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Supplementary Information

Photoinduced Reversible Formation of a Superhydrophilic Surface by Crystal Growth of Diarylethene

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General Information

¹H- (400 MHz), ¹³C- (100 MHz) and ¹⁹F-NMR (376.32 MHz) spectra were recorded on JEOL JNM-400 spectrometer. Chemical shifts are reported in ppm from the signals of solvent peak for ¹H- and ¹³C- NMR, and C₆F₆ for ¹⁹F-NMR CH₃CN (¹H NMR: d = 1.94 ppm) in CD₃CN, CH₃CN (¹³C NMR: d = 118.26 ppm) in CD₃CN, ^{S1} C₆F₆ (¹⁹F NMR: d = -114.93 ppm) in CD₃CN. Electronic absorption spectra were recorded on Hitachi UH-4150 spectrometer. XRD spectra were measured on Rigaku RINT2500. SEM images were monitored on Keyence VE-8800. Contact angle measurements were carried out on Kyowa Interface Science Co., Ltd., Drop Master 500. The volume of the water droplet was 1.5 μ L. Melting point was observed on Yanaco MP-500D and DSC curves were recorded on Perkin-Elmer DSC 8500. For the light irradaition to the microcrystalline surfaces, an UV hand lamp SPECTROLINE Model EB-280C/J (λ = 313 nm) and 500W Xe-arc lamp (Ushio SX-UI501XQ) attached with Toshiba Y-48, Y-43 color filters were used. For the quantum yeild measurements, Ushio 500 W Hg-lamp (SX-UI501HQ) and Xe-arc lamp (Ushio SX-UI501XQ) were used as light source attached with a monochromator (Jobin Yvon UV-10). Elemental analysis of the compounds were carried out at Graduate School and Faculty of Pharmaceutical Sciences, Kyoto University.

Preparation of 1,2-Bis(2-methyl-5-[*N*-methylpyridin-3-yl]-thien-3-yl)perfluoro-cyclopentene trifluorophenylborate (20)^{S2}



A diarylethene derivative **30** was prepared according to privious paper.^{S3} Complexiation of **20** with trifluorophenylborate was carried out as follows.

A mixture of 1.26 g (2.41 mmol) of **20** and 0.15 mL (24.1 mmol, 10 eq.) of 1-iodomethane in 30 mL of acetonitrile anhydrous was stirred for 17 h at room temperature in the dark. After the reaction was over, the solvent was removed in vacuo. The obtained brown oil (1.90 g) was purified with silicagel chromathography (Kanto Chemical) by use of a mixture of acetonitrile, water, and saturated sodium nitrate aq. with 10: 1: 0.1 v/v to obtain 1.61 g of brownish solid as the crude product. The solid was dissolved to 40 mL of acetonitrile, and 0.98 g (5.30 mmol, 2.2 eq.) of KBF₃Ph, 10 mL of water were added and stirred for 18 h at room temperature. After the solvent was removed in vacuo.

on sodium sulfate anhydrous. After removal of sodium sulfateby filtration, solvent was evaporated. The remained dark brownish solid (1.72 g) was dissolved to 30 mL of acetonitrile and 1.72 g of activated carbon and stirred for 12 h at room temperature. After the activated carbon was removed by filtration, solvent was removed and 1.64 g of yellow solid was obtained. The solid was recrystallized from the mixture of 80 mL of ethanol and 60 mL of acetone to obtain the 1.01 g (41.5%) of **20** as pale yellow plates. From the elemental analysis, **20** consists **20**: KBF₃Ph = 1 :0.9.

20: m.p. 203.2°C (by DSC), ¹H NMR (400 MHz, CD₃CN, ppm) δ 2.04 (s, 6H), 4.30 (s, 6H), 7.07 (d, J = 7.6 Hz, 2H), 7.13 (dd, J = 7.6, 7.2 Hz, 4H), 7.39 (d, J = 7.2 Hz, 4H), 7.75 (s, 2H), 7.97 (dd, J = 8.2, 6.1 Hz, 2H), 8.16 (d, J = 6.1 Hz, 2H), 8.54 (d, J = 8.2 Hz, 2H), 8.89 (s, 2H). ¹³C NMR (100 MHz, CD₃CN) δ 15.0, 49.3, 126.2, 126.9, 127.4, 128.6, 129.1, 132.3(q, J = 1.9 Hz), 134.5, 134.8, 137.8, 141.8, 142.9, 144.3, 147.4. ¹⁹F NMR (376 MHz, CD₃CN) δ -61.4 (t, J = 4.3 Hz, 4F), -82.8 (quin, J = 4.3 Hz, 2F), -92.3 (q, J = 55.6 Hz, 6F), Anal. Calcd. for C₃₉H₃₂B₂F₁₂N₂S₂+ 0.9(C₆H₅BF₃K): C, 52.90; H, 3.65; N, 2.78; Found: C, 52.91; H, 3.67; N, 2.70.

The preparation of 2c: 10 mg of 2o was dissolved in 700 mL of acetonitrile, then it was divided into 10 bottles of 100 mL of glass tubes in each 70 mL solution. To the bottles, UV light (313 nm) was irradiated with stirring the solutions for 30 s. The solvents was combined and evaporated, and the residue was recrystallized from the mixture of 4 mL of ethanol and 1 mL of acetone to obtain 7.2 mg of 2c as dark blue cubic crystals. 2c: m.p. 190.2°C.

Crystal Data of **20** and **2c**. X-ray crystallographic analysis was performed with a CCD-based X-ray diffractometer (Bruker AXS, SMART APEX2 Ultra-Cu) with Cu K_{α} radiation ($\lambda = 1.54178$ Å). The crystal was cooled using a low temperature controller (Japan Thermal Engineering, TC-190CP-CS-K). The diffraction frames were integrated with the Bruker SAINT program. The cell constants were determined by the global refinement. The structure was solved by the direct method using the SHELXS-97 program and refined by the full-matrix least-squares method using the SHELXL-2014 program. The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

Crystal Data for Plate-Shaped Crystals of **20**. $C_{39}H_{32}B_2F_{12}N_2S_2$, M = 860.42, monoclinic, a = 17.8505(5) Å, b = 8.3333(2) Å, c = 13.1813(3) Å, $\beta = 104.6708(10)^\circ$, U = 1896.84(8) Å³, T = 93(2) K, space group P2/c (no. 13), Z = 2, 12585 reflections measured, 3334 unique ($R_{int} = 0.0309$), which were used in all calculations. R_1 ($I > 2\sigma(I)$) = 0.0799, wR_2 ($I > 2\sigma(I)$) = 0.2034, R_1 (all data) = 0.0815, wR_2 (all data) = 0.2049, CCDC 1436375.

Crystal Data for Rod-Shaped Crystals of **2c**. $C_{39}H_{32}B_2F_{12}N_2S_2$, M = 860.42, monoclinic, a = 9.7143(2) Å, b = 32.9243(7) Å, c = 11.9342(3) Å, $\beta = 96.4166(10)^\circ$, U = 3793.08(15) Å³, T = 93(2) K, space group $P2_1/c$ (no. 14), Z = 4, 26200 reflections measured, 6560 unique ($R_{int} = 0.0282$), which were used in all calculations. R_1 ($I > 2\sigma(I)$) = 0.0338, wR_2 ($I > 2\sigma(I)$) = 0.0891, R_1 (all data) = 0.0349, wR_2 (all data) = 0.0900, CCDC 1436376.

These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

DSC mesurements

To make phase diagram, compounds **20** and **2c** were weighed to make total amounts of **20** + **2c** are 6.0 mg with changing the ratio. And the mixtures of **20** and **2c** were pound up in an agate mortar (30 mm ϕ) for 1 h in the dark, and the DSC were mesured. In order to avoid the thermal cycloreversion reaction of **2c** to **20**, melting points of the mixtures were recorded between 0~210 °C with heating rate of 10 °C/min. Measurements of grass transition temperatures (T_g) were carried out as second heating after the fitst heating to each melting points of the mixture. However, the all samples after secon heating was all coverted to **20** due to the cycloreversions and could not obtain the T_g of the mixtures. For **2c**, after DSC measurement (peak was observed at 175.2 °C), it was convered to the mixture of **20**: **2c** = 49: 51. Therefore the melting point of **2c** was obtained by Yanaco melting point determination apparatus MP-500D only putting **2c** on heated stage with changing the temperature and obtained the melting point of 190.2 °C.



Fig. S1 DSC measurement of T_g of **20**. DSC curves of the 1st and 2nd heating cycle of **20** with a heating rate of 10 K min⁻¹.



Fig. S2. XRD spectra of microcrystalline surfaces of **20.** Black line: asprepared coated film of **20**, Green line: flat surface after UV (313 nm) irradiation for 5 min, Red line: After visible light (λ >430 nm) irradiation for 5 min to the surface followed by keeping the film at 70 °C for 24 h. The reflections are attributed to **20** crystals.



Fig. S3. The SEM images (gold coated) of the cross-section of the flat surface generated by UV (313 nm) light irradiation for 5 min (a, b) and the appropriate trace curves (c, d). CA of a water droplet on the surface was 59.5±2.6°. (a), (c): ×1000, (b) , (d): ×3000.



Fig. S4. A SEM image (gold coated) (a) of the cross-section of the rough surface generated by visible light (λ>430 nm) irradiation for 5 min to the flat surface followed by keeping at 70 °C for 24 h. (b) The trace curve of the SEM image. (CA of a water droplet was = 0°). ×3000.



Fig. S5. SEM images with extended scale of rough surface of **20** microcrystals generated by storage at 70 °C for 24 h in the dark.



Fig. S6. Thickness dependency of microcrystalline film of 20 on the photoinduced topographical changes were monitored on the films with different thickness of (a): 5.22 µm, (b) 7.76 µm, and (c) 53.0 µm. Same photoinduced topographical changes with CA changes of water droplet were observed. These results indicated that the CA changes dependent on surface properties.



Fig. S7. Reversible CA changes (with optical images of the water droplets) on the surface by alternate irradiation with UV ($\lambda = 313$ nm) light irradiation for 5 min and visible ($\lambda > 430$ nm) light irradiation followed by storage at 70 °C for 24 h.

Table 1. Contact angles measured on the flat surface after UV irradiation (313 nm, 5 min) with water droplets of deionized water (volume 1.5 μL)

	1	2	3	4	5	6	7	8	9	10	Av. CA/°
1st cycle	62.7	59.2	59.2	56.0	54.8	58.8	65.3	52.6	57.8	57.2	58.2±2.4
2nd cycle	57.8	66.7	66.7	59.6	60.5	63.5	61.5	56.1	59.9	54.0	60.7 ± 3.3
3 rd cycle	57.8	63.3	67.8	56.5	54.7	57.0	67.1	56.7	57.0	59.0	59.3±3.9



Fig. S8. The estimated crystal shapes from the crystal units of 2o (above) and 2c(below).

References

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