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Photo-induced reversible topographical changes of photochromic dithienylethene microcrystalline surfaces†

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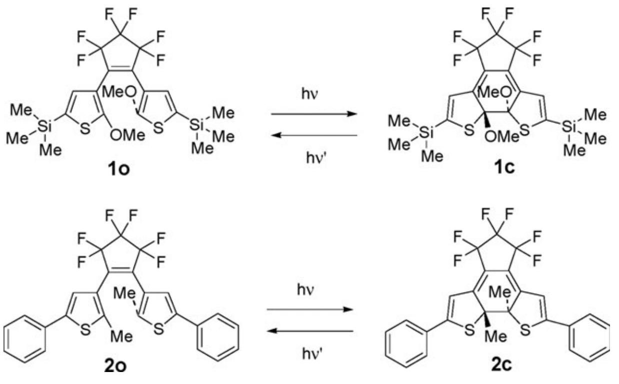
Upon alternating UV and visible light irradiation, the surface of a coated film of 1,2-bis(2-methyl-5-phenylthien-3-yl)perfluorocyclopentene showed reversible surface topographical changes between a lumpy surface with small structures ($\sim$1.0 μm) and a smoother surface with larger structures (5$\sim$10 μm), accompanied by changes in the water droplet contact angle.

Photochromic compounds undergo reversible color changes by alternating UV and visible light irradiation.[1] Diarylethenes, which are some of the most well known photochromic compounds, show thermally stable photochromic performances with high fatigue resistance.[2] Therefore, the study of diarylethenes has especially concentrated on their properties that are directly related to applications for molecular switches and memory devices.[3] Recently, however, we have seen progress in using such photochromic compounds for other applications. For example, reversible bending of rod-like or thin film-like crystals has been observed.[4] Additionally, the selective deposition of Mg atoms and their control has been shown using a diarylethene thin film substrate.[5] The discovery of the photo-controlling of surface wettability is one example of this remarkable progress; *i.e.*, we have demonstrated the reversible formation and deformation of micrometer-scale fibrils on microcrystalline films of diarylethenes **1**, accompanied by changes in the water droplet contact angle (CA).[6] This finding is thus applicable for the photo-control of surface wettability changes. The reversible changes to the CA were attributed to reversible changes in the surface roughness, which was estimated by fractal analysis, obtained by the box-counting method.[6b] In this Letter, we report the reversible topographical changes of a surface of a coated film of **2o** (Scheme 1) to show that such reversible topographical changes are universal phenomena in the diarylethene compound family.

Diarylethenes undergo reversible photoisomerization, even in their crystalline states.[7] The photochromism of **2** in solution and in the crystalline state has already been reported, and its crystals maintain a clear, transparent character during coloration/decoloration cycles at room temperature;[7e,f] photo-induced surface changes were not observed at elevated temperatures. The phase diagram of diarylethene **2** is shown in Fig. 1. The melting points of **2o** and **2c** are 140 and 193 °C, respectively. The eutectic point is 115 °C, where the ratio of **2o** to **2c** is 80 : 20.

Based on the results of the micro-fibril formation of **1**,[6] the photo-induced reversible topographical changes of **2** were expected to occur above 115 °C. Before UV irradiation, the surface of the coated film with **2o** was monitored by SEM, and the image is shown in Fig. 2a. Even before UV irradiation, some rough structures were observed that may be attributable to microcrystals of **2o**, generated when the solvent was evaporated. The surface was irradiated with UV light (254 nm) for 10 min while stored at 115 °C, and then kept in the dark for 6 h at the same temperature. The surface was monitored by SEM and found to be covered by small lumps with a diameter around 1 μm (Fig. 2b); some of the surface looked hexagonal-shaped. Then, the surface was irradiated with visible light ($\lambda > 500$ nm) while the temperature was kept at 115 °C on the hot stage. Because of the lower quantum yield (0.0081 (600 nm)) of the cycloreversion reaction of **2c** compared with the cyclization quantum yield (0.52 (286 nm)) of **2o**,[7f] irradiation was carried out for the initial 1 h of heating. After 90 min, the small lumps disappeared and a different type of rough surface was observed (Fig. 2c and d); time profiles are shown in Fig. 3.



Scheme 1

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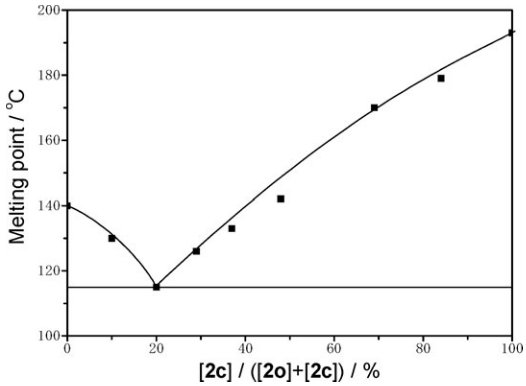

Fig. 1 The phase diagram of mixtures of open (**2o**)- and closed (**2c**)-ring isomers formed upon UV light (313 nm) irradiation.

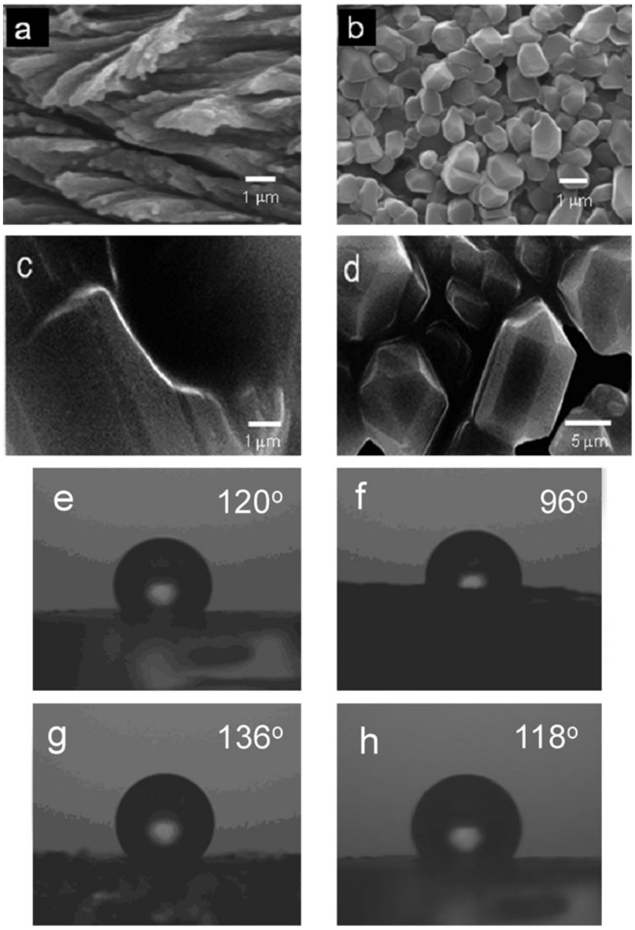

Fig. 2 Surface topographical changes of a diarylethene film of **2**. SEM images: (a) before UV irradiation (×10 000), (b) after UV irradiation (×10 000), (c) after visible light irradiation (×10 000) and (d) after visible light irradiation (×2000). The CAs of a water droplet (e) before UV irradiation, (f) after UV irradiation for 10 min, (g) 6 h after UV light irradiation and (h) after visible light irradiation.

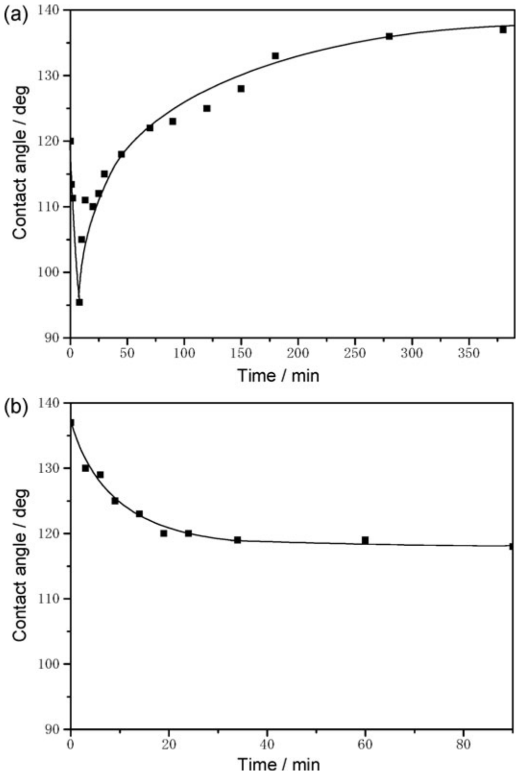

Fig. 3 Time profiles of the water droplet CA on the diarylethene surface. UV irradiation was carried out for an initial 10 min, while visible light irradiation was carried out for an initial 60 min. (a) The time profile of the CA during the micro meter scale cubic structure generation process. (b) The time profile of the CA during the cubic structure disappearance process upon irradiation of the colored structured surface with visible light.

At the same time, the CA of the water droplet changed during both processes (Fig. 2e–h). The angle of a water droplet (1.2 mm ϕ) at the initial surface of **2o** was 120° (Fig. 2e). Upon UV light irradiation, the CA rapidly decreased to 96° in 10 min (Fig. 2f and 3a) as the surface melted, because it was in the eutectic state; a similar phenomenon was observed for **1**.[6] 6 h later, the angle reached a constant value of 136° (Fig. 2g). The CA of the water droplet was enhanced due to the smaller lumpy structures of **2c**, compared with the structures of the initial surface. The smaller angle compared with the surface of diarylethene **1c** is attributable to the crystal shape differences between the closed-ring isomers **1c** and **2c**. Closed-ring isomer **1c** formed needle-like crystals, while **2c** formed cubic-like ones. Upon visible light irradiation of the surface while maintaining the temperature, larger structures (1.0–5.0 μm) had grown on the surface and the CA had been decreased to 118°.

The dipole moment changes of diarylethenes accompanying the photochromism are much smaller than those of azobenzenes and spiropyranes. By the B3LYP/6-31G(d) method, the dipole moment of **2o** and **2c** were calculated to be 3.8768 D and 4.3181 D, respectively. Therefore the CA changes, as shown in Fig. 3, are not attributable to the dipole changes of the diarylethene but to surface topographical changes. Upon alternating UV and visible light irradiation and while maintaining the eutectic temperature, a surface with small lumps (Fig 2b) and another with larger structures (Fig 2c,d) was alternately observed by SEM for two cycles.

To understand the crystal shapes, we estimated the Bravais, Friedel, Donnay and Harker (BFDH) crystal morphology of **2o** and **2c** using Mercury CSD 2.0. The estimated crystal shape of **2o** is a rectangular parallelepiped and that of **2c** is a

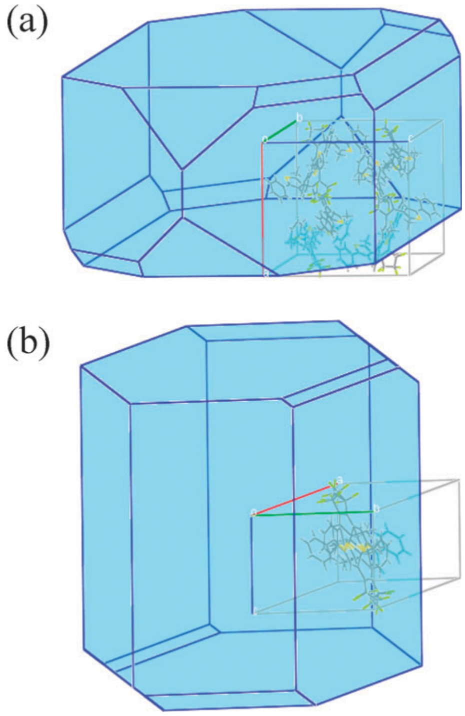

Fig. 4 The estimated crystal shapes from the crystal units of (a) **2o** and (b) **2c**.

hexagonal pillar (Fig. 4). While larger block-like structures could be observed on the surface of **2o**, smaller lumpy structures were observed for **2c**. This difference may reflect the higher melting point of the closed-ring isomer, **2c**. The temperature difference between the eutectic temperature and the melting point of **2o** is 25 °C, while the difference for **2c** is 78 °C. Nucleation would be faster for **2c** because of the larger temperature difference between its melting point and the surroundings (115 °C). Therefore, many smaller crystals would grow due to the larger population of nuclei for **2c**.

In conclusion, photo-induced reversible topographical changes were observed above the eutectic point of open- and closed-ring isomers of a diarylethene-coated film surface, whose crystalline photochromism has already been reported; no surface changes were observed at room temperature. The topographical changes seen on the surface above the eutectic temperature should be universal phenomena in organic photochromic systems.

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Experimental

The film was prepared by coating a chloroform solution containing **2** (100 mg ml^{-1}) onto the substrate (glass, resin or metal), and the solvent was evaporated *in vacuo*. The film thickness, which was approximately 20–30 μm, was measured by observing the scratched surface by SEM. A scanning electron microscope (JEOL JSM-5200) and an optical microscope (Leica DMLP) were used to study the surface microstructure. Static CAs were measured on an optical contact angle meter (Kyowa Interface Science Co., Ltd., Drop Master 500) by the $\theta/2$ method at 25 °C. De-ionized water (1.5 μl) was dropped carefully onto the surface. An average CA value was obtained by measuring the same sample at five to ten different positions (see ESI†). Photoirradiation (visible light: $\lambda > 500$ nm) was carried out using a Ushio 500 W xenon lamp with a cut-off filter (Toshiba color filter Y-50), and UV irradiation was carried out using a Topcon PU-2 (12 W) UV lamp. Photoirradiation experiments at the eutectic temperature were carried out on a Mettler Toledo FP90 instrument attached to a FP82HT hot stage. The crystal data have already been reported in a previous paper.[7e]

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