o}C. Short fibrils are disappeared on visible light irradiation (blue and white arrows), but the long fibrils turned to be prism shaped (attributable to the crystal shape of **1o**) and the fibrils are broken (orange arrow) within 10 min. (a) before visible light (λ > 500 nm) irradiation, (b) after 1 min irradiation with the visible light, (c) after 2min irradiation with the visible light, (d) after 4min irradiation with the visible light, (e) after 6 min irradiation with the visible light, (f) after 8 min irradiation with the visible light, (g) after 10 min irradiation with the visible light