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Temperature dependence of the photoinduced microcrystalline surface topography of a diarylethene[†]

Noriko Fujinaga,^a Naoki Nishikawa,^a Shingo Sakiyama,^a Seiji Yamazoe,^{ab} Yuko Kojima,^c Tsuyoshi Tsujioka,^d Satoshi Yokojima,^e Shinichiro Nakamura^f and Kingo Uchida^{*a}

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By alternate irradiation with UV and visible light, reversible topographical changes were observed. Step and valley formation while keeping the crystal confinement was observed below the glass transition temperature (T_g), while crystal growth *via* a softened state was observed above the T_g on the same diarylethene crystalline surface.

Photochromic compounds undergo reversible colour changes upon alternating irradiation with UV and visible light.^{1,2} Such photochromic compounds have been applied for photoinduced surface shape changes.^{3–11} Diarylethenes, which are amongst the most studied photochromic compounds, are thermally stable in both coloured and colourless states and show high fatigue resistance.^{12,13} Due to the relatively minor extent of structural change that accompanies the photochromism of the diarylethene derivatives, they can undergo photoisomerization even in the crystalline state, where the distance between the two reactive carbon atoms of the open-ring isomer in the crystalline state is less than 4 Å.¹⁴ Irie *et al* reported the photoinduced formation and deformation of steps and valleys on the surface of a diarylethene single crystal.¹⁵ The colourless single crystals of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (10) turned blue without a change in the shape of the crystal upon irradiation with UV light at room temperature. The colour change is a manifestation of the formation of the closed-ring isomer (1c).¹⁶ Upon irradiation with UV (366 nm) light, new steps appeared on the (100) surface of the crystal which disappeared again upon irradiation with visible light ($\lambda > 500$ nm). The step height of *ca*. 1 nm corresponds to one molecular layer. Irradiation with UV light formed valleys on the (010) surface that also disappear upon irradiation with visible light ($\lambda > 500$ nm). The changes to the surface morphology can be rationalised by the changes to the molecular structure of diarylethenes in the single crystal (Fig. S1, ESI[†]).

Recently, we have shown that topographical changes of the surface can be achieved by the growth and regrowth of crystals of the open-ring or closed-ring isomers upon alternate irradiation with UV and visible light at the eutectic temperature for both isomers.^{17–19} However, such crystal growth was observed previously below the eutectic temperature in a particular diarylethene derivative.¹⁹ This observation raises an important question as to the factors that determine the transition temperature for the two photo-induced changes in the surface (step and valley formation reported by Irie and crystal growth *via* the eutectic state reported by our group). In the present contribution, we report the temperature dependence of the topographical changes observed on single crystals of **10**.

The melting points of mixtures of **10** and **1c** were determined by DSC and the phase diagram obtained is shown in Fig. 1. The melting points of **10** and **1c** are 130 and 189 °C, respectively. The eutectic temperature is 121 °C, where the ratio of **10** to **1c** is 86:14.

Our previous studies^{17,18} indicated that reversible photoinduced topographical changes of **1** were expected to occur above 121 °C. Prior to irradiation with UV light, the surface coated with the film of **10** was characterized by SEM. Upon irradiation with UV light, a relatively rough surface structure

^a Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194, Japan. E-mail: uchida@rins.ryukoku.ac.jp; Fax: +8177 543 7483; Tel: +81 77 543 7462

^b Department of Chemistry, School of Science, the University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 221-0033, Japan

^c Mitsubishi Chemical Group Science and Technology Research Center, INC., 1000 Kamoshida, Yokohama 227-8502, Japan

^d Department of Arts and Sciences, Faculty of Education, Osaka Kyoiku University, 4-698-1 Asahigaoka, Kashiwara, Osaka 582-8582, Japan

^e School of Pharmacy, Tokyo University of Pharmacy and Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan

^f Nakamura Laboratory, RIKEN Research Cluster for Innovation, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

 $[\]dagger$ Electronic supplementary information (ESI) available: estimated crystal shapes from the crystal units of **10** and **1c**, DSC curves of the 1st and 2nd heating of **10** with heating rate of 10 K min⁻¹, and XRD spectra of microcrystalline surface of **10** before and after heating processes. See DOI: 10.1039/c3ce41336e



Fig. 1 The phase diagram of mixtures of open (1o)- and closed (1c)-ring isomers formed by irradiation at 313 nm.

was observed (Fig. 2a) that is ascribed to the presence of microcrystals of **10**, generated upon solvent evaporation. The microcrystalline surface was irradiated with UV light (313 nm) for 5 min at room temperature followed by heating at the



Fig. 2 Surface topographical changes of a film of diarylethene **1o**. (a–g: ×3000, h: ×500) SEM images: (a) before UV irradiation, (b) after UV irradiation for 5 min followed by storage at 121 °C for 5 h in the dark, (c) after UV irradiation and stored at 121 °C for 24 h in the dark, (d) after irradiation with visible light (λ > 480 nm) for 5 min at 121 °C, (e) after irradiation with UV light for 5 min followed by storage at 100 °C for 5 h in the dark, (f) after irradiation with UV light followed by storage at 100 °C for 5 h in the dark, (g) after irradiation with UV light and storage at 50 °C for 5 h in the dark, (h) after irradiation with UV light and storage at 50 °C for 5 h in the dark, (h) after irradiation with UV light and storage at 50 °C for 5 h in the dark.

eutectic temperature of 121 °C for 5 h in the dark. The surface turned blue and micron sized structures, formed from crystals of 1c, were observed on the surface by SEM (Fig. 2b). Prolonged heating (total 24 h) of the surface at the eutectic temperature resulted in further growth of the micro-crystals (Fig. 2c). Irradiation with visible light ($\lambda > 480$ nm) for 5 min at 121 °C resulted in complete decolouration and a pronounced change in the shape of the crystals (Fig. 2d). However, the growth of crystals of 1c was observed even below the eutectic temperature. Indeed, at 100 °C, albeit more slowly than at the eutectic temperature, crystal growth was observed (Fig. 2e, f). At 50 °C, crystallization was not observed within 24 h (Fig. 2g). However, rapid crystallization like "flowering on chocolate" was observed after 48 h (Fig. 2h).²⁰

The Bravais, Friedel, Donnay and Harker (BFDH) crystal morphology²¹ of **10** and **1c** was estimated using Mercury CSD 2.0, to ascertain whether or not the crystals formed upon irradiation with visible and UV light were due to the formation of the crystals of **1c** and **10**, respectively, and to understand the crystal shapes.^{22–24} The estimated crystal shape of **10** is a rectangular parallelepiped and that of **1c** is a hexagonal pillar (Fig. S2, ESI†). These morphologies are clearly found in Fig. 2b (cubic shape of **10** crystals) and Fig. 2c (hexagonal shape of **1c** crystals).

Since the mobility of molecules on the crystal surface is significantly different from that of the same species in the bulk or within the film because of their high surface energy, we used the atomic force microscopy (AFM) force curve $(FC)^{25-28}$ to understand the state of the surface. The results are summarized in Fig. 3. The FC for the surfaces before and after UV irradiation at 22 °C did not present a hysteresis (Fig. 3a and b). These data indicate that the surface was still hard even after irradiation with UV light.

At 30 °C, the FC showed a slight hysteresis without UV irradiation, indicating that the crystal surface softens at that temperature. The FCs for the surfaces before and after UV irradiation at 22 °C are indicative of a relatively hard surface. The slopes (A-B) of the FCs were 36 and 37 nN nm⁻¹, respectively. On the other hand, at 30 °C, the surface prior to irradiation with UV light shows a slope of A–B of only 6.2 nN nm⁻¹. These data indicate that the hard surface softens dramatically at around 30 °C. Above 50°C, the surfaces were too soft to measure the slopes. These data are in agreement with the lowest temperature at which photoinduced topographical changes were observed, with the glass transition temperature of 10 determined to be 27.9 °C by DSC measurements (Fig. 4). At higher temperatures (50, 100 °C), the hysteresis became larger, as shown in Fig. 3d, e. In particular, the FC at 100 °C is not stable and it changed every second. The surface was soft and could not support the cantilever. In contrast, the FC became unstable after UV irradiation even at 30 °C, as shown in Fig. 3f. The FC resembles that of Fig. 3e. Generation of 1c by irradiation with UV light results in softening of the surface. Irie and his co-workers have noted that the crystal surface was considered to be hard, even when irradiated with UV light.¹⁵ The glass transition temperature (T_g) of 10 was determined by



Fig. 3 Force curves obtained by AFM on single crystalline surfaces of **1o** ((a) before and (b) after irradiation with UV light at 22 °C. (c) Before irradiation with UV light at 30 °C. (d) Before irradiation with UV light at 50 °C. (e) Before irradiation with UV light at 100 °C. (f) After irradiation with UV light at 30 °C.) Approach and release processes are depicted as red and blue lines, respectively. The speed of the approach and the release of the cantilever were both 100 nm s⁻¹. The spring constant was 42 N m⁻¹.

DSC to understand the reason why the surface switches from hard at 22 °C to soft at 28 °C upon irradiation with UV light. DSC curves of the 1^{st} and 2^{nd} heating cycle of **10** are shown in Fig. 4.

When heated for the first time, the crystals melted at 133 °C and became amorphous (solidification without crystallization) upon cooling. The T_g was observed at 27.86 °C in the second cycle.

Samples of **10** and **1c** were dissolved in chloroform in various mole ratios and the mixed samples were prepared by solvent evaporation to allow for the determination of T_{g} . For example, for the measurement of a **10**:1c = 85:15 mixture, 8.6 mg of **10** and 1.4 mg of **1c** (the sum of **10** and **1c** is 10 mg) were dissolved into ca. 4 mL of dichloromethane,



Fig. 4 DSC curves of the 1^{st} and 2^{nd} heating cycle of **10** with a heating rate of 10 K min⁻¹.

followed by evaporation *in vacuo* in the dark. Additionally, mixtures with other ratios (10:1c = 71:29 and 10:1c = 55:45) were prepared. The first heating and cooling processes were performed in the same way as for 10. The second heating cycle was performed up to 60 °C. The obtained T_g values were similar to those of 10 (Fig.S3, ESI†).

The microcrystalline surface of **10** was characterized by XRD. Prior to heating, several diffraction peaks were observed, which were not observed after the second heating cycle (up to 50 °C), confirming the change of the crystalline film to an amorphous state during the first heating cycle (Fig. S4, ESI†).

These data indicate that the molecules are strongly confined in the lattice in the crystalline state and reversible step and valley formation was observed upon irradiation with UV light below T_{g} . In contrast, the liquidity of the film increased above the T_{g} and the molecules are able to move and photogenerated **1c** self-aggregates to form lumpy crystals on the surface. This is a common feature in the photoinduced topographical changes that we observe.

Conclusions

In conclusion, reversible photo-induced topographical changes by crystal growth of 1c and 1o occurs via softening of the surfaces of single crystals and microcrystalline film is observed above the T_{g} of the open-ring isomer. While step and valley formation on the crystalline surface was observed below the $T_{\rm g}$, these phenomena are switched at the $T_{\rm g}$ where molecular confinement is drastically changed. Below the T_{g} , the confinement within the crystalline lattice is effective even with the formation of 1c in the crystals upon irradiation with UV light. Therefore, formation of step and valley microstructures was observed on single crystalline surfaces. In contrast, the confinement is relaxed above the T_{g} upon irradiation with UV light and photogenerated 1c self-aggregates to form the microcrystals of 1c on the surface via the softened state. These observations of the intricate relation between the $T_{\rm g}$ and surface mobility hold broader significance for surface topographical changes in photo-control of self-aggregation and surface modification and solid state photo-control in supramolecular systems.

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