

Construction of photo-switchable functional surface by photoinduced crystal growth

March 2020

Ryo Nishimura

Construction of photo-switchable functional surface by photoinduced crystal growth

(光応答性分子の光誘起結晶成長による
新規表面機能材料の創成)

March 2020

Graduate School of Science and Technology

Ryukoku University

龍谷大学 理工学研究科

Ryo Nishimura

西村 涼

Abstract

This thesis describes construction of photo-reactive biomimetic functional surface consisting of photochromic diarylethenes. By controlling the parameters in photoinduced crystal growth technique and vapor deposition method, I succeeded to mimic the surface structures of plants and insects, and regenerated their specific functions.

The thesis consist of two parts, i.e., one is for the biomimetic superhydrophobic surface mimicking the surface structures of some creatures by photoinduced crystal growth technique (chapters 2-4) and the other is for a photo-controllable object transportation system consists of diarylethene platelet crystals mimicking the cilia's motion of paramecium aurelia prepared by the vapor deposition method (chapter 5).

In chapter 2, the preparation of superhydrophobic surface having double roughness structures (DRS) by mimicking the surface structures of lotus leaf is described. The DRS was successfully reproduced on a diarylethene microcrystalline surface. Static superwater-repellency and dynamic waterdrop-bouncing were observed on the surface and were comparable to those on natural lotus leaves.

In chapter 3, we optimised the size and intervals of DRS to improve the bouncing ability. We fabricated a surface structure that closely resembles the natural lotus leaf's characteristic controlling factors of the Laplace pressure. We thus clarified the importance of the double roughness structure of the surface. Moreover, this work clarifies the exquisiteness of the double roughness structure of the leaf.

In chapter 4, the regeneration of the dual wettability on diarylethene microcrystalline surface mimicking a termite wing is described. Upon irradiation with UV light to the microcrystalline surface of mixture of two diarylethene derivatives, two types of needle-shaped crystals of distinctly different sizes are generated. The surface shows the termite wing's dual-wettability.

In chapter 5, we design an object transportation system exploiting the bending behaviour of surface-assembled diarylethene crystals. A photo-actuated smart surface realized transportation of a polystyrene bead to the desired area depending on the direction of the incident light.

In chapter 6, the conclusion is given with a list of my publications.

Contents

Chapter 1

Introduction

1.1 Biomimetic functional materials	1
1.2 Photochromism	5
1.3 The application of photochromic compounds	7
1.4 Photochromic reaction in the crystalline state	9
1.5 Photoinduced crystal growth of diarylethene	13
1.6 Photoinduced bending of diarylethene	15
1.7 Scope of this thesis	17
1.8 References	19

Chapter 2

Fractal Surfaces of Molecular Crystals Mimicking Lotus Leaf with Phototunable Double Roughness Structures

2.1 Introductions	27
2.2 Experimental Section	
2.2.1 Preparation of the diarylethene microcrystalline films and their characterization	29
2.2.2 Fractal analysis of superhydrophobic surfaces	29
2.2.3 Contact angle measurement	30
2.3 Results and Discussion	
2.3.1 Preparation and characterization of double roughness surface	30
2.3.2 Reversibility of the photoinduced double roughness structures	33
2.3.3 Different preparation of the surface and the importance of making thick rod-shaped crystal for the double roughness structure	34
2.3.4 Water droplet bouncing phenomena	35
2.3.5 Theoretical explanation of bouncing of a water droplet	36

2.4 Conclusion	38
2.5 References	39

Chapter 3

Crystal Growth Technique for Formation of Double Roughness Structures Mimicking Lotus Leaf

3.1 Introductions	41
3.2 Experimental Section	
3.2.1 Preparation and observation of the microcrystalline surface	44
3.2.2 Photo-irradiation and heating methods	44
3.2.3 Procedure to prepare double-roughness surface	45
3.2.4 Observation method of contact angle and bouncing phenomena of water droplets	45
3.3 Results and Discussion	
3.3.1 Preparation of double roughness structure (1): Controlling the interval between the structures (rod-shaped crystalline pillars); 1st UV irradiation and 1st annealing	47
3.3.2 Preparation of double roughness structure (2): Controlling the size of the rod-shaped pillars; 2nd UV irradiation	49
3.3.3 Preparation of the double-roughness structures (3): Visible light irradiation to form needle-shaped crystals over entire surface; 1st Vis irradiation	51
3.3.4 Water-droplet bouncing phenomena on the double-roughness surfaces	53
3.3.5 Preparation of double roughness structures (4): Controlling the growth and size of needle-shaped crystals; 3rd UV irradiation and 3rd annealing	56
3.3.6 Theoretical understanding of DRS surface and CGT based on viscous friction in bouncing droplets	58
3.4 Conclusion	60
3.5 References	61

Chapter 4

Dual Wettability on Diarylethene Microcrystalline Surface Mimicking a Termite Wing

4.1 Introductions	63
4.2 Experimental Section	
4.2.1 General information	66
4.2.2 Preparation and characterization of the film	67
4.3 Results and Discussion	
4.3.1 Preparation of crystalline films mimicking the termite wing	68
4.3.2 Water dropping test	71
4.3.3 Water spraying test	73
4.3.4 Theoretical explanation of dual wettability	77
4.4 Conclusion	83
4.5 References	84

Chapter 5

Object transportation system mimicking the cilia of paramecium aurelia making use of the light-controllable crystal bending behaviour of a photochromic diarylethene

5.1 Introductions	86
5.2 Experimental Section	
5.2.1 General information	88
5.3 Results and Discussion	
5.3.1 Photoinduced bending behavior of platelet crystal of 3o	89
5.3.2 Measurement of Young's modulus of the platelet crystal of 3o	91
5.3.3 Preparation of object transportation system	92
5.3.4 The effect of dotted structures for crystal growth	96
5.3.5 Photo-actuation of the surface growing standing platelet crystal	96

5.3.6 Object transportation by the light	98
5.4 Conclusion	99
5.5 References	99

Chapter 6

Conclusions	102
List of publication	104
Acknowledgement	107

Chapter 1

Introduction

1.1 Biomimetic functional materials

In nature, there are many creatures and plants having specific surface structures showing various excellent functions as a strategy to survive safely. By mimicking such surface structures and systems, many researchers investigated to make the functional materials showing specific functions.¹ In general, such research field is called “Biomimetics”. Biomimetics was proposed by Otto H. Schmitt in 1957, by mimicking the shapes, processes and ecological systems of nature to create low environmental loading and sustainable design.² Before advocating this term, velcro tape inspired by a burdock fruit was developed as functional bio-inspired material, and superhydrophobic surface of lotus leaf,³⁻⁶ superhydrophilic surface of snail shell,⁷⁻⁹ non-reflective surface of moth eye,¹⁰⁻¹³ high adhesive materials of gecko’s foot,¹⁴⁻¹⁸ structural colour of morpho butterfly,¹⁹⁻²³ low water resistance of shark skin^{24,25} and so on, were investigated for a long time by many researchers (Fig. 1.1). As mentioned above, environmental load is lower than other artificial materials by using biomimetic materials, therefore, it is necessary to use biomimetic materials for realizing sustainable society. It will be an important research subject.

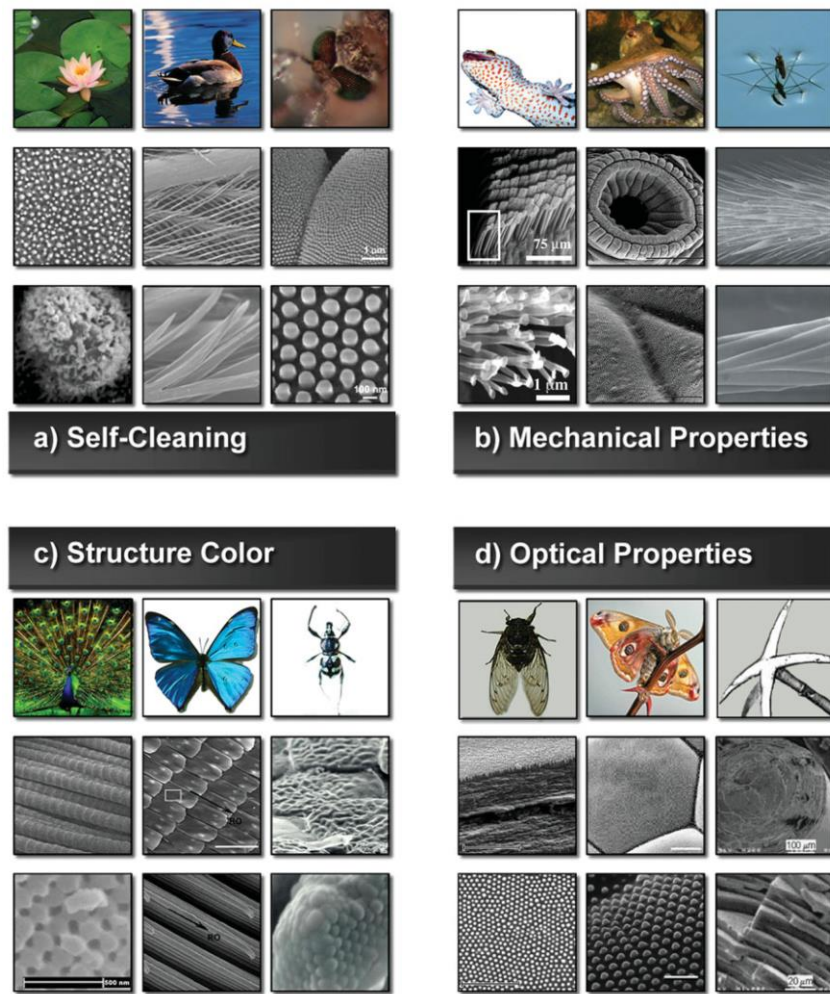


Figure 1.1 Biological functions observed in nature. a) Micro structures showing self-cleaning phenomena of lotus leaf, duck feather and mosquitos' eye. b) Micro structures showing mechanical properties of gecko feet, octopus's suckers and water strider. c) Micro structures showing structural color of peacock feather, butterfly wings and beetle shells. d) Micro structures showing cicada wings, moth compound eyes and sponge spur.

Many researches on biomimetics have been reported. Especially, the superhydrophobic materials mimicking the surface structures of lotus leaf and rose petal were gathering much attention.^{3-6,26} Jiang *et al.* reported biomimetic surfaces showing lotus effect and rose petal effect.²⁶ Lotus leaf has micro- and submicro-structures called Double Roughness Structure (DRS). Owing to the DRS, the surface of a lotus leaf show superhydrophobicity. The contact angle (CA) and sliding angle (SA) of a water droplet on the lotus leaf was 161° and 2° , respectively. This effect is called lotus effect. The superhydrophobicity is also known as self-cleaning effect of

lotus leaf. On the other hand, rose petal shows superhydrophobicity, however, water droplets pinned to the surface. The droplet cannot roll off, even when the petal is turned upside down. It is called rose petal effect. The SEM images of both surfaces were shown in Fig. 1.2.

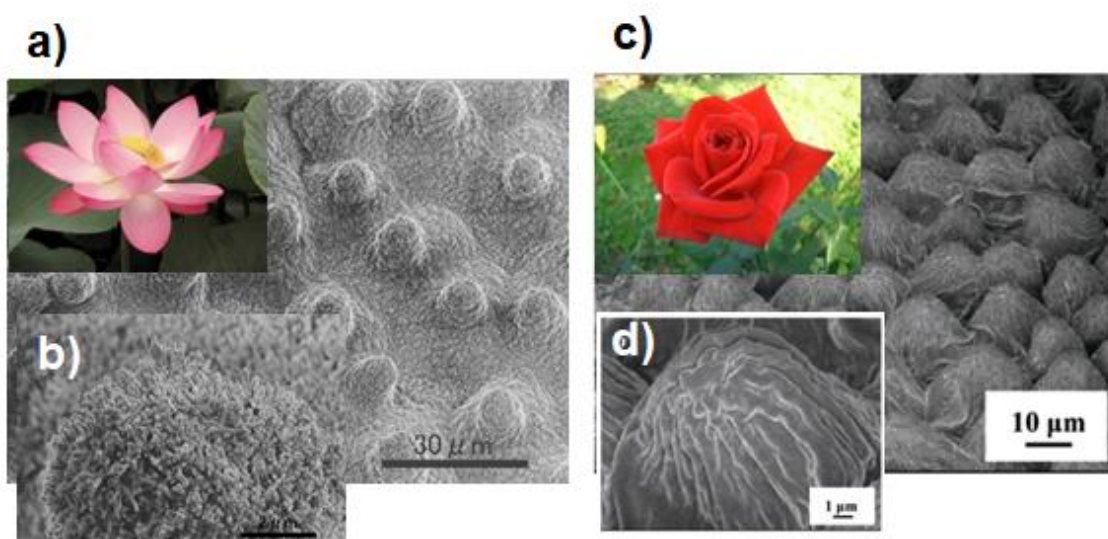


Figure 1.2 The SEM images of lotus leaf and rose petal surface. a) SEM image of lotus leaf, b) magnified SEM image of lotus leaf. c) The SEM image of rose petal surface, d) magnified SEM image of rose petal surface. Scale bars: a) 30 μm , b) 2 μm , c) 10 μm , d) 1 μm .

Unlike the surface structures of lotus leaf, rose petal having micropapillae and nanofolds. These structural differences on the surfaces resulted in different dynamic wetting property. In 2015, Uchida *et al.* reported when the wax tubes on the larger projections were removed by washing the lotus leaf with ethanol, the CA on the surface was reduced from 161° to 122° , i.e., the lotus effect was disappeared (Figs. 1.3, 1.4).²⁷ From this result, the nano-structures on the large projections of DRS are indispensable for realizing the lotus effect.

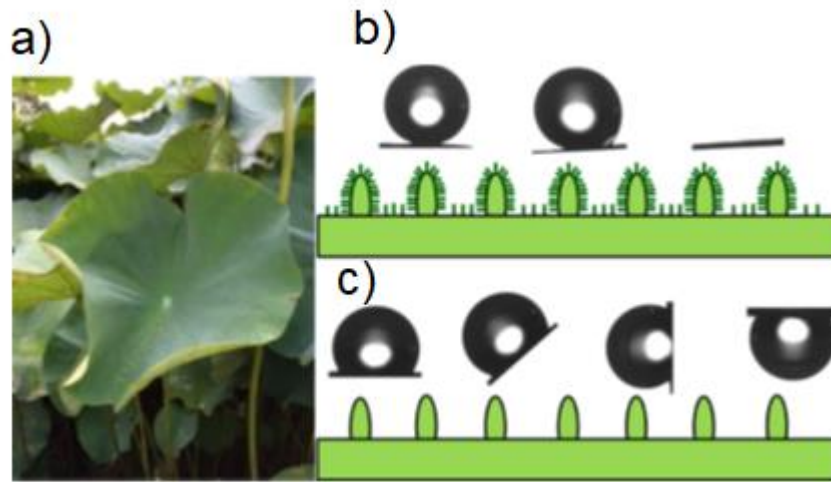


Figure 1.3 A picture of lotus leaf and schematic illustration of lotus leaf with and without DRS. a) A picture of lotus leaf. b) The schematic illustration of lotus leaf with DRS, c) the schematic illustration of lotus leaf without DRS.²⁷

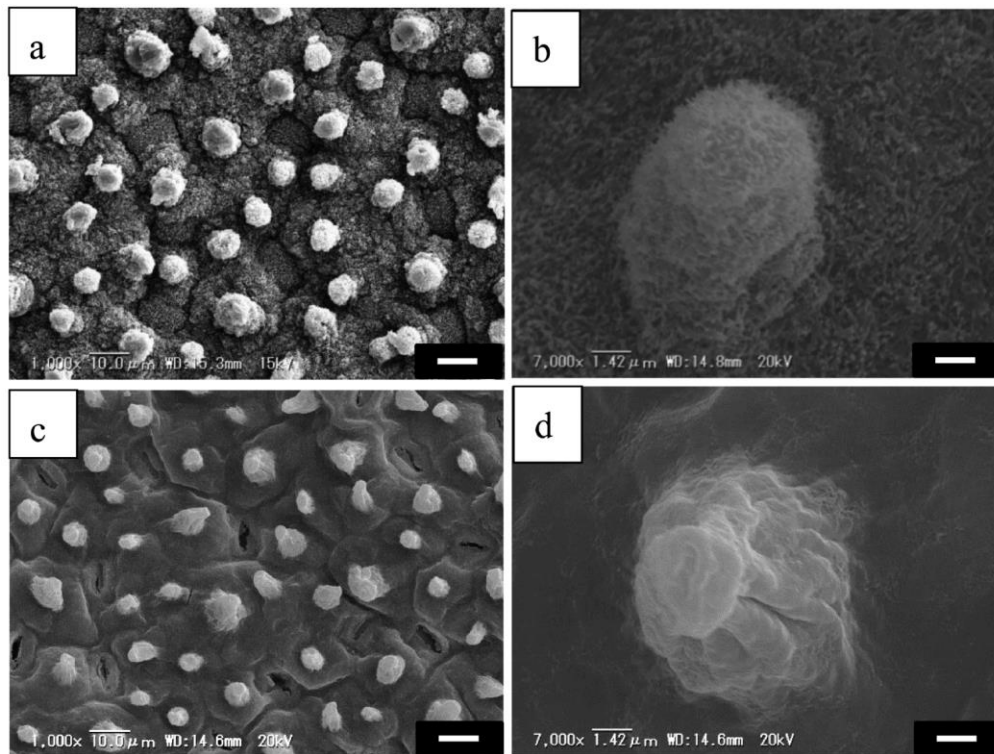


Figure 1.4 The SEM images of surface structures of lotus leaf before and after dipping in ethanol. a) The SEM image and b) magnified SEM image of surface structures of lotus leaf. c) The SEM image and b) magnified SEM image of surface structures of lotus leaf after dipping in ethanol.

As mentioned in above works, the DRS was essential and important for lotus

leaf and superhydrophobic materials. For this reason, superhydrophobic surfaces having DRS were produced, and superhydrophobicity was actually realized.²⁸⁻³¹ However, the making method, for instance, dry- or wet-etching, is not good for environment. Therefore, clean process which doesn't create chemical waste was required.

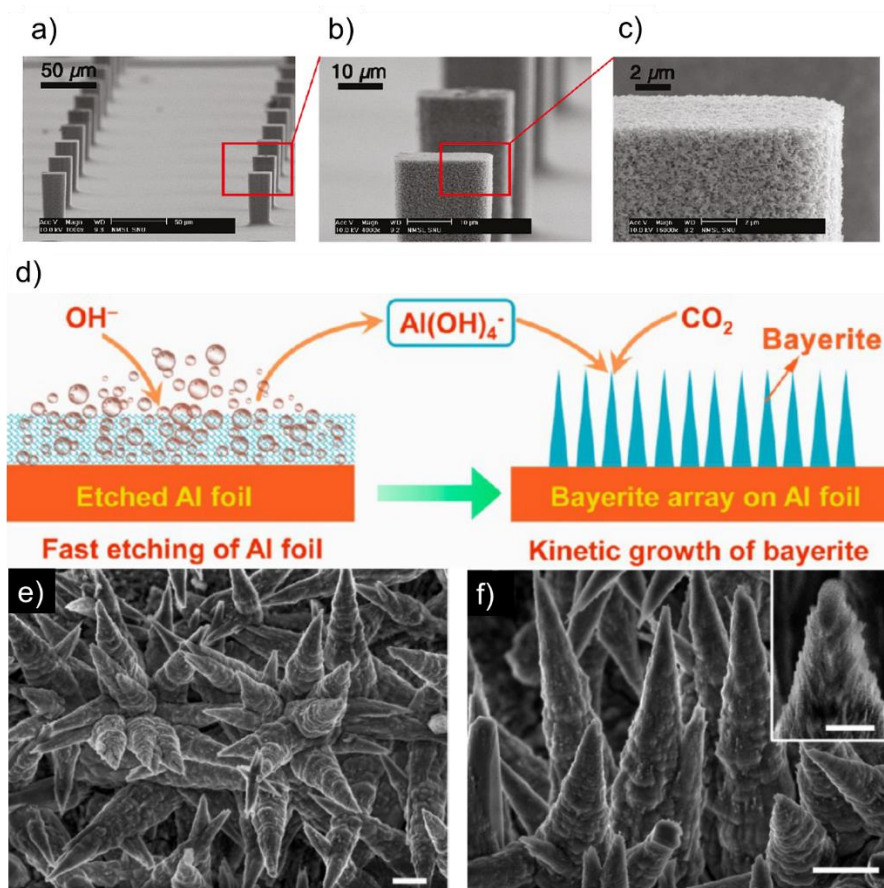


Figure 1.5 Superhydrophobic surfaces having DRS prepared by etching method. a-c) Superhydrophobic surface consist of Si pillar prepared by dry etching method using XeF₂ gas.²⁸ d-f) Superhydrophobic surface consist of Al pillar prepared by wet etching using typical etching aqueous solution.²⁹

1.2 Photochromism

Photochromism is defined as “a reversible transformation of a single chemical species being induced in one or both directions by electromagnetic radiation between two states having different distinguishable absorption spectra.”³² There are many photochromic compounds having varied specific properties. Among them, thermal

stability of both isomers was one of the important points to use them for any environment. The compounds undergo the photochromic reaction reversibly by only use of light stimuli called P type photochromic compounds, on the other hand, reverted to the original isomer through the thermal reaction due to thermal instability of photogenerated isomer called T type photochromic compounds. The typical photochromic compounds are shown in Fig. 1.6.

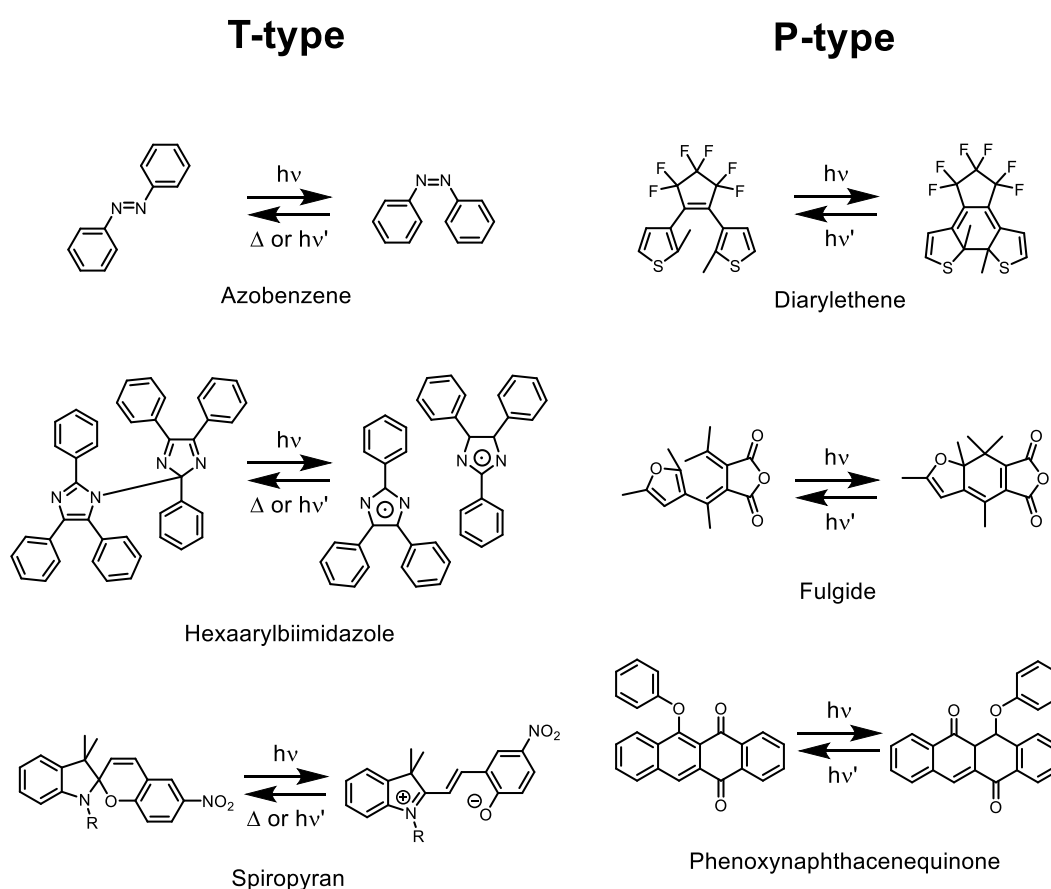
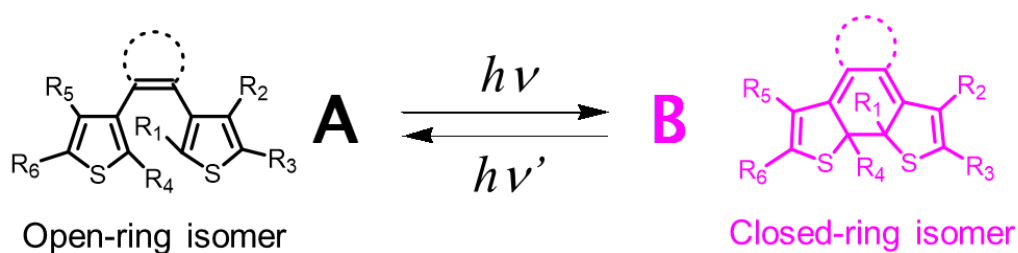


Figure 1.6 Molecular structures of typical thermally stable (right) and unstable (left) photochromic compounds.

Among them, diarylethene classified as P-type photochromic compound has excellent properties such as high thermal stability of both isomer, high fatigue resistance, rapid response time, high reactivity and photochromic reactivity in the crystalline state.^{33,34}



Scheme 1.1 Photo-isomerization of photochromic diarylethene.

Owing to these excellent properties, diarylethene has a possibility to apply for various scientific and industrial field such as optical memory, photo-actuator, bioimaging and so on. Especially, photochromic reaction occur in the crystalline and polymer media is worthy point because of their photo-mechanical properties. Therefore, it is expected to apply to photo-actuator.

1.3 The application of photochromic compounds

Photochromic compounds, especially, azobenzene, spiropyran and diarylethene have been studied as on-off switches to change biological,³⁵⁻⁴¹ optical,⁴²⁻⁴⁷ wetting⁴⁸⁻⁵² and aggregation⁵³⁻⁶¹ properties of various systems owing to their molecular motion, polarity change, absorption change through the photo-isomerization. Hell and Irie reported fluorescent photo-switchable diarylethenes for biolabeling and single-molecule localization microscopies with optical superresolution.⁴⁰ They introduced the carboxylic acid to the turn-on type fluorescent switching diarylethene to increase the water-solubility for the fluorescent probe of single-molecule based fluorescence nanoscopy (STORM). This molecule showed relatively large stokes shift of ~100 nm compared with conventional systems based on STORM. The property of photo-switchable fluorescence is valuable for superresolution imaging because conventional fluorescent probe needed chemical additives for on-off fluorescence switching.

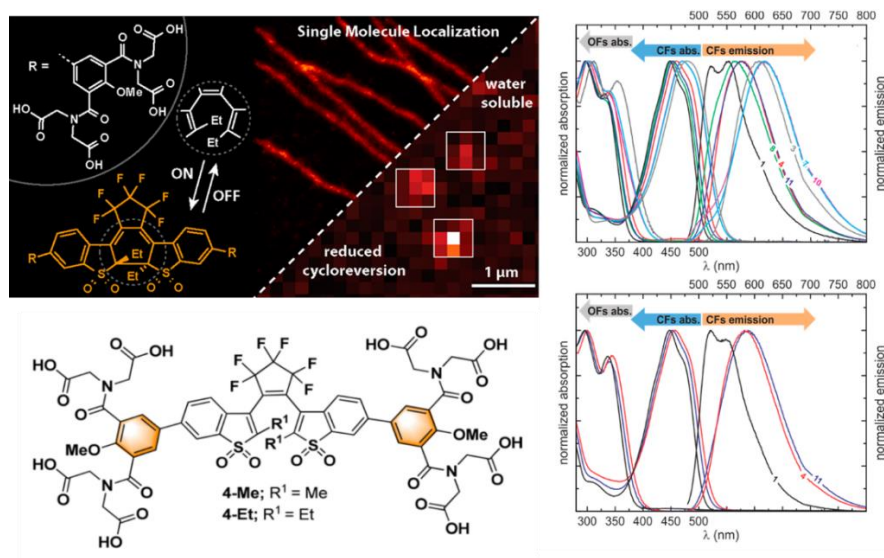


Figure 1.7 Fluorescent switching system for biolabeling and single-molecule localization microscopies with optical superresolution.⁴⁰

Matsuda *et al.* reported reversible photoinduced macroscopic transformation between the microspheres and fibers via photoisomerization of amphiphilic diarylethene derivative.⁵⁸ The amphiphilic diarylethene with nonyloxy chain as the hydrophobic moiety and triethylene glycol unit as the hydrophilic moiety was added in water to obtain the assemblies consist of diarylethenes, a few micrometer sized spheres were generated. Upon irradiation with UV light to the colorless **4o** microsphere, division of spheres were observed and colored **4c** fibers were formed. Furthermore, upon irradiation with visible light to the colored **4c** fibers, the colorless **4o** spheres were restored to the original position. These phenomena were controllable by changing the temperature of solution. Thus, in this work, photoisomerization of photochromic moieties completely change the structure of assemblies.⁵⁸⁻⁶¹

spatially large molecular changes cannot react in the solid state such as molecules with *cis-trans* isomerization. In 1971, Schmidt reported the experimentally observed limit of centre-to-centre distance of double bonds of photo-dimerized monomers.⁶⁷ From the experimental results, they found that the photo-reactive distance between the double bonds is $4.2 \text{ \AA} > d > 3.5 \text{ \AA}$. From these results, when the distance between the reactive atoms or bond is less than $4.2 \text{ \AA}$, photochromic reaction occurred in the solid phase. Photochromic compounds showing photochromic reactivity in the solid state are rare, and in most cases, colored isomers are thermally unstable (e.g. 2,3,4,4-tetrachloronaphthalen-1(4H)-one, salicylideneanilines, hexaarylbiimidazolyl derivatives and so on). If the both isomers are thermally stable, it will have potential to realize various applications in photonic devices. Irie *et al.* reported the relationship between the reactivity and distance between the reactive carbon atoms of diarylethene derivatives in the crystalline state.^{63,64}

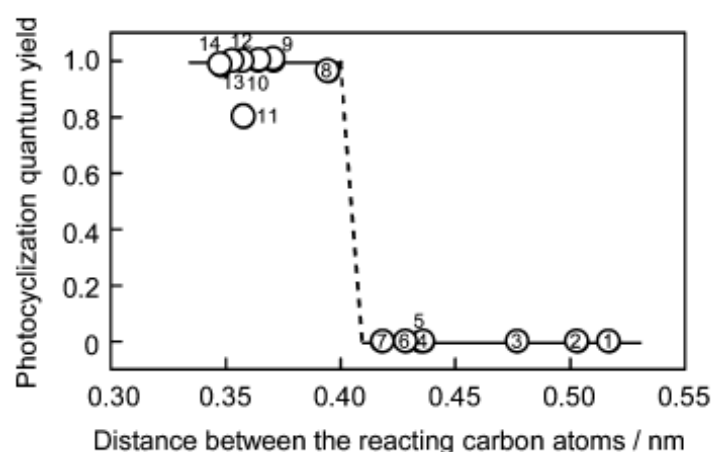


Figure 1.9 The relationship between the photo-cyclization quantum yield and distance between the reacting carbon atoms.⁶³

Similarly, in the case of photochromic reaction of diarylethenes in the crystalline state, the border of reactivity in distance between the reacting carbon atoms is almost $4.2 \text{ \AA}$. Furthermore, the quantum yield of photocyclization reaction is almost unit in the crystalline state.

Recently, Photochromism of diarylethene in the crystalline state have been studied not only reversible colour change as one of the functional dyes but also as functional crystalline systems switching the various optical and mechanical properties.⁸⁰⁻⁸² Irie *et al.* reported the diarylethene crystal showing different photo-reactivity between the two crystals polymorphism having anti-parallel and parallel conformation.⁸⁰ The diarylethene **5o**- α crystal turned green from colourless by UV irradiation, and reverted to the colourless form by visible light irradiation, because the **4o** - α crystal having anti-parallel conformation in the crystal. On the other hand, **5o** - β crystal is packed in parallel conformation; therefore, it cannot undergo photocyclization reaction.

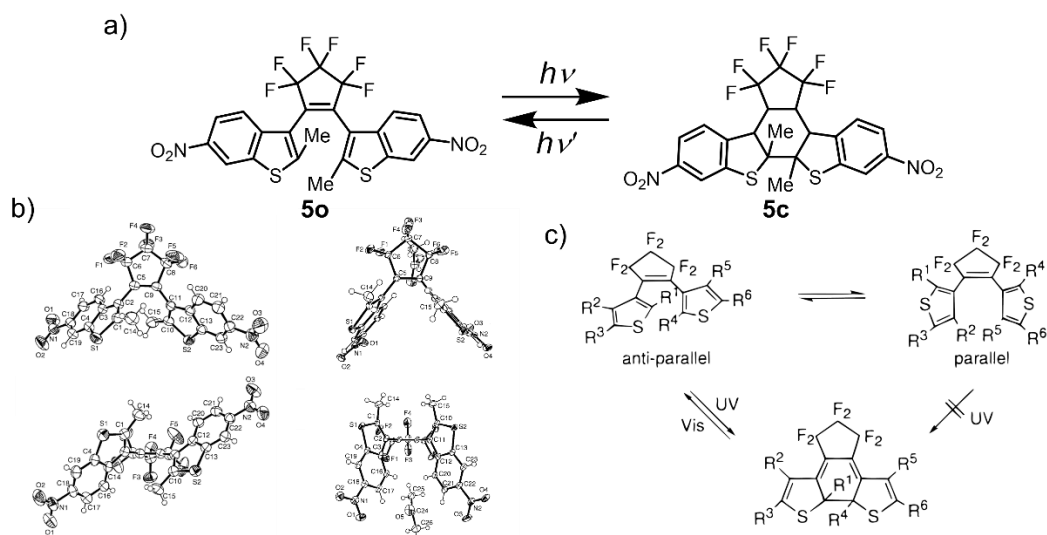


Figure 1.10 Photochromic reaction depending on the molecular conformation in the crystal.

Recently, reversible fluorescent switching of photochromic crystals have been studied.⁸²⁻⁸⁴ Efficient luminescence property in the crystalline state is important ability for application of sensors, electroluminescent display, memory device and bioimaging. Morimoto *et al.* reported turn-on mode fluorescence photo-switchable diarylethene single crystals with high quantum yields.⁸² The turn-off luminescence mode which is initially luminescent and gradually quenched by UV irradiation due to the generation of closed-ring isomers, is not suitable for applications due to the limitation of contrast of on/off switching. On the other hand, the turn-on luminescence mode which is

initially non luminescent and photoluminescence ability is activated by UV irradiation, is suitable due to the high on/off switching contrast.

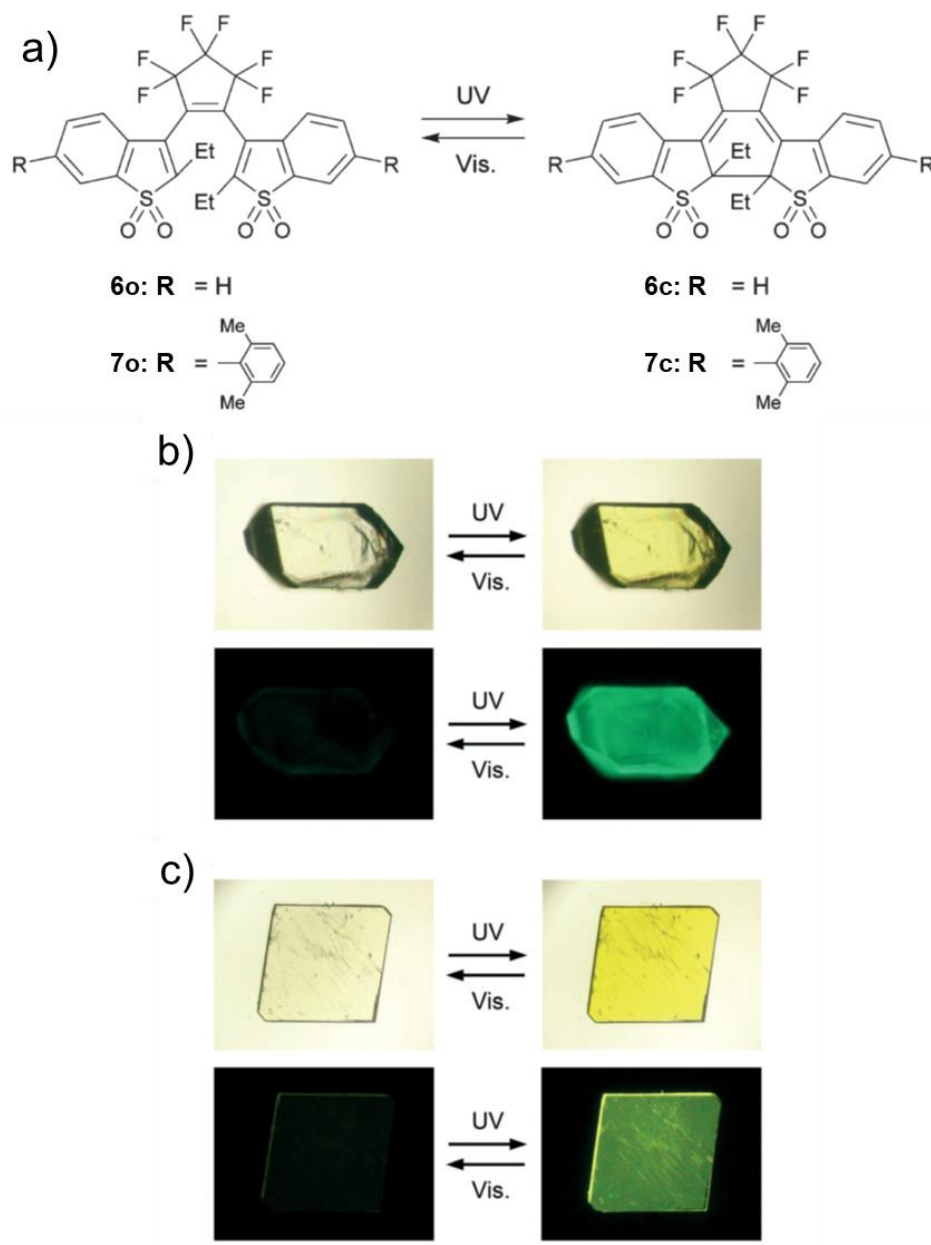


Figure 1.11 Molecular structures and optical images of diarylethenes. a) photo-isomerization of diarylethene molecules. b) Optical images of diarylethene crystal of **6o** and c) **7o**. Top: photoinduced photoisomerization by irradiation with UV ($\lambda = 365$ nm) and visible ($\lambda > 460$ nm) light, bottom: photoinduced fluorescence changes under dark-field observation. The excitation wavelength for fluorescence detection were 450 and 480 nm for **6o** and **7o**, respectively.⁸²

The colourless and non-fluorescent crystals of **6o** and **7o** were isomerized yellow coloured crystals, and they showed green and yellow-green fluorescence, respectively. By using this high contrasted turn-on mode fluorescent switching system, reversible rewritable patterned fluorescent switching with spatially patterned light was realized. As shown above, diarylethene crystal expected to applied in many fields as optical materials.

1.5 Photoinduced crystal growth of diarylethene

The photochromic reaction of diarylethenes undergo even in the crystalline state, which satisfy the condition of Schmidt's empirical rule.⁶⁷ The investigation of photochromic reactions of diarylethenes in the crystalline state have been studied during the past two decades.^{44,62-66,80-84,95-111} Among them, photo-switching of surface properties of diarylethene crystal such as geometry and wettability is considerably attractive from the view point of memory devices,⁸⁵⁻⁹⁴ optical materials^{44,65,82} and self-cleaning materials.⁹⁵⁻⁹⁹ Irie *et al.* reported photoinduced morphological changes of a diarylethene single crystal depending on the crystal surface planes observed by atomic force microscopy (AFM).¹⁰⁰ Upon irradiation with UV ($\lambda = 366$ nm) light to the (100) plane of single crystal of **8o**, step (2.0 and 3.0 nm) appeared on the surface, and disappeared by visible light ($\lambda > 500$ nm) irradiation (Figs. 1.12d-f). On the other hand, on the surface of (010) crystal surface, the valley (10 to 50 nm in depth) was appeared and disappeared by alternate UV and visible light irradiation (Figs. 1.12g-i). These morphological changes were explained by the decreasing of distance between the edges of phenyl rings from 1.41 to 1.39 nm and of c axes of unit cell, and generation of vacancies corresponding to the molecular layers.

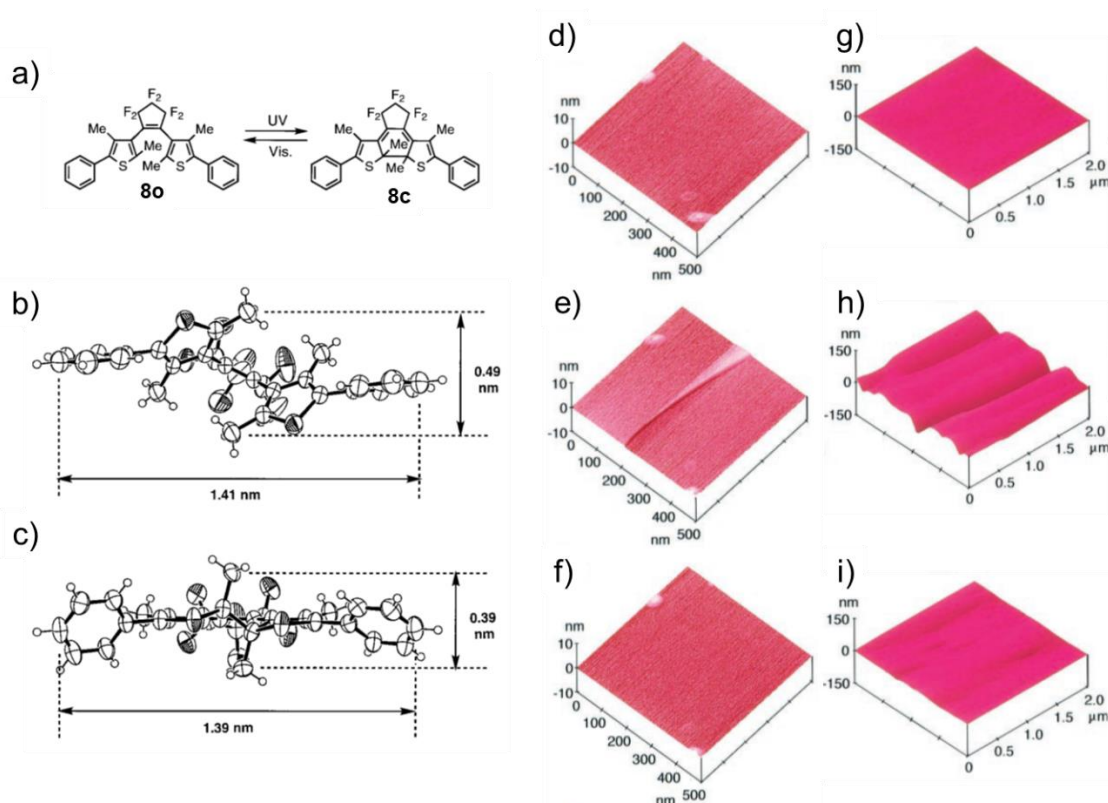


Figure 1.12 ORTEP drawing of diarylethene from the X-ray analysis and AFM images of the (100) crystal surface and (010) crystal surface before and after UV irradiation. a) Molecular structures of diarylethenes, b, c) ORTEP drawing of **8o** b) and **8c** c). d-f) AFM images of (100) crystal surface before and after UV irradiation. g-i) AFM images of (010) crystal surface before and after UV irradiation.¹⁰⁰

Following this work, photoinduced topographical changes were reported.^{95-99,101-113} Uchida *et al.* reported the reversible topographical changes of diarylethenes alternate UV and visible light irradiation.⁹⁵ Upon irradiation with UV light to the surface of **1o** single crystal and kept it at room temperature in the dark, the needle-shaped crystals were generated onto the surface, and the crystals were melted and reverted to the original flat surface followed by visible light irradiation. Furthermore, by changing the heating temperature higher, the sizes of crystals became larger via the Ostwald ripening of the small needle-shaped crystals.⁹⁶ By using this crystal growth technique (CGT), we have realized several biomimetic surfaces such as superhydrophobic surface, superhydrophilic surface and anti-reflection surfaces using several diarylethene derivatives.^{95-98,108}

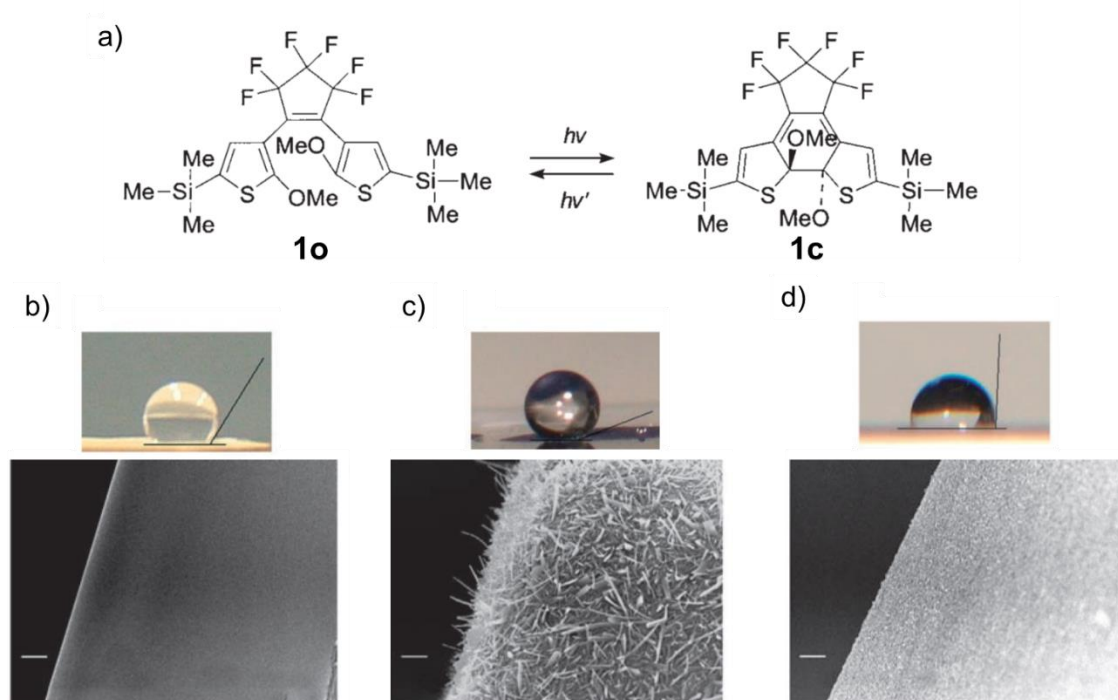


Figure 1.13 Molecular structures of diarylethene **1** and reversible topographical changes of diarylethene single crystalline surface. a) Molecular structures of diarylethene **1o**. b) SEM image and surface wettability of single crystalline surface of **1o** before UV irradiation, c) after UV irradiation followed by heating at room temperature, d) after visible light irradiation.⁹⁵

1.6 Photoinduced bending of diarylethene crystal

The photochromic molecule undergoes the photochromic reaction in the crystalline state has a possibility for the light driven actuator.¹¹⁴⁻¹²³ Among them, diarylethene can be a candidate for light driven actuator. Recently, the fundamental and applied research of photomechanical crystals have been studied. There are many external stimuli responsive materials, among them, the photo-responsive materials have some advantages as readily controllable photo-reactivity by using light with different wavelength, usable synergistically photo and thermal effect by only photoirradiation and they can work without any contact to the materials. Reversible photo-induced shape and size changes of diarylethene crystals were initially reported by Irie.¹¹⁸ The single crystal of **9o** and **10o** reversibly changes their shapes and sizes upon alternate irradiation with UV and visible light irradiation. The response time is

25 microseconds, it is about five order of magnitude faster than that of azobenzene based polymer systems.¹²⁴⁻¹²⁶ Furthermore, the rod-shaped crystal of **10o** bent towards the direction of incident light, and it can move the microscopic objects by photoinduced bending motion of rod-shaped crystal.

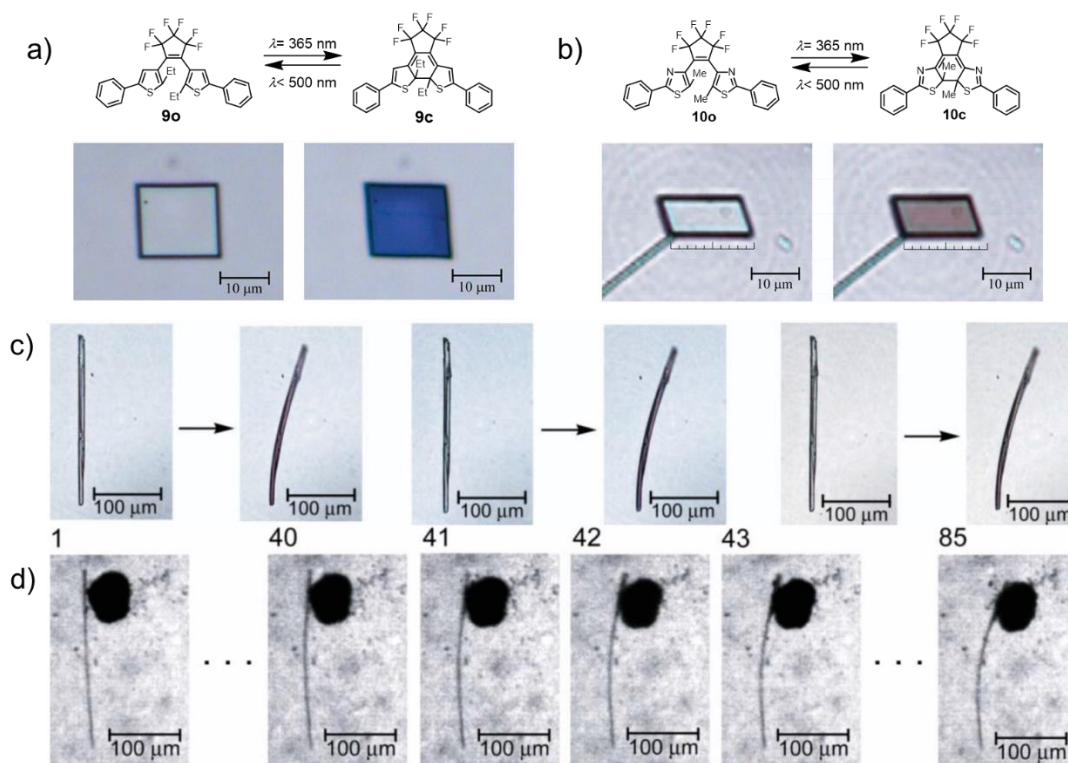


Figure 1.14 Reversible shape and size changes of diarylethene crystals via photoisomerization. a) A single crystal of **9o** changed corner angle of crystal from 88° and 92° to 82° and 98° upon UV irradiation. b) A rectangular single crystal of **10o** reversibly shrinking and expanded by as much as 7%. c) Reversible bending of rod-shaped crystal of **10o** upon alternate UV and visible light irradiation. d) Movement of a gold micro-particle by bending behaviour of rod-shaped crystal of **10o** upon UV light.

After this report, many photoinduced crystal bending of diarylethene derivatives has been reported.^{122-123,127-137} Kobatake reported many works relating to the photomechanical behaviour of diarylethene derivatives.¹³¹⁻¹⁴⁰ They have been studied about quantitative evaluation of photoinduced crystal bending of diarylethene,¹³¹⁻¹³³ specific bending motions of diarylethene crystals e.g. twisting and multi-step bending motion,¹³⁴⁻¹³⁷ response to polarized light,¹³⁸ photo-fragmentation of crystal¹³⁹ and

application for light driven actuator.¹⁴⁰ The mechanisms of photoinduced bending behaviour were almost clarified, therefore, the application of bending crystals was required.

1.7 Scope of this thesis

The fundamental studies of photochromic diarylethenes has been well studied by many researchers in the past thirty years. Many attractive studies have been studied in a various range of scientific field, for example, photochromic reactivity depending on the phase of diarylethenes, molecular assembly, fluorescence property, biological application, surface topographical changes, photomechanical properties and so on. However, it seems that the studies having potential applicable to real society are relatively few examples. The author considers the reason of this, as a one of them, the results has been observed in small region in micro- or nano-order. Then, the author constructs the system showing viewable macroscopic change or motion caused by changes in molecular level such as photo-isomerization of diarylethene molecules. Especially, the author focused on the “biomimetics” mimicking the fine surface structure and motion of plant and creatures. From the view point of this concept, we design and regenerate the functional molecular system showing macroscopic output.

In this doctoral thesis, we reported four topics relation to the development of biomimetic functional material by using the photochromic diarylethenes.

In chapter 2, we described about preparation of superhydrophobic surface having double roughness structures (DRS) by mimicking the surface structures of lotus leaf. The DRS, the origin of the lotus effect of natural lotus leaf, was successfully reproduced on a diarylethene microcrystalline surface by clean method. Static superwater-repellency and dynamic waterdrop-bouncing were observed on the surface, in the manner of natural lotus leaves. DRS was essential for water-drop bouncing ability. This ability was not observed on a microcrystalline with single roughness structures (SRS) showing the lotus effect of the same diarylethene derivative. The double roughness structure was reversibly controlled by alternating irradiation with UV and visible light.

In chapter 3, we optimised the size and intervals of DRS to improve the bouncing ability. We have developed a crystal growth technique (CGT) over the past decade,

and from this we fabricated a surface structure that closely resembles the natural lotus leaf's characteristic of controlling the Laplace pressure and clarified the importance of the double roughness structure of the surface. Moreover, this work clarifies the exquisiteness of the double roughness structure of the leaf. We also show that CGT is a versatile technique with the potential to fabricate desired structured surfaces.

In chapter 4, we regenerate the dual wettability on diarylethene microcrystalline surface mimicking a termite wing. The termite wing has a specific property of wetting in contact with a water droplet. It adsorbs water mist while larger water droplets are bounced on the surface. This is due to the survival strategy of termites. Here, we reproduce the termite wing's dual-wettability by a photoinduced crystal growth technique. Upon UV irradiation to a microcrystalline surface of a mixture of two diarylethenes, two types of needle-shaped crystals of distinctly different sizes are observed to grow. The surface shows the termite wing's dual-wettability. The bouncing ability of a water droplet is attributed to the smaller-sized needle crystals, while the adhesive property is due to the larger-sized ones, explaining the microstructures of the termite wing. Considering dissipation energy and adhesion energy, the bouncing ability and dual wettability can be explained theoretically. The surface could potentially be used as collectors of mists to get water.

In chapter 5, we design the object transportation system mimicking the cilia of *Paramecium aurelia* by using photo-controllable crystal bending behaviour of photochromic diarylethene. The design of an object transportation system exploiting the bending behaviour of surface-assembled diarylethene crystals is reported. A photoactuated smart surface based on this system can transport polystyrene beads to a desired area depending on the direction of the incident light. Two main challenges were addressed to accomplish directional motion along a surface: first, the preparation of crystals whose bending behaviour depends on the direction of incident light; second, the preparation of a film on which these photochromic crystal plates are aligned. Nuclei generation and nuclear growth engineering were achieved by using a roughness-controlled dotted micro-structured substrate. This system demonstrates how to achieve a mechanical function as shown by remote-controlled motion along a surface.

1.7 References

- 1) F. Xia L. Jiang, *Adv. Mater.* **2008**, 20, 2842–2858.
- 2) J. M. Harkness, *Phys. perspect.* **2002**, 4, 456–490.
- 3) M. Xiang, A. Wilhelm, C. Luo, *Langmuir* **2013**, 29, 7715–7725.
- 4) W. Barthlott, C. Neinhuis, *Planta* **1997**, 202 1–8.
- 5) L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, 14, 1857–1860.
- 6) V. Zorba, E. Stratakis, M. Barberoglou, E. Spanakis, P. Tzanetakis, S. H. Anastasiadis, C. Fotakis, *Adv. Mater.* **2008**, 20, 4049–4054.
- 7) J. M. C. Hutchinson, *Biol. J. Linneun Soc.* **2000**, 70, 161–187.
- 8) N. Isu, *J. Soc. Cosmet. Chem. Japan* **2006**, 40, 187–194.
- 9) N. Isu, *J. Jpn. Weld. Soc.* **2009**, 78, 187–190.
- 10) P. B. Clapham, M. C. Hutley, *Nature* **1973**, 244, 281–282.
- 11) W-L. Min, B. Jiang, P. Jiang, *Adv. Mater.* **2008**, 20, 3914–3918.
- 12) S. Giselsbrecht, M. Reinhardt, T. Mappes, M. Börner, E. Gottwald, C. van Blitterswijk, V. Saile, R. Truckenmüller, *Adv. Mater.* **2011**, 23, 4873–4879.
- 13) C-M. Chen, C-L. Chiang, C-L. Lai, T. Xie, S. Yang, *Adv. Funct. Mater.* **2013**, 23, 3813–3823.
- 14) K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, R. J. Full, *Nature* **2000**, 405, 681–685.
- 15) J. Lee, B. Bush, R. Maboudian, R. S. Fearing, *Langmuir* **2009**, 25, 12449–12453.
- 16) A. Y. Y. Ho, L. P. Yeo, Y. C. Lam, I. Rodri'guez, *ACS Nano* **2011**, 5, 1897–1906.
- 17) J. Yu, S. Chary, S. Das, J. Tamelier, N. S. Pesika, K. L. Turner, J. N. Israelachvili, *Adv. Funct. Mater.* **2011**, 21, 3010–3018.
- 18) K. Liu, J. Du, J. Wua, L. Jiang, *Nanoscale* **2012**, 4, 768–772.
- 19) M. Srinivasarao, *Chem. Rev.* **1999**, 99, 1935–1961.
- 20) Y. Zheng, X. Gao, L. Jiang, *Soft Matter* **2007**, 3, 178–182.
- 21) M. Liu, Y. Zheng, J. Zhai, L. Jiang, *Acc. Chem. Res.* **2010**, 43, 368–377.
- 22) C. Liu, J. Ju, Y. Zheng, L. Jiang, *ACS nano* **2014**, 8, 1321–1329.
- 23) Z. Han, Z. Mu, B. Li, Z. Wang, J. Zhang, S. Niu, L. Ren, *ACS Nano* **2016**, 10, 8591–8602.

- 24) P. Ball, *Nature* **1999**, *400*, 507–509.
- 25) W. Kaiyaded, E. Wimolmala, W. Harnnarongchai, W. Sitticharoen, N. Sombatsompop, *J. Appl. Polym. Sci.* **2012**, *125*, 2312–2321.
- 26) L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, L. Jiang, *Langmuir* **2008**, *24*, 4114–4119.
- 27) M. Yamamoto, N. Nishikawa, H. Mayama, Y. Nonomura, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2015**, *31*, 7355–7363.
- 28) Y. Kwon, N. Patankar, J. Choi, J. Lee, *Langmuir* **2009**, *25*, 6129–6136.
- 29) L. Liu, X. Feng, M. Guo, *J. Phys. Chem. C* **2013**, *117*, 25519–25525.
- 30) P. Wang, T. Zhao, R. Bian, G. Wang, H. Liu, *ACS Nano* **2017**, *11*, 12385–12391.
- 31) Y. Li, M. Zheng, L. Ma, M. Zhong, W. Shen, *Inorg. Chem.* **2008**, *47*, 3140–3143.
- 32) H. Dürr, H. B-Laurent, *Photochromism Molecules and Systems*, studies in organic chemistry 40, **1990**, p5.
- 33) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.
- 34) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.
- 35) U. A-Atar, R. Fernandes, B. Johnsen, D. Baillie, N. R. Branda, *J. Am. Chem. Soc.* **2009**, *131*, 15966–15967.
- 36) R. Kodama, K. Sumaru, K. Morishita, T. Kanamori, K. Hyodo, T. Kamitanaka, M. Morimoto, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Commun.* **2015**, *51*, 1736–1738.
- 37) J. Okuda, Y. Tanaka, R. Kodama, K. Sumaru, K. Morishita, T. Kanamori, S. Yamazoe, K. Hyodo, S. Yamazaki, T. Miyatake, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Commun.* **2015**, *51*, 10957–10960.
- 38) P. Shi, E. Ju, Z. Yan, N. Gao, J. Wang, J. Hou, Y. Zhang, J. Ren, X. Qu, *Nat. Commun.* **2016**, *7*, 13088.
- 39) J. Zhang, Y. Fu, H.-H. Han¹, Y. Zang, J. Li, X.-P. He, B. L. Feringa, H. Tian, *Nat. Commun.* **2017**, *8*, 987.
- 40) B. Roubinet, M. Weber, H. Shojaei, M. Bates, M. L. Bossi, V. N. Belov, M. Irie, S. W. Hell, *J. Am. Chem. Soc.* **2017**, *139*, 6611–6620.
- 41) J. Qi, C. Chen, X. Zhang, X. Hu, S. Ji, R. T. K. Kwok, J. W. Y. Lam, D. Ding, B. Z. Tang, *Nat. Commun.* **2018**, *9*, 1848.

- 42) J. Su, T. Fukaminato, J.-P. Placial, T. Onodera, R. Suzuki, H. Oikawa, A. Brosseau, F. Brisset, R. Pansu, K. Nakatani, R. Métivier, *Angew. Chem. Int. Ed.* **2016**, 55, 3662–3666.
- 43) S. Ishida, T. Fukaminato, D. Kitagawa, S. Kobatake, S. Kim, T. Ogata, S. Kurihara, *Chem. Commun.* **2017**, 53, 8268–8271.
- 44) S. Ishida, D. Kitagawa, S. Kobatake, S. Kim, S. Kurihara, T. Fukaminato, *Chem. Commun.* **2019**, 55, 5681–5684.
- 45) J. Bu, K. Watanabe, H. Hayasaka, K. Akagi, *Nat. Commun.* **2014**, 5, 3799.
- 46) S. Kim, S.-J. Yoon, S. Y. Park, *J. Am. Chem. Soc.* **2012**, 134, 12091–12097.
- 47) M. Sakai, T. Seki, Y. Takeoka, *Small* **2018**, 1800817.
- 48) S. Samanta, J. Locklin, *Langmuir* **2008**, 24, 9558–9565.
- 49) G. Joseph, J. Pichardo, G. Chen, *Analyst* **2010**, 135, 2303–2308.
- 50) D. Wang, P. Jiao, J. Wang, Q. Zhang, L. Feng, Z. Yang, *J. Appl. Polym. Sci.* **2012**, 125, 870–875.
- 51) P. Tannouri, K. M. Arafah, J. M. Krahn, S. L. Beaupré, C. Menon, N. R. Branda, *Chem. Mater.* **2014**, 26, 4330–4333.
- 52) Y. Yang, T. Zhang, J. Yan, L. Fu, H. Xiang, Y. Cui, J. Su, X. Liu, *Langmuir* **2018**, 34, 15812–15819.
- 53) S. Yagai, K. Iwai, M. Yamauchi, T. Karatsu, A. Kitamura, S. Uemura, M. Morimoto, H. Wang, F. Würthner, *Angew. Chem. Int. Ed.* **2014**, 53, 2602–2606.
- 54) B. Adhikari, Y. Yamada, M. Yamauchi, K. Wakita, X. Lin, K. Aratsu, T. Ohba, T. Karatsu, M. J. Hollamby, N. Shimizu, H. Takagi, R. Haruki, S. Adachi, S. Yagai, *Nat. Commun.* **2017**, 8, 15254.
- 55) T. Kobayashi, Y. Kitamoto, Y. Hirai, T. Kajitani, T. Seki, S. Yagai, *Commun. Chem.* **2018**, 1, 58.
- 56) B. Adhikari, T. Suzuki, L. Xu, M. Yamauchi, T. Karatsu, S. Yagai, *Polymer* **2017**, 128, 356e362.
- 57) B. Adhikari, K. Aratsu, J. Davis, S. Yagai, *Angew. Chem. Int. Ed.* **2019**, 58, 3764–3768.
- 58) K. Higashiguchi, G. Taira, J. Kitai, T. Hirose, K. Matsuda, *J. Am. Chem. Soc.* **2015**, 137, 2722–2729.
- 59) A. Sakaguchi, K. Higashiguchi, H. Yotsuji, K. Matsuda, *J. Phys. Chem. B* **2017**,

- 121, 4265–4272.
- 60) H. Yotsuji, K. Higashiguchi, R. Sato, Y. Shigeta, K. Matsuda, *Chem. Eur. J.* **2017**, *23*, 15059–15066.
- 61) A. Sakaguchi, K. Higashiguchi, K. Matsuda, *Chem. Commun.* **2018**, *54*, 4298–4301.
- 62) M. Irie, K. Uchida, T. Eriguchi, H. Tsuzuki, *Chem. Lett.* **1995**, *24*, 899–900.
- 63) S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Commun.* **2002**, 2804–2805.
- 64) S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195–210.
- 65) M. Morimoto, M. Irie, *Chem. Commun.* **2005**, 3895–3905.
- 66) S. Takami, L. Kuroki, M. Irie, *J. Am. Chem. Soc.* **2007**, *129*, 7319–7326.
- 67) G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678.
- 68) W. Marckwald, *Z. Physk. Chem.* **1899**, *30*, 140.
- 69) W. C. Clark, G. F. Lothian, *Trans. Faraday Soc.* **1958**, *54*, 1790–1796.
- 70) M. Scherl, D. Haarer, J. Fischer, A. DeCian, J.-M. Lehn, Y. Eichen, *J. Phys. Chem.* **1996**, *100*, 16175–16186.
- 71) A. Schmidt, S. Kababya, M. Appel, S. Khatib, M. Botoshansky, Y. Eichen, *J. Am. Chem. Soc.* **1999**, *121*, 11291–11299.
- 72) J. Harada, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.* **1999**, *121*, 5809–5810.
- 73) A. Takanabe, M. Tanaka, K. Johmoto, H. Uekusa, T. Mori, H. Koshima, T. Asahi, *J. Am. Chem. Soc.* **2016**, *138*, 15066–15077.
- 74) T. Taniguchi, H. Sugiyama, H. Uekusa, M. Shiro, T. Asahi, H. Koshima, *Nat. Commun.* **2018**, *9*, 538.
- 75) T. Taniguchi, H. Sato, Y. Hagiwara, T. Asahi, H. Koshima, *Commun. Chem.* **2019**, *2*, 19.
- 76) H. Sugiyama, K. Johmoto, A. Sekine, H. Uekusa, *Cryst. Growth Des.* **2019**, *19*, 4324–4331.
- 77) K. Maeda, T. Hayashi, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 429.
- 78) M. Kawano, T. Sano, J. Abe, Y. Ohashi, *J. Am. Chem. Soc.* **1999**, *121*, 8106–8107.
- 79) M. Kawano, T. Sano, J. Abe, Y. Ohashi, *Chem. Lett.* **2000**, *29*, 1372–1373.
- 80) S. Kobatake, M. Yamada, T. Yamada, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 8450–8456.
- 81) K. Morimoto, H. Tsujioka, D. Kitagawa, S. Kobatake, *Bull. Chem. Soc. Jpn.* **2019**,

- 92, 1299–1304.
- 82) M. Morimoto, R. Kashihara, K. Mutoh, Y. Kobayashi, J. Abe, H. Sotome, S. Ito, H. Miyasaka, M. Irie, *CrystEngComm* **2016**, *18*, 7241–7248.
 - 83) D. Kitagawa, T. Nakahama, K. Mutoh, Y. Kobayashi, J. Abe, H. Sotome, S. Ito, H. Miyasaka, S. Kobatake, *Dyes Pigm.* **2017**, *139*, 233–238.
 - 84) T. Nakahama, D. Kitagawa, H. Sotome, S. Ito, H. Miyasaka, S. Kobatake, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 153–157.
 - 85) K. Uchida, M. Saito, A. Murakami, S. Nakamura, M. Irie, *ChemPhysChem* **2003**, *4*, 1124–1127.
 - 86) K. Uchida, M. Saito, A. Murakami, S. Nakamura, M. Irie, *Adv. Mater.* **2003**, *15*, 121–125.
 - 87) M. Saito, T. Miyata, A. Murakami, S. Nakamura, M. Irie, K. Uchida, *Chem. Lett.* **2004**, *33*, 786–787.
 - 88) K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura, M. Irie, *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 31–36.
 - 89) K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura, M. Irie, *Chem. Eur. J.* **2005**, *11*, 534–542.
 - 90) A. Takata, M. Saito, S. Yokojima, A. Murakami, S. Nakamura, M. Irie, K. Uchida, *Jpn. J. Appl. Phys.* **2007**, *45*, 7114–7120.
 - 91) A. Takata, S. Yokojima, H. Nakagawa, Y. Matsuzawa, A. Murakami, S. Nakamura, M. Irie, K. Uchida, *J. Phys. Org. Chem.* **2007**, *20*, 998–1006.
 - 92) H. Li, S. Pu G. Liu, W. Liu, B. Yao, *Front. Chem. China* **2010**, *5*, 234–240.
 - 93) K. Mori, Y. Ishibashi, H. Matsuda, S. Ito, Y. Nagasawa, H. Nakagawa, K. Uchida, S. Yokojima, S. Nakamura, M. Irie, H. Miyasaka, *J. Am. Chem. Soc.* **2011**, *133*, 2621–2625.
 - 94) T. Nakahama, D. Kitagawa, H. Sotome, S. Ito, H. Miyasaka, S. Kobatake, *Dyes Pigm.* **2019**, *160*, 450–456.
 - 95) K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura, M. Irie, *Angew. Chem. Int. Ed.* **2006**, *45*, 6470–6473.
 - 96) K. Uchida, N. Nishikawa, N. Izumi, S. Yamazoe, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii, M. Irie, *Angew. Chem. Int. Ed.* **2010**, *49*, 5942–5944.

- 97) N. Nishikawa, H. Kiyohara, S. Sakiyama, S. Yamazoe, H. Mayama, T. Tsujioka, Y. Kojima, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2012**, *28*, 17817–17824.
- 98) N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2013**, *29*, 8164–8169.
- 99) D. Kitagawa, S. Kobatake, *Chem. Sci.* **2012**, *3*, 1445.
- 100) M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769–1772.
- 101) N. Izumi, N. Nishikawa, S. Yokojima, Y. Kojima, S. Nakamura, S. Kobatake, M. Irie, K. Uchida, *New J. Chem.* **2009**, *33*, 1324–1326.
- 102) N. Nishikawa, A. Uyama, T. Kamitanaka, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii, K. Uchida, *Chem. Asian J.* **2011**, *6*, 2400–2406.
- 103) A. Uyama, S. Yamazoe, S. Shigematsu, M. Morimoto, S. Yokojima, H. Mayama, Y. Kojima, S. Nakamura, K. Uchida, *Langmuir* **2011**, *27*, 6395–6400.
- 104) S. Sakiyama, S. Yamazoe, A. Uyama, M. Morimoto, S. Yokojima, Y. Kojima, S. Nakamura, K. Uchida, *Cryst. Growth Des.* **2012**, *12*, 1464–1468.
- 105) N. Fujinaga, N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, T. Tsujioka, S. Yokojima, S. Nakamura, K. Uchida, *CrystEngComm* **2013**, *15*, 8400–8403.
- 106) N. Nishikawa, H. Mayama, Y. Nonomura, N. Fujinaga, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2014**, *30*, 10643–10650.
- 107) N. Fujinaga, N. Nishikawa, R. Nishimura, K. Hyodo, S. Yamazoe, Y. Kojima, K. Yamamoto, T. Tsujioka, M. Morimoto, S. Yokojima, S. Nakamura, K. Uchida, *CrystEngComm* **2016**, *18*, 7229–7235.
- 108) K. Takase, K. Hyodo, M. Morimoto, Y. Kojima, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Commun.* **2016**, *52*, 6885–6887.
- 109) K. Uchida, R. Nishimura, E. Hatano, H. Mayama, S. Yokojima, *Chem. Eur. J.* **2018**, *24*, 8491–8506.
- 110) K. Tawa, T. Kadoyama, R. Nishimura, M. Toma, K. Uchida, *J. Photochem. Photobiol. A* **2018**, *356*, 397–402.
- 111) T. Kadoyama, R. Nishimura, M. Toma, K. Uchida, K. Tawa, *Langmuir* **2018**, *34*, 4217–4223.
- 112) R. O. Nuñez, D. Fragouli, F. Pignatelli, A. Scarpellini, E. Gigliotti, E.

- Samoylova, A. Athanassiou, *Langmuir* **2014**, *30*, 13058–13064.
- 113) G. Nanni, L. Ceseracciu, R. O. Nuñez, C. Canale, P. Salvatore, D. Fragouli, A. Athanassiou, *Langmuir* **2015**, *31*, 6072–6077.
- 114) L. Zhu, R. O. Al-Kaysi, R. J. Dillon, F. S. Tham, C. J. Bardeen, *Cryst. Growth Des.* **2011**, *11*, 4975–4983.
- 115) H. Koshima, R. Matsuo, M. Matsudomi, Y. Uemura, M. Shiro, *Cryst. Growth Des.* **2013**, *13*, 4330–4337.
- 116) O. S. Bushuyev, A. Tomberg, T. Friščić, C. J. Barrett, *J. Am. Chem. Soc.* **2013**, *135*, 12556–12559.
- 117) L. Zhu, F. Tong, C. Salinas, M. K. Al-Muhanna, F. S. Tham, D. Kisailus, R. O. Al-Kaysi, C. J. Bardeen, *Chem. Mater.* **2014**, *26*, 6007–6015.
- 118) N. K. Nath, L. Pejov, S. M. Nichols, C. Hu, N. Saleh, B. Kahr, P. Naumov, *J. Am. Chem. Soc.* **2014**, *136*, 2757–2766.
- 119) N. K. Nath, T. Runčevski, C. Y. Lai, M. Chiesa, R. E. Dinnebier, P. Naumov, *J. Am. Chem. Soc.* **2015**, *137*, 13866–13875.
- 120) A. Takanabe, M. Tanaka, K. Johmoto, H. Uekusa, T. Mori, H. Koshima, T. Asahi, *J. Am. Chem. Soc.* **2016**, *138*, 15066–15077.
- 121) T. Taniguchi, A. Kubota, T. Moritoki, T. Asahi, H. Koshima, *RSC Adv.* **2018**, *8*, 34314–34320.
- 122) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778–781.
- 123) M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172–14178.
- 124) Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, 145.
- 125) T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, *Adv. Mater.* **2003**, *15*, 201–205.
- 126) Y. Yu, M. Nakano, A. Shishido, T. Shiono, T. Ikeda, *Chem. Mater.* **2004**, *16*, 1637–1643.
- 127) K. Uchida, S. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y. Kojima, S. Nakamura, J. Areephong, A. Meetsma, B. L. Feringa, *Chem. Commun.* **2008**, 326–328.
- 128) E. Hatano, M. Morimoto, K. Hyodo, N. Yasuda, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Eur. J.* **2016**, *22*, 12680–12683.

- 129) E. Hatano, M. Morimoto, T. Imai, K. Hyodo, A. Fujimoto, R. Nishimura, A. Sekine, N. Yasuda, S. Yokojima, S. Nakamura, K. Uchida, *Angew. Chem. Int. Ed.* **2017**, 56, 12576–12580.
- 130) Y. Nakagawa, M. Morimoto, N. Yasuda, K. Hyodo, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Eur. J.* **2019**, 25, 7874–7880.
- 131) D. Kitagawa, S. Kobatake, *J. Phys. Chem. C* **2013**, 117, 20887–20892.
- 132) D. Kitagawa, C. Iwaihara, H. Nishi, S. Kobatake, *Crystals* **2015**, 5, 551–561.
- 133) A. Hirano, T. Hashimoto, D. Kitagawa, K. Kono, S. Kobatake, *Cryst. Growth Des.* **2017**, 17, 4819–4825.
- 134) D. Kitagawa, H. Nishi, S. Kobatake, *Angew. Chem. Int. Ed.* **2013**, 52, 9320–9322.
- 135) D. Kitagawa, R. Tanaka, S. Kobatake, *CrystEngComm* **2016**, 18, 7236–7240.
- 136) D. Kitagawa, K. Kawasaki, R. Tanaka, S. Kobatake, *Chem. Mater.* **2017**, 29, 7524–7532.
- 137) D. Kitagawa, H. Tsujioka, F. Tong, X. Dong, C. J. Bardeen, S. Kobatake, *J. Am. Chem. Soc.* **2018**, 140, 4208–4212.
- 138) A. Hirano, D. Kitagawa, S. Kobatake, *CrystEngComm* **2019**, 21, 2495–2501.
- 139) D. Kitagawa, T. Okuyama, R. Tanaka, S. Kobatake, *Chem. Mater.* **2016**, 28, 4889–4892.
- 140) D. Kitagawa, S. Kobatake, *Chem. Commun.* **2015**, 51, 4421–4424.

Chapter 2

Fractal Surfaces of Molecular Crystals Mimicking Lotus Leaf with Phototunable Double Roughness Structures

2.1 Introductions

In nature, many plants and insects have superhydrophobic surfaces (water contact angles (CAs) larger than 150°) with double roughness structure. For example, the lotus leaf and legs of a water strider have the double roughness structure. Here, the double roughness structure is the origin of the superhydrophobic lotus effect which is useful for self-cleaning materials and floating ability on a water surface. We started this research to clarify the importance of the structure.¹⁻⁴ Historically, the most important finding is the “lotus effect” by Barthlott and Neinhuis.^{2,3} They investigated the superwater-repellent and self-cleaning effect of the lotus leaf and attributed it to the double roughness surface structure with micro- and nanostructures (trichomes, cuticular folds, and wax crystals), together with the hydrophobic properties of epicuticular wax.^{5,6} Since air pockets are maintained in the structure, a water droplet can move more easily, and the structure induces the self-cleaning effect. On the other hand, the bouncing of a water drop on the lotus leaf also plays an important role in self-cleaning, and artificial double roughness structures have been prepared.⁷⁻¹³ Parkin et al. fabricated superhydrophobic self-cleaning surfaces with the dual-scale nature of TiO_2 nanoparticles, and demonstrated that self-cleaning is based on surface micro/nanomorphologies.⁷ Here, we report a guiding principle to prepare the double roughness structure of a diarylethene microcrystalline surface with superhydrophobicity and the ability to bounce a water droplet on it. Recently, much attention was paid to the stimuli-responsive organic crystals. Naumov et al. discovered photo- and thermosalient organic crystals, and many types of mechanically responsive molecular crystals were reviewed.¹⁴⁻¹⁶ Burgess et al. reported the phototunable wetting of hybrid materials with inverse opal structures.¹⁷ In previous papers, we controlled surface topography on the microcrystalline surface of a thermally irreversible photochromic diarylethene **1o** (Fig. 2.1),¹⁸⁻²⁰ which has the photoreactivity in the

crystalline state.^{21,22} Upon UV irradiation to the microcrystalline **1o** film, needle-shaped crystals of **1c** grew on the surface, and a superhydrophobic lotus effect was observed. Then these crystals were melted upon irradiation with visible light, and the lotus effect disappeared. Surface wettability depends on crystal sizes. While controlling the needle-shaped crystals of **1c** to around 1–2 μm in diameter and 10 μm in length by keeping the surface at 30 $^{\circ}\text{C}$ for 24 h in the dark, a superwater-repellant lotus effect was observed (contact angle (CA) and the sliding angle (SA) of a water droplet was about 163 $^{\circ}$ and 2 $^{\circ}$, respectively). In contrast, a surface covered with needle-shaped crystals and rod-shaped crystals (diameters and lengths approximately 5–10 μm and 20–30 μm , respectively) was prepared by two steps of UV irradiation and thermal control. The surface showed the property to adhere a water droplet, i.e., the rose-petal effect (CA = 154 $^{\circ}$ but with a water droplet pinned on the surface).^{19,20} The topography of those superhydrophobic surfaces was single roughness structures.²³⁻²⁹

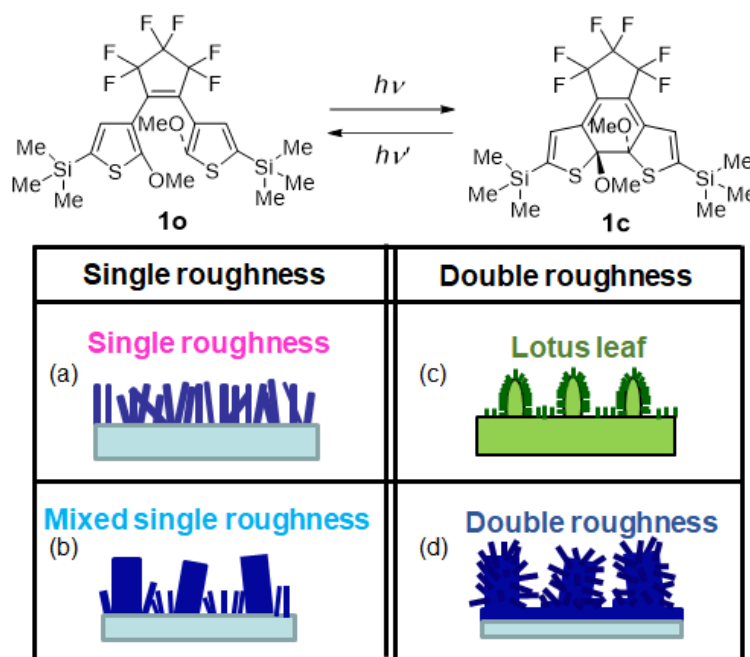


Figure 2.1 Molecular structures of the open- and closed-ring isomers of a photochromic diarylethene **1**, and four different surface structures. A single roughness surface of the diarylethene (a), a mixed single roughness surface of the diarylethene (b), the double roughness surface of natural lotus leaf (c), a double roughness surface of the diarylethene (d).

2.2 Experimental section

2.2.1 Preparation of the diarylethene microcrystalline films and their characterization.

The thin films of diarylethene **1** were prepared by a solution casting by using a chloroform solution (100 mg/ml) on a brass plate, and solvent was evaporated in vacuo. The films were stored in the dark at room temperature. The film thickness was approximately 20 μm by measuring the cross-section of the microcrystalline films from the side view by a scanning electron microscope (KEYENCE VK-8800). The SEM was also used to study the surface microstructures. Photoirradiation (visible light: $\lambda > 480\text{ nm}$) was carried out using an Ushio 500-W xenon lamp with a cut-off filter (Toshiba color filter Y-48), and UV irradiation was carried out with a TOPCON UV lamp (PU21; $\lambda = 254, 312, 365\text{ nm}$, 23 W (distance: 1 cm)). Photoinduced crystal growth experiments after UV irradiation were performed in a house-made hot stage with temperature controller. The crystal data were already reported in a previous paper.¹⁸

2.2.2 Fractal analysis of superhydrophobic surfaces

For the fractal analysis, the sample on a cover glass was set on the electron microscope stage with conductive carbon tape. The cross-section was observed for the sample that was cracked with the cover glass and set perpendicularly on the stage and observed by the SEM after the Au-Pd alloy was evaporated onto the sample surface. The fractal dimension of the cross-section of the rough solid surfaces was calculated from the trace curves of the surfaces by the box-counting method. A two-dimensional space containing the above trace curve was divided by identical boxes of side size r like a piece of cross section paper. The number of boxes containing trace curve $N(r)$ was counted, and then side size r was changed. The number of boxes was counted again for new side size r , and the above process was repeated. Based on the box-counting method the fractal dimension can be calculated from the following relationship:

$$N(r) \propto r^{-D} \quad (\text{S1})$$

where D is the fractal dimension. Dimension D in Eq. (S1) is the fractal dimension of

the cross-section.

2.2.3 Contact angle measurement

Static contact angles (CAs) and sliding angles (SAs) were measured on an optical contact angle meter (Drop Master 500, Kyowa Interface Science Co., Ltd.) with a water droplet with 1.5 μL . For the dropping test, we dropped a water droplet (7.6 ± 0.6 μL of ion-exchanged water) from 4 mm high (speed=1.2 m/s) to natural lotus leaves and diarylethene microcrystalline surfaces with observing on an optical contact angle meter (Drop Master 501, Kyowa Interface Science Co., Ltd.) attached with Hamiltonian micro syringe (1700 series, Luer tip normal syringe with inner diameter of 0.15 mm). The motion of the droplet was captured using a high-speed camera (attached with Drop Master 501) at 1000 frames per second. Measurements were carried out for 10 times for each surface sample.

2.3 Results and discussion

2.3.1 Preparation and characterization of double roughness surface

Here, we prepared a photo-responsive superhydrophobic surface with double roughness structures using the same diarylethene **1o** shown in Fig. 2.1. Initially the microcrystalline surface of **1o** (Fig. 2.2-1) was irradiated with UV light. Due to photoisomerization, the colorless **1o** near the surface became blue **1c** (Fig. 2.2-2). Then, the needle-shaped crystals of **1c** grew on the surface by storage at 50 °C (Fig. 2.2-3). After storage for 24 h at 50 °C in the dark, the surface was covered with rod-shaped crystals of **1c** (Fig. 2.2-4). The topographical change on the surface is due to Ostwald ripening.¹⁹ To make the double roughness structure, we assumed that thicker rod-shaped crystals would not melt upon visible light irradiation and could play the role of a larger-sized structure of the double roughness structure.

In order to make fat (thick) rod-shaped crystals of **1c**, we further applied this Ostwald ripening. We again irradiated the surface in Fig. 2.2-4 with UV light and stored it at 70 °C for 3 h in the dark (Fig. 2.2-5): the small rod-shaped crystals of **1c** grew from the newly generated **1c** on the surface (Fig. 2.2-6), and they were incorporated in the larger rod-shaped crystals (Fig. 2.2-7a). The rod-shaped crystals, especially small ones, grew in size. The average width and length of these rod-shaped

crystals at the state shown in Fig. 2.2-7a were 10 and 21 μm , respectively.

Upon visible light irradiation to the surface of the Fig. 2.2-7a state, cycloreversion reaction from **1c** to **1o** proceeded, and the surface was covered with cubic-shaped crystals of **1o** (Fig. 2.2-8a) on the 10 μm rough structures. The size of each bumpy rod-shaped crystal was almost the same as that of a projection on a lotus leaf covered with plant wax tubes. As expected, the enlarged crystals were not melted: otherwise, the smaller rod-shaped crystals of **1c** would be lost due to Ostwald ripening or melted to form a flat surface upon visible light irradiation.¹⁹⁻²⁰ Upon UV irradiation to the surface, each rod-shaped crystal was covered with needle-shaped crystals of **1c** of 0.2-0.5 μm width and 3-5 μm length, and double roughness structures were prepared (Fig. 2.2-9a). The needle-shaped crystals were much smaller than those grown on the flat microcrystalline surface of **1o**. This is due to the small supply of **1c** crystals to form needle-shaped crystals on each projection. Fig. 2.2-7b,8b,9b shows SEM images of the surfaces of the states shown in Fig. 2.2-7a,8a,9a, and Fig. 2.2-7c,8c,9c shows SEM images of cross sections of samples in Fig. 2.2-7b,8b,9b. The distribution of the sizes of the microstructures on natural lotus leaf was reported by using box-counting fractal analysis.³⁰ The size distribution of the double roughness structure was very similar to that of natural lotus leaf (Fig. 2.3). The CAs of water droplets on the surfaces of rod-shaped crystals of **1c** (Fig. 2.2-7a,7b,7c) and cubic crystals of **1o** (Fig. 2.2-8a,8b,8c) were around 130°, and water droplets were pinned on the surface, even when the surfaces were upside down (Fig. 2.2-7d, 8d). After formation of double roughness structures, CA and SA on the surface changed to $161.9 \pm 2.0^\circ$ and 2° , respectively. The advanced (CA_{ad}) and receding (CA_{rec}) CAs of a water droplet were $162.0 \pm 1.6^\circ$ and $158.3 \pm 1.4^\circ$, respectively. Thus, a remarkable lotus effect was observed (Fig. 2.2-9d).

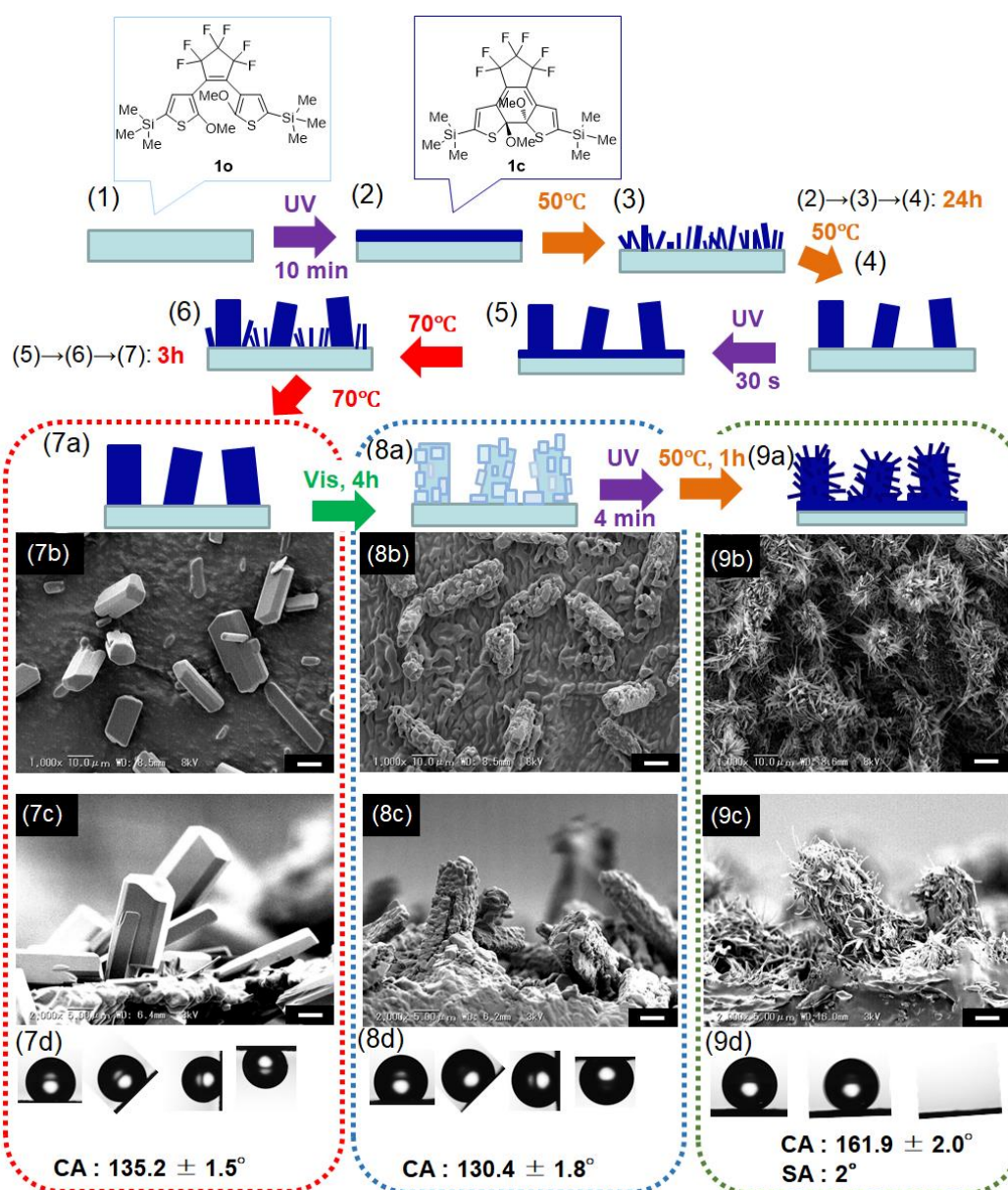


Figure 2.2 Preparation of lotus surface with double roughness structures (1-9a): pale blue and dark blue parts correspond to crystals of **1o** and **1c**, respectively. SEM images of each surface: (7b) surface with rod-shaped crystals of **1c**, (8b) after visible light irradiation to surface of 7b, (9b) after second UV irradiation to the surface of 7b followed by storing at 50 °C for 1 h in dark; (7c, 8c, 9c) the side view of the surfaces of 7b, 8b, 9b, respectively; (7d, 8d, 9d) water droplet (1.5 μ L) on surfaces of 7b, 8b, and 9b, respectively. Scale bars, 10 μ m for 7b-9b images, which are magnified 1000 times; 5 μ m for 7c-9c images, which are magnified 2000 times.

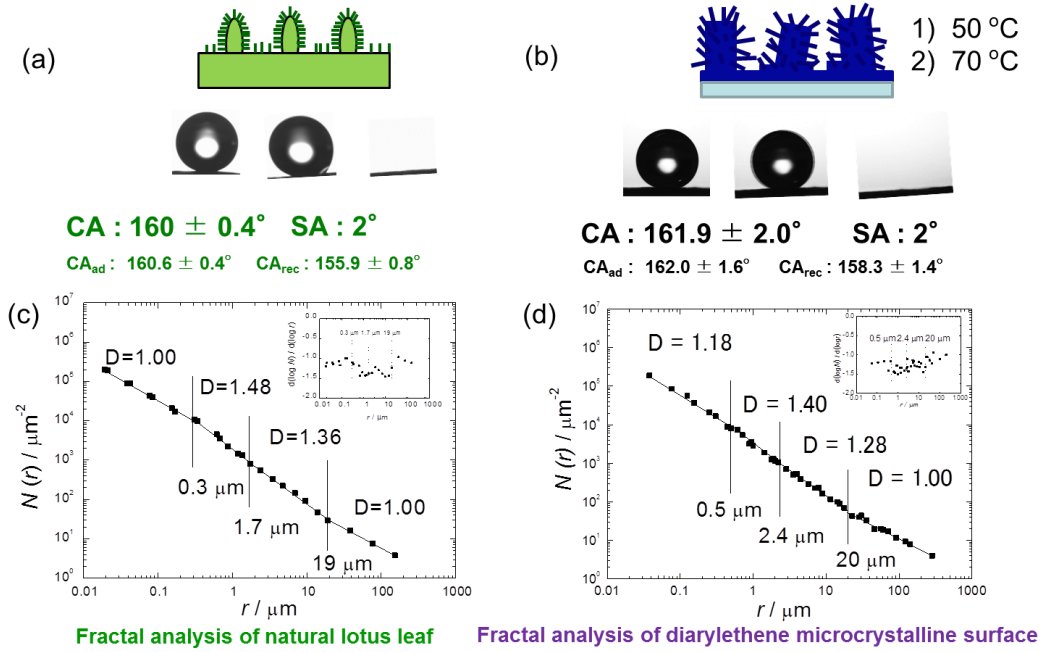


Figure 2.3 Comparison of the size-distribution of the double roughness microstructures on natural lotus leaf and diarylethene microcrystalline film. (a) a water droplet on the natural lotus leaf ^[S4] and (b) that on diarylethene microcrystalline surface. Size distributions of microstructures on (c) natural lotus leaf, and (d) diarylethene microcrystalline film (Fig. 2-9a, 9b, 9c). The insets show the dependence of the differentiation $d(\log N)/d(\log r) = -D$ on scale.

2.3.2 Reversibility of the photoinduced double roughness structures

The reversibility of the melting and reformation of double roughness structure by alternate well (Fig. 2.4). Upon visible light irradiation for 4 h at 30 °C, the double roughness structure was lost, accompanied with the loss of lotus effect, then UV light irradiation for 4 min followed by storage at 50 °C for 1 h in the dark reproduced the double roughness structure with lotus effect. This is due to the reversibility of the formation and disappearance of the needle-shaped microcrystals on each rod-shaped crystal.

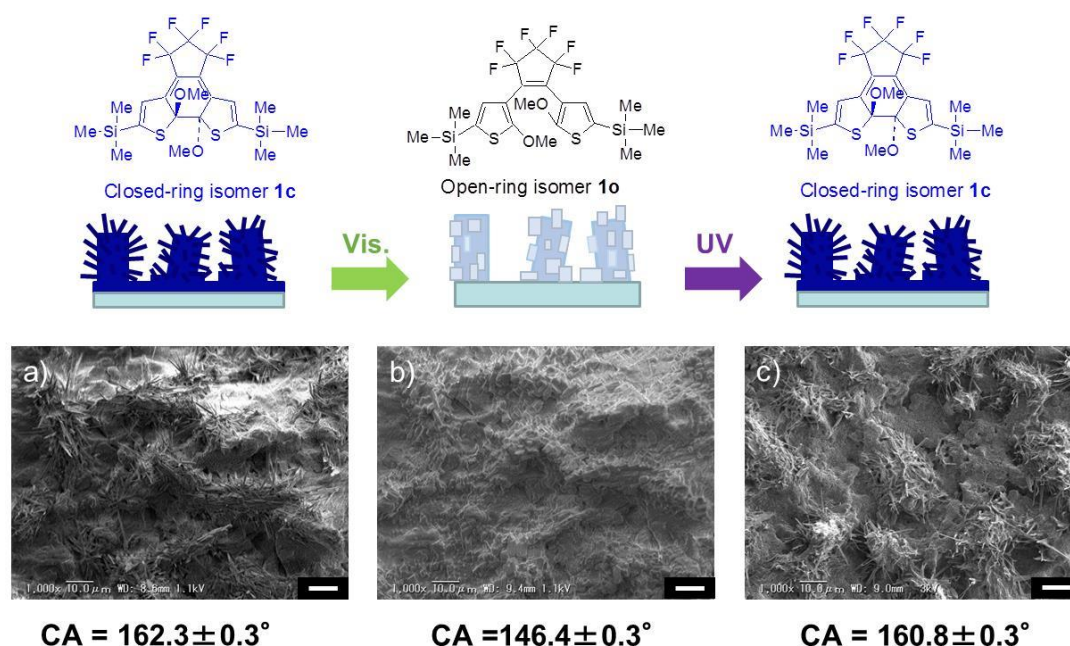


Figure 2.4 Reversibility of the photoinduced double roughness structures at the same place. (a) Initial surface with double roughness structures (corresponding to Fig. 2-9a, 9b, 9c), (b) visible light irradiation for 4 h at 30 °C to surface of (a); (c) UV light irradiation for 5 min after storage at 50 °C for 1 h in the dark to surface of (b). Scale bars: 10 μm for all images, which are magnified 1000 times.

2.3.3 Different preparation of the surface and the importance of making thick rod-shaped crystal for the double roughness structure

With a change to the sequence of the irradiation of visible and UV light (Fig. 2.5), no surface with double roughness prepare thick rod-shaped crystals to form a double roughness structure. The surface with thinner rod-shaped crystals resulted in a surface with a single roughness structure (Fig. 2.5-5a). The distinct difference between the surface wettability of Fig. 2-9b and Fig. 2.5-5b shows the critical role of the double roughness structures in wettability. This difference is attributable for the larger fractal dimension of double roughness structures in a 0.5-2.4 μm sized area. Also, existence of large air pockets allows intrusion of water to the pockets.

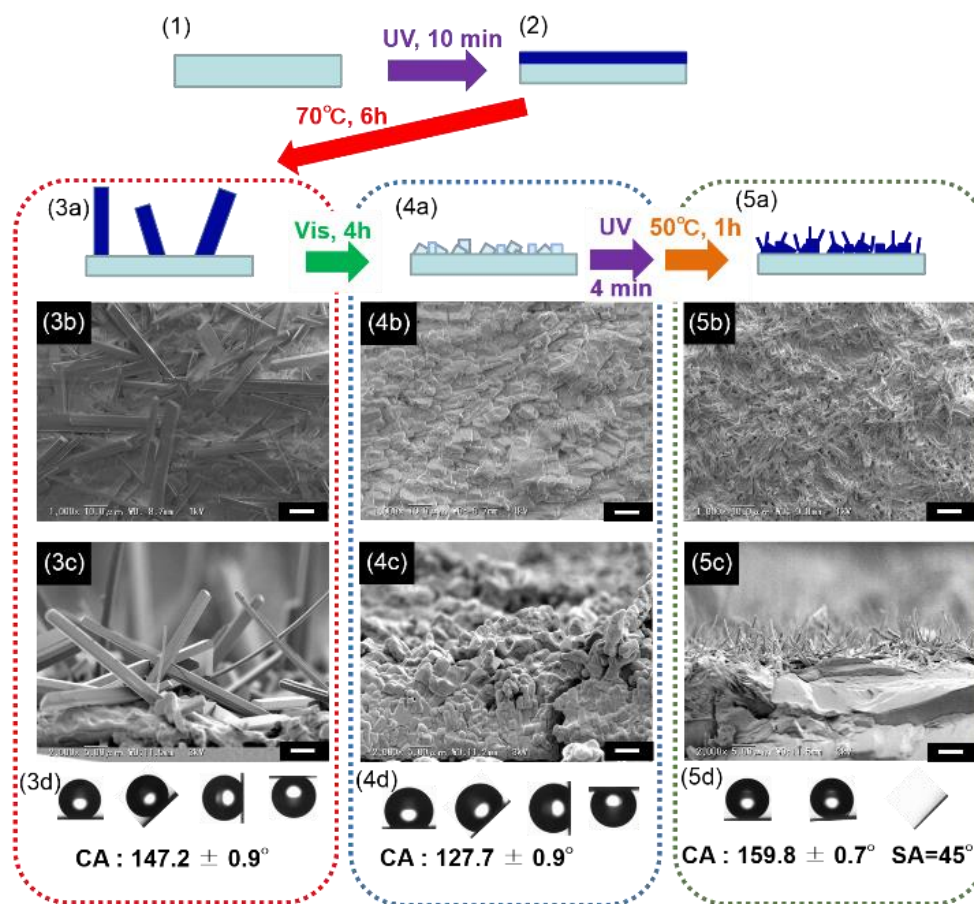


Figure 2.5. Procedure for making rod-shaped crystals (1-5a). By heating the (2) state at 70 °C followed by UV irradiation of initial surface of **1o** (1), a rough surface covered with rod-shaped **1c** was formed (3a). A surface covered with cubic crystals of **1o** was generated upon visible light irradiation to (3a) for 4 h (4a). The surface (5a) was prepared by 4 min UV irradiation and crystal growth of **1c** by storage at 40 °C for 1 h in dark. SEM images corresponding to (3a), (4a), and (5a) are shown in (3b), (4b), and (5b), respectively. And the cross-section images of (3b), (4b), and (5b) are shown in (3c), (4c), and (5c), respectively. Water droplet (1.5 μ L) on surfaces (3b), (4b), and (5b) are shown in (3d), (4d), and (5d), respectively. Scale bars, 10 μ m for (3b)-(5b) images, which are magnified 1000 times; 5 μ m for (3c)-(5c) images, which are magnified 2000 times.

2.3.4 Water droplet bouncing phenomena

The static CAs and SAs of the microcrystalline surface with double roughness structure strongly resembled those observed on single roughness surfaces of the same diarylethene **1** in previous papers.¹⁸⁻²⁰ As reported previously, double roughness structures having micro/nano-morphologies show water-droplet-bouncing phenomena that contribute to superhydrophobic and self-cleaning.⁷⁻¹³ We thus

performed a water-droplet bouncing experiment from 1.8 mm high on the diarylethene microcrystalline surface with double roughness structures and compared the results with those of diarylethene with single roughness structure and natural lotus leaf (Fig. 2.6). On the lotus leaf, water droplets bounced (Fig. 2.6a); by contrast, bouncing was not observed on a diarylethene microcrystalline surface with single roughness structure (Fig. 2.6b).¹⁸⁻²⁰ Indeed, the phenomenon was reproduced in the diarylethene microcrystalline surface only with double roughness structure (Fig. 2.6c). This result indicates that these two surfaces even with the same static CA and SA may show differences in bouncing.

2.3.5 Theoretical explanation of bouncing of a water droplet

Let us consider the reasons why non-bouncing and bouncing are differentiated on the surfaces having the same static CA and SA values. To understand the bouncing on the multipillar surface, the magnitude of Laplace pressure P_L and dynamic pressure P_d provide a clue, where P_L represents the magnitude of suppression factor, and P_d does that of a driving force. If $P_L > P_d$, bouncing occurs. The former is reflecting characteristic sizes of surface structure such as spacing between surface structures $P_L = 16\gamma_L H / (\sqrt{2}p - D)^2$ [γ_L , surface tension; H and D , height and diameter of surface structures; p , pitch between surface structures], whereas the latter is determined by an impacting droplet ($P_d = (1/2)\rho V^2$; ρ density; V , velocity).³¹

There are three critical points to be taken into account, when we deal with experimental results (Fig. 2.6d-f). (i) The theory cannot be applied directly to the current system because of the randomness of the current surface structure in tilting angle and direction; however, it is possible to estimate the magnitude of P_L from the effective pitch p_{eff} between almost perpendicularly standing crystals on the single roughness and that between the larger-sized structures on double roughness surface and lotus leaf. (ii) p_{eff} could be roughly estimated from the SEM images of single and double roughness surfaces and lotus leaf. (iii) The estimated magnitude of P_L can be used as a criterion to determine whether there is nonbouncing or bouncing from the surface structures in comparison with P_d (17.6 Pa). On the single roughness surface, almost all the crystals were tilting; therefore, we could not find suitable needle-shaped

crystals. As a result, we concluded that p_{eff} values are over 500 μm (Fig. 2.6e) on a single roughness surface and $PL < 17.6 \text{ Pa}$ by the above equation using p_{eff} instead of p (Table 2.1). In contrast, on the double roughness surface and lotus leaf (Fig. 2.6d, f), p_{eff} is estimated to be 35 and 20 μm due to the pitch of the larger sized structures, respectively (Table 2.1). Laplace pressure (PL) due to p_{eff} is estimated to be $1.4\text{--}2.5 \times 10^3 \text{ Pa}$ using the above relation. We obtained $PL > 17.6 \text{ Pa}$, which explains the bouncing on double roughness surface and lotus leaf consistently. To verify the arguments together with the magnitude of PL , we carried out further experiments: water droplets ($7.0 \mu\text{L}$) go down from higher positions h (50, 100, 150 mm). The magnitudes of PL and P_d are summarized in Table 1. As a result, the magnitude of PL is explained by P_d , and the bouncing occurs when PL is larger than P_d .

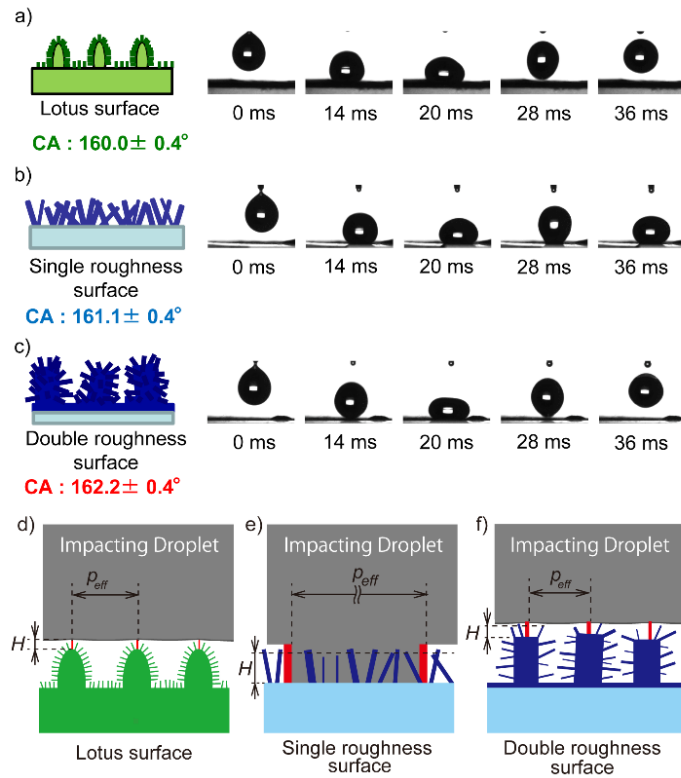


Figure 2.6. Water-droplet ($7.6 \mu\text{L}$) bouncing phenomena on natural lotus leaf (a), diarylethene microcrystalline surfaces with single (b) and double roughness structure (c) ($h=1.8 \mu\text{m}$). Schematic representations of Laplace pressure (P_L) on lotus leaf (d), single roughness structures (e) and double roughness structure (f). P_L is determined by height H of surface structures and effective pitches p_{eff} between almost perpendicularly standing needles shown by red.

Table 2.1. Numerical results under actual conditions

	Single Roughness	Double Roughness	Lotus
H (μm)	7.6	<u>3</u>	<u>1.7</u>
D (μm)	1	0.2	0.03
h (mm)	1.8	1.8	1.8
P_d (Pa)	17.6	17.6	17.6
p_{eff} (μm)	> 500	35 ^{*1}	20 ^{*1}
P_L (Pa)	17.6 <	1.4×10^3	2.5×10^3
Behavior	Non-bouncing	Bouncing	Bouncing

*1: Obtained from the SEM images.

We succeeded in generating the double roughness structure. It is a significant advance in mimicking the structural complexity of natural lotus leaves. Actually, the above discussion explains bouncing raindrops on lotus leaf structure.³² By further adjustment to size, height, and spacing, a full reproduction has come into scope.

2.4 Conclusion

In summary, we prepared the double roughness structure by using diarylethene **10** and showed the importance of the double roughness structure on its super-water-repellence by mimicking the structure of a natural lotus leaf. The results support the importance of the double roughness structure to form the water-droplet-bouncing phenomenon which is the origin of self-cleaning on a lotus leaf. The double roughness structure was reversibly photo-controlled by alternate irradiation with UV and visible lights (Fig. 2.4). The diarylethene microcrystalline system can provide versatile surface functions and will be a useful tool for understanding natural surface properties by controlling the sizes of rod- and needle-shaped crystals with changing UV irradiation periods. By using the metal deposition technique, we can immobilize the structures of the surface. Then they will be applicable self-cleaning smart materials for industrial use.

2.5 References

- 1) F. Xia, L. Jiang, *Adv. Mater.* **2008**, *20*, 2842–2858.
- 2) W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1–8.
- 3) C. Neinhuis, W. Barthlott, *Ann. Bot.* **1997**, *79*, 667.
- 4) X. F. Gao, L. Jiang, *Nature* **2004**, *432*, 36.
- 5) L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, *14*, 1857–1860.
- 6) Tian, Y.; Su, B.; Jiang, L. *Adv. Mater.* **2014**, *26*, 6872–6897.
- 7) Y. Lu, S. Sathasivam, J. Song, C. R. Crick, C. J. Carmalt, I. P. Parkin, *Science* **2015**, *347*, 1132–1135.
- 8) X. Deng, L. Mammen, H. J. Butt, D. Vollmer, *Science* **2012**, *335*, 67–70.
- 9) J. C. Bird, R. Dhiman, H. M. Kwon, K. K. Varanasi, *Nature* **2013**, *503*, 385–389.
- 10) Y. Kwon, N. Patankar, J. Choi, J. Lee, *Langmuir* **2009**, *25*, 6129–6136.
- 11) X. Yao, Y. Song, L. Jiang, *Adv. Mater.* **2011**, *23*, 719–734.
- 12) B. Bhushan, Y. C. Jung, K. Koch, *Philos. Trans. R. Soc. A* **2009**, *367*, 1631–1672.
- 13) Z. Guo, F. Zhou, J. Hao, W. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 15670–15671.
- 14) S. C. Sahoo, M. K. Panda, N. K. Nath, P. Naumov, *J. Am. Chem. Soc.* **2013**, *135*, 12241–12251.
- 15) P. Naumov, S. C. Sahoo, B. A. Zakharov, E. V. Boldyreva, *Angew. Chem. Int. Ed.* **2013**, *52*, 9990–9995.
- 16) P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath, E. Boldyreva, *Chem. Rev.* **2015**, *115*, 12440–12490.
- 17) T. A. Singleton, I. B. Burgess, B. A. Neger, A. G. Hanssens, N. Koay, C. J. Barrett, J. Aizenberg, *Soft Matter* **2014**, *10*, 1325–1328.
- 18) K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura, M. Irie, *Angew. Chem. Int. Ed.* **2006**, *45*, 6470–6473; *Angew. Chem.* **2006**, *118*, 6620–6623.
- 19) K. Uchida, N. Nishikawa, N. Izumi, S. Yamazoe, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii, M. Irie, *Angew. Chem. Int. Ed.* **2010**, *49*, 5942–5944; *Angew. Chem.* **2010**, *122*, 6078–6080.
- 20) N. Nishikawa, A. Uyama, T. Kamitanaka, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii, K. Uchida, *Chem. - Asian J.* **2011**, *6*, 2400–2406.
- 21) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.

- 22) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.
- 23) L. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 2966–2967.
- 24) J. Zhang, X. Sheng, L. Jiang, *Langmuir* **2009**, *25*, 1371–1376.
- 25) L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, *14*, 1857–1860.
- 26) Y. Tian, B. Su, L. Jiang, *Adv. Mater.* **2014**, *26*, 6872–6897.
- 27) L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, L. Jiang, *Langmuir* **2008**, *24*, 4114–4119.
- 28) E. Bormashenko, T. Stein, R. Pogreb, D. Aurbach, *J. Phys. Chem. C* **2009**, *113*, 5568–5572.
- 29) M. Yamamoto, N. Nishikawa, H. Mayama, Y. Nonomura, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2015**, *31*, 7355–7363.
- 30) N. Nishikawa, H. Mayama, Y. Nonomura, N. Fujinaga, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2014**, *30*, 10643–10650.
- 31) Y. C. Jung, B. Bhushan, *Langmuir* **2008**, *24*, 6262–6269.
- 32) B. J. Mason, *The Physics of Clouds* (Oxford Classic Texts in the Physical Sciences), 2nd ed.; Clarendon Press: Oxford, U.K., **2010**; p 594.

Chapter 3

Crystal Growth Technique for Formation of Double Roughness Structures Mimicking Lotus Leaf

3.1 Introductions

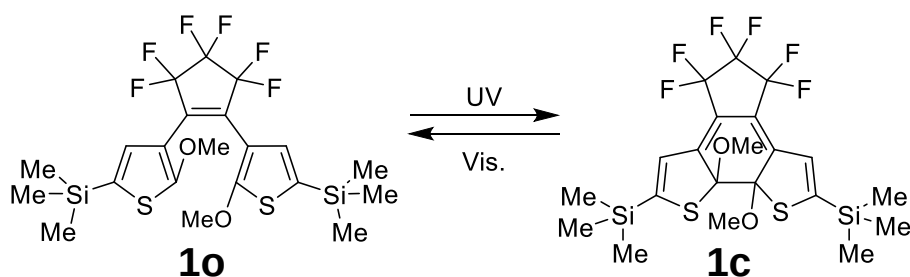
Biomimetics generally aims to mimic the structures and morphologies of biological systems and thus reproduce their functions. Recently, biomimetics has received much attention in the field of material sciences for practical applications requiring new functions and technology. Xia and Jiang classified the biomimetic function into four categories: selfcleaning, mechanical properties, structure color, and optical properties.¹ Adhesion properties were studied by Autumn *et al.*,² who clarified that the adhesive force is due to the van der Waals force. The system was reproduced by Crosby *et al.* and commercially produced by Nippon Denso Company using single-walled carbon fibers.³ Structure colors, for example, those on the wings of the Morpho butterfly, have also been reproduced by biomimetics.^{4,5} Such a development was achieved by mimicking the structures and morphologies of natural plants and insects.

Barthlott and Neinhuis initially reported the Lotus effect,⁶⁻⁸ which is now familiar as super-water repellency with the selfcleaning ability of the lotus leaf, and the effect is attributed to the double roughness structure (DRS) on the surface of the natural lotus leaf, which is a hierarchical structure in which 100 nm-scaled structures cover the surface with several micrometer-scaled roughness. The appearance of superhydrophobicity on the surface is explained by the solid-liquid surface tension incorporating the air space between a water droplet and the nanostructured wax crystals. For self-cleaning materials, the ability to bounce a water droplet plays an important role because such bouncing with momentum washes off the dust on the leaf surface and maintains a clean surface

Barthlott and Neinhuis initially reported the Lotus effect,⁶⁻⁸ which is now familiar as super-water-repellency with the self-cleaning ability of the lotus leaf, and the effect is attributed to the double roughness structure (DRS) on the surface of the natural lotus leaf, which is a hierarchical structure in which 100-nm-scaled structures

cover the surface with several μm -scaled roughness. The appearance of superhydrophobicity on the surface is explained by the solid-liquid surface tension incorporating the air space between a water droplet and the nanostructured wax crystals. For self-cleaning materials, the ability to bounce a water drop plays an important role because such bouncing with momentum washes off the dust on the leaf surface and maintains a clean surface.

In this study, we aimed to reproduce the DRS of a natural lotus leaf by a crystal growth technique (CGT). For the CGT materials, we used a photochromic diarylethene crystalline system that we have developed. Photochromic molecules, which reversibly change their physical properties accompanied with color changes by alternating irradiation with UV and visible lights, are very attractive as a means to control the surface properties without any physical contact. This study used one of the photochromic compounds, diarylethene, whose open- and closed-ring isomers are thermally stable and have fatigue resistance, high reactivity, rapid response, and photoreactivity in the crystalline state.^{9,10} We compare the superhydrophobicity, Laplace pressure, and water-bouncing ability of the surface with those properties of a natural lotus leaf. Furthermore, we clarified what is necessary to reproduce the nature of the surface structures through the CGT procedure.



Scheme 3.1 Molecular structures of open- and closed-ring isomers of diarylethene **1**.

In the system, the photoinduced crystal growth of the needle-shaped crystals of the closed-ring isomer **1c** proceeded on the microcrystalline surface of open-ring isomer **1o** (Scheme 3.1) prepared by a solution coating; this was carried out via eutectic mixtures upon UV irradiation by keeping the temperature above the glass transition temperatures (T_g), and thus, the photogenerated rough surfaces covered with needle

shaped crystals showed superhydrophobicity.^{11–13} Subsequently, upon irradiation to this surface with visible light, the needle-shaped crystals of **1c** melted, and the surface reverted to one covered with cubic crystals of **1o**, while the contact angle (CA) reverted to its initial value. The reversible photocontrol of crystal growth (making a surface topography) and melting (erasing the surface topography) is a useful technique to fabricate the desired surface topography with specific functions, which we have established.

By using the above CGT, we have studied photoinduced crystal growths to reproduce bio-inspired functions of insects and plants. In fact, we have fabricated several bio-inspired materials in the last few years.^{14–18} Very recently, we prepared a prototype of a DRS surface mimicking the natural lotus leaf; however, the ability of dynamic water-drop bouncing on our surface was somewhat inferior to that on the natural lotus leaf.¹⁶ In this study, we successfully controlled the DRS precisely, where rod-shaped crystals were covered with needle-shaped crystals, by controlling the irradiation periods of UV light and the annealing temperature after UV irradiation as well as the Laplace pressure of the surfaces. The newly prepared surfaces showed the bouncing phenomena of a water droplet released from a 15 cm height, which nearly correspond to the bouncing property of a natural lotus leaf when it bounces rainfall, indicating the optimization of such surface structures.¹⁶ In this paper, we describe the optimization of a surface structure to increase the Laplace pressure. For the purpose, it was necessary to shorten the intervals between rod-shaped crystals and lengthen the crystals by controlling the irradiation periods of UV and visible lights as well as the storage period and temperature for Ostwald ripening. We assumed that long crystals could be formed by increasing the UV irradiation periods and increasing the temperatures for Ostwald ripening, but we found that when the storage temperature was elevated, the crystals melted during the visible light irradiation. Although it is not related to the Laplace pressure, crystal thickness, as another hidden factor, should be controlled at the same time. This determines the optimum temperature for Ostwald ripening.

Weak nonspecific interactions are dominant in the molecular crystals, and it is very difficult to control the surface topography. Such topographical changes have typically been controlled by changing the molecular structures. In our system, since

one of the photochromic molecules, diarylethene, has thermal stability in both isomers and photoreactivity in the crystalline state, we could control the surface structure by photocontrol of the ratio of two isomers having different crystal habits. Our developed CGT provides an important contribution to the fundamental work on the crystal growth technique for molecular crystals. Here, we show new crystal engineering mimicking the DRS of the natural lotus leaf, while considering the increment of Laplace pressure, by tuning the diameter, intervals of rod-shaped crystalline pillars of DRSs, lengths of fine needle-shaped crystals on each pillar, UV irradiation periods, heating temperatures, and control of the self-assembling passage of the molecules. Finally, we attained a water-bouncing ability comparable to that of a natural lotus leaf. The results show a guideline for designing the surface topography controlling crystal growth, a guideline inspired by nature.

3.2 Experimental section

3.2.1 Preparation and observation of the microcrystalline surface

A compound of photochromic diarylethene **1o** was synthesized as previously reported. The crystal data of open- and closed-ring isomers were previously reported. The microcrystalline surface of **1o** was prepared by a solution-coating method. The chloroform solution of the **1o** (100 mg/mL) was coated on a glass substrate (1 cm²) and stored in the dark at room temperature for about 12 h, and then a thin crystalline film of **1o** was obtained. The film thickness was found to be approximately 20 μ m by measuring the cross-section of the microcrystalline films from the side view by a scanning electron microscope (KEYENCE VK-8800). The SEM was also used to study the surface microstructures. We observed the cross-section of a sample that was cracked along with the glass substrate and set perpendicularly on a stage, which was then observed by the SEM after the Au-Pd alloy evaporated on the sample surface.

3.2.2 Photo-irradiation and heating methods

Photo-irradiation to the microcrystalline surface of diarylethene derivative **1** was carried out using a TOPCON UV lamp (PU21; λ = 254 nm, 23 W (distance: 1 cm)) as a UV light and an Ushio 500-W Xe arc-lamp with a cutoff filter (Toshiba color filter Y-48) as a visible light (λ > 480 nm). Photoinduced crystals growth experiments after the UV light irradiation were performed using a hot stage constructed in-house along

with a temperature controller. Observations of crystal growth were made using a digital microscope (KEYENCE DIGITAL MICROSCOPE VHX-500) and a temperature- controllable hot stage (Lincam MK600).

3.2.3 Procedure to prepare double-roughness surface (Fig. 3.1)

First, the **1o** on the glass substrate (Fig. 3.1a) was irradiated by UV light for 10 min to form a surface layer of **1c** (1st UV, Fig. 3.1b). Then, it was annealed in the dark for 24 h at a suitable temperature for the growth of needle-shaped crystals, and the growth of rod-shaped crystals from these needle-shaped crystals by Ostwald ripening (1st annealing, Fig. 3.1b-d). Here, the temperature of the 1st annealing determines the interval between the larger-sized structures. Next, the surface covered with the rod-shaped crystals was irradiated by UV light for 10 min to form the surface layer of **1o** in the flat surface of **1c** between the rod-shaped crystals (2nd UV, Fig. 3.1e). Then, it was annealed for 3 h in the dark again for 70 °C to prepare the needle-shaped crystals first and then to form the large rod-shaped crystals by Ostwald ripening (2nd annealing, Fig. 3.1e-g). After that, it was irradiated by visible light for 4 h to form **1o** (Fig. 3.1g). Finally, it was irradiated by UV light (3rd UV, Fig. 3.1h) and annealed for an arbitrary time at a suitable temperature to form needle-shaped crystals over the surface (3rd annealing, Fig. 3.1h-j).

3.2.4 Observation method of contact angle and bouncing phenomena of water droplets

Static contact angles (CAs) and sliding angles (SAs) were measured on an optical contact angle meter (Drop Master 500, Kyowa Interface Science Co., Ltd.) with a water droplet of 1.5 μ L. For the dropping test, we dropped a water droplet (5.4 μ L of distilled water) and observed it using the same apparatus with a high-speed camera (1000 frames / sec).

3.3 Results and discussion

The most important factor to achieve high bouncing ability is the Laplace pressure (P_L)^{16,19} which is determined by the characteristic scales of DRSs according to $P_L = 16\gamma_L H / (\sqrt{2}p - D)^2$ (where γ_L is the surface tension; H and D are the height and diameter of surface structures respectively, and p is the pitch between surface structures).¹⁶ The Laplace pressure is the pressure difference between the inside and the outside of a curved surface that forms the boundary between a gas region and a liquid region. The pressure difference is caused by the surface tension between liquid and gas.¹⁶ The procedure to fabricate a microcrystalline surface having DRSs is shown in Fig. 3.1. To generate a larger P_L , it is important to design the intervals (p) between the rod-shaped crystals to be smaller and the length (H) of needle-shaped crystals on the rod-shaped crystals to be longer. As shown below, the points of the CGT for the current study are the 1st annealing, the 2nd and the 3rd UV irradiations. The storage temperature and storage period of the 1st annealing determine p because the seeds of the rod-shaped crystals in DRS are formed by Ostwald ripening in the 1st annealing. Further steps of UV light irradiation and annealing promote the growth of the rod-shaped crystals. On the other hand, the 2nd and the 3rd UV irradiations are also important for controlling H .

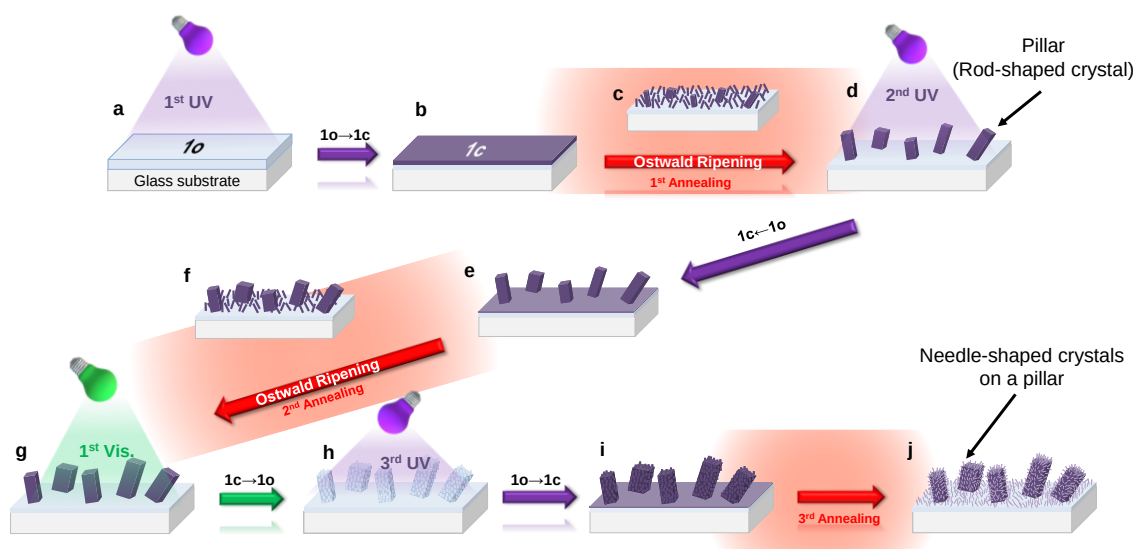


Figure 3.1 Procedure to prepare double-roughness surface by CGT. a) 1st UV light irradiation onto the flat surface of **1o**. b) Flat surface of **1c** formed by 1st UV light irradiation before 1st annealing. c) Intermediate surface with needle-shaped and rod-shaped crystals of **1c** during 1st annealing to grow rod-shaped crystals by Ostwald ripening of needle-shaped crystals. d) Rod-shaped crystals of **1c** and flat surface of **1o** between the rod-shaped crystals by 1st annealing and then 2nd UV light irradiation. e) Rod-shaped crystals and flat surface of **1c** after 2nd UV light irradiation and before 2nd annealing. f) Intermediate surface with needle-shaped crystals during 2nd annealing to induce Ostwald ripening to fatten rod-shaped crystals of **1c** by supplying of **1c** from flat surface. g) Rod-shaped crystals of **1c** fatten by Ostwald ripening and then 1st Vis light irradiation. h) Surface with rod-shaped crystals of **1o** after 1st Vis light irradiation, where rod-shaped crystals are covered with cubic-shaped crystals of **1o**, and 3rd UV light irradiation. i) Surface of **1c** after 3rd UV light irradiation. j) Double roughness structures formed by 3rd UV light irradiation. Interval between rod-shaped crystals can be controlled by 1st annealing as shown in Fig. 3.2. Furthermore, size of rod-shaped crystals can be controlled by 1st and 2nd annealing as shown in Fig. 3.3.

3.3.1 Preparation of double roughness structure (1): Controlling the interval between the structures (rod-shaped crystalline pillars); 1st UV irradiation and 1st annealing

In order to shorten the interval between the rod-shaped crystals, we raised the storage temperature slightly higher in the 1st annealing than that in our previous report.¹⁶ In the previous report, the storage temperature of the 1st annealing in the dark after the 1st UV irradiation for 10 min was 50 °C, and the diameter and length of the rod-shaped pillars resulting from Ostwald ripening of the needle-shaped crystals were

10 μm and 21 μm , respectively.¹⁶ However, due to the larger intervals between larger crystals (30 μm) compared with those (20 μm) of DRSs on a lotus leaf, the bouncing ability of water droplets was inferior to that on a lotus leaf. To control the intervals, crystal growth of **1c** and average intervals were monitored at six storage temperatures in the 1st annealing at 45, 50, 55, 60, 65, and 70 °C for 48, 24, 20, 18, 12, and 6 h, respectively, in the dark, after irradiation with the 1st UV light for 10 min (Movie S1). The storage temperature dependence of the average intervals evaluated from the SEM images is summarized together with the average interval of the larger projections of a lotus leaf in Fig. 3.2a. With increasing storage temperature, the intervals became smaller, while the rod-shaped crystals became longer and narrower (Fig. 3.2b-g). On the other hand, the volume of the rod-shaped crystals decreased with increasing storage temperature of the 1st annealing (Fig. 3.3a, b). The dependences of the interval and volume on the storage temperature indicate that the number of crystal growth points of the rod-shaped crystals increased at elevated temperatures of the 1st annealing. The interval and size of the rod-shaped crystals can thus be controlled by storage temperature. In particular, the intervals on the surfaces obtained at 55, 60, 65, and 70 °C were smaller than that of a lotus leaf. However, the narrower rod-shaped crystals generated at 60, 65, and 70 °C were melted and made to disappear by irradiation with visible light ($\lambda > 480 \text{ nm}$) for 4 h (1st Vis irradiation, described later) due to the small sizes of the crystals. These results indicate that a suitable storage temperature should be ensured, that is, not too high for preparing the double roughness structures. Therefore, we adopted a storage temperature at 55 °C for 20 h for the condition of the 1st annealing.

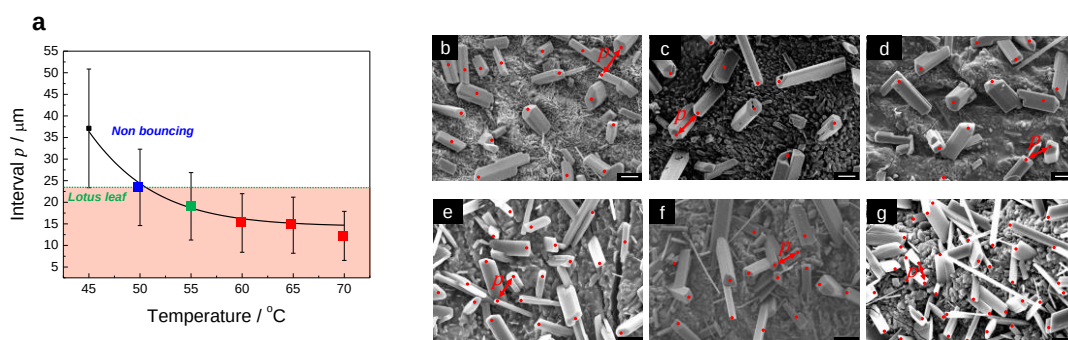


Figure 3.2 Dependence of intervals of rod-shaped crystals of **1c** on storage temperature in 1st annealing (CGT). **a** Average intervals between rod-shaped crystals generated at storage temperature of 45, 50, 55, 60, 65 and 70 °C for 48, 24, 20, 18, 12, and 6 h in the dark, respectively. Values of intervals were measured from SEM images. Heating temperature represented by the blue dot is the poor condition for preparing a surface with bouncing ability in the previous paper¹⁶, and that represented by the green dot is the best condition to prepare a surface with bouncing ability in this paper. **b** SEM image of rod-shaped crystals of **1c** generated at 45 °C, **c** 50 °C, **d** 55 °C, **e** 60 °C, **f** 65 °C, and **g** 70 °C in 1st annealing (Fig. 3.1d before 2nd UV light irradiation). Measurement of intervals was carried out from SEM images. Scale bars are 10.0 μm for all SEM images, which are magnified 1000 times.

3.3.2 Preparation of double roughness structure (2): Controlling the size of the rod-shaped pillars; 2nd UV irradiation

After the 1st annealing, we tried to enlarge the rod-shaped crystals to prevent melting and to form the DRSs, since **1c** molecules in the needle-shaped crystals should be transferred to the rod-shaped crystals to make them thicker to form the DRS surface. In this section, we report how to control the sizes of the rod-shaped crystals by the 2nd UV irradiation periods through the formation of needle-shaped crystals and Ostwald ripening. The surface after the 1st annealing was irradiated with UV light for 1, 4, 10 min independently (2nd UV irradiation), where **1a** between the rod-shaped crystals isomerized to **1c** by the 2nd UV irradiation. This was the source of supply to grow the rod-shaped crystals in the 2nd annealing (70 °C for 3 h in the dark), and the amount of the source was determined by the 2nd UV irradiation period. The results were summarized in Fig. 3.3c, e. The volume of the rod-shaped pillars was proportional to the irradiation period. The longer the irradiation periods of the 2nd UV irradiation were, the larger was the rod-shaped crystals.

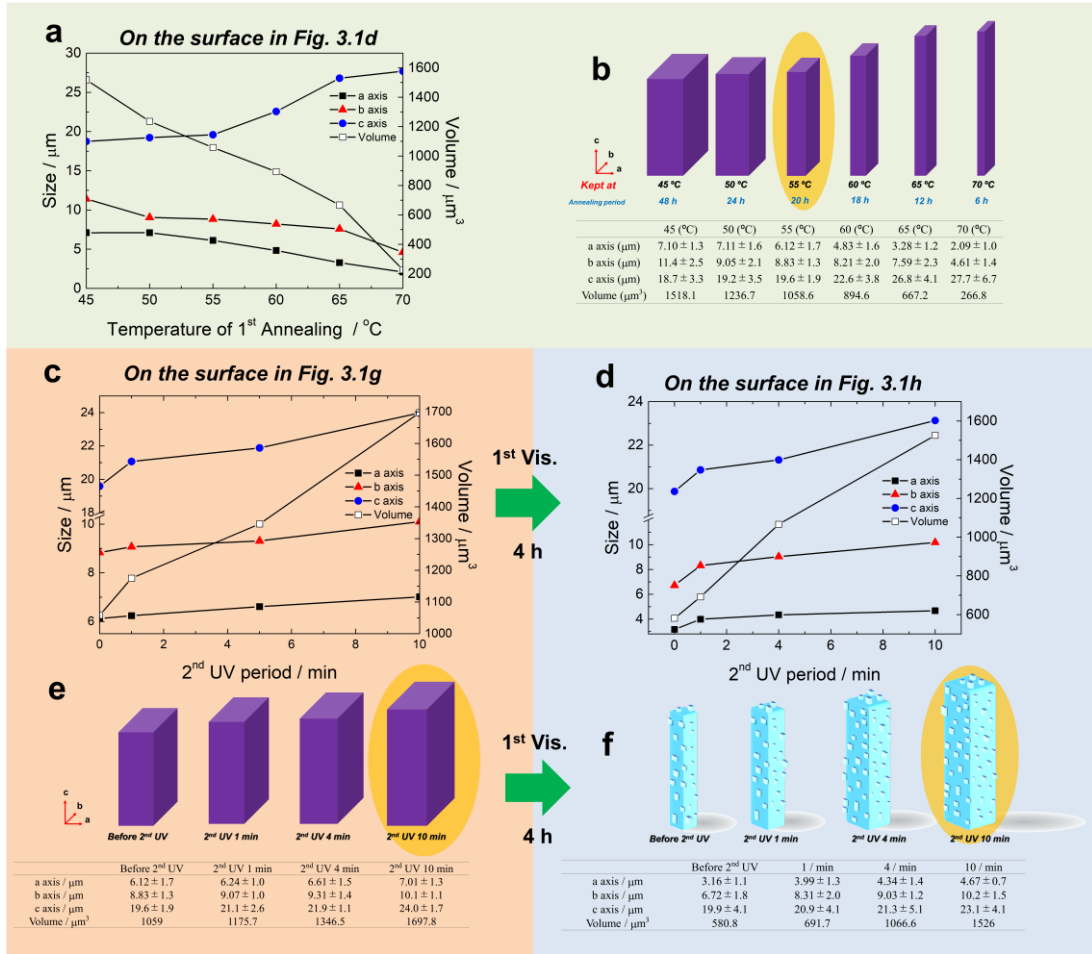


Figure 3.3 Control of the sizes of rod-shaped crystal by CGT after 1st annealing (before 2nd UV light irradiation in Fig. 3.1d), 2nd annealing (before 1st Vis light irradiation in Fig. 3.1g) and 1st Vis light irradiation (before 3rd UV light irradiation in Fig. 3.1h). Values of crystal size were measured from SEM images. a) Dependence of sizes of rod-shaped crystals on 1st annealing temperature. We kept the temperature of microcrystalline surfaces at 45, 50, 55, 60, 65 and 70 °C for 48, 24, 20, 18, 12 and 6 h, respectively, after 1st UV light irradiation. b) Schematic illustration of obtained crystals corresponding to (a). c) Dependence of average sizes of rod-shaped crystals on 2nd UV light irradiation period for surface prepared by heating at 55 °C in 1st annealing (highlighted in Fig. 3.3b). We kept the temperature of all surfaces at 70 °C for 3 h after 2nd UV light irradiation. d) Dependence of average sizes of rod-shaped crystals on 1st Vis light irradiation period for surface prepared by heating at 55 °C (the same as 1st annealing). e) Schematic illustration of obtained crystals corresponding to (c). f) Schematic illustration of obtained crystals corresponding to (d). Schematic illustrations with yellow background indicate optimized conditions in this paper.

3.3.3 Preparation of the double-roughness structures (3): Visible light irradiation to form needle-shaped crystals over entire surface; 1st Vis irradiation

To grow the needle-shaped crystals on the surface after the 2nd annealing, the entire surface, including that of the rod-shaped crystals, must be covered with crystals of **1o**. The surface was prepared by irradiation with visible light ($\lambda > 480$ nm) for 4 h (the 1st Vis irradiation). By this irradiation, the roughly structured rod-shaped crystals covered with **1o** were formed and the sizes depended on the period of the 2nd UV irradiation as shown in Fig. 3.3d, f. A slightly roughly structured surface of rod-shaped crystals is formed due to the formation of cubic-shaped crystals of **1o**. The size of the rod-shaped structure of **1o** was measured from the SEM images (Fig. 3.3d, f). The size of each axis and the volume of the rod-shaped crystals increased with the increasing period of the 2nd UV irradiation.

To grow the needle-shaped crystals on the surface of rod-shaped crystals covered with **1o** (Fig. 3.1h), a 3rd UV irradiation to the surface was carried out. We irradiated with UV light for 4 min to the surface after 1st Vis irradiation, and kept it at 50 °C in the dark for 1 h to form DRSs (Fig. 3.4). After heating, the DRSs were generated on the microcrystalline surface. The surface showed superhydrophobicity with CA of a water droplet around 160° (Table 3.1). The Laplace pressure P_L , which is one of the wetting properties, was higher than that of Lotus leaf (Fig. 3.5b, c). The Laplace pressure was calculated from the average values of the crystal sizes.

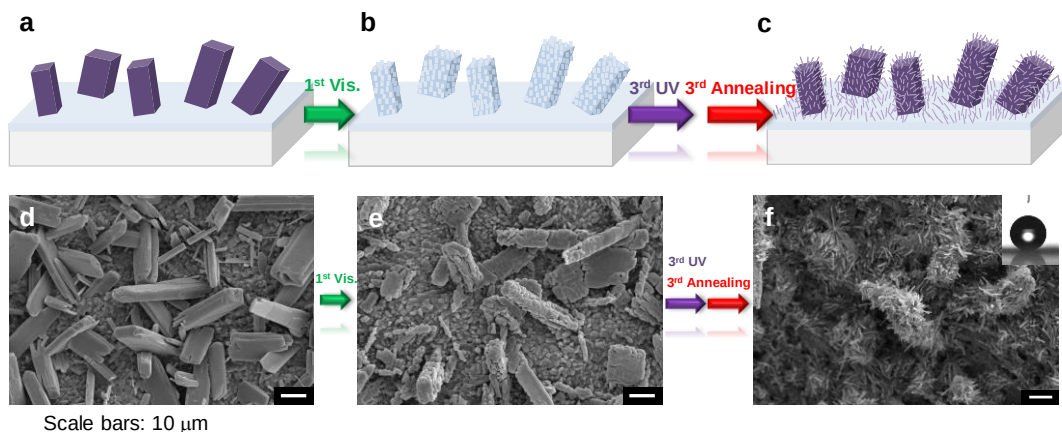


Figure 3.4 Formation of double-roughness structure by heating at 55 °C as 1st annealing, 10-min UV irradiation as 2nd UV and 10 min irradiation as 3rd UV (**DRS 55-10-4**). d-f) SEM images of microcrystalline surface covered with three types of crystals corresponding to schematic illustrations a-c). Scale bars are 10.0 μm for all SEM images, which are magnified 1000 times. The inset in **f** shows the water droplet with static CA $163.8 \pm 1.3^\circ$.

Table 3.1 Static and dynamic CA of a water droplet on each double roughness surface.

Surface	CA / deg.	Advancing CA / deg.	Receding CA / deg.
DRS 55-10-2^{*1}	156.7 $\pm$ 2.6	159.3 $\pm$ 2.5	151.7 $\pm$ 4.1
DRS 55-10-4^{*1}	159.6 $\pm$ 1.9	162.0 $\pm$ 1.9	157.9 $\pm$ 2.4
DRS 55-10-6^{*1}	159.7 $\pm$ 1.9	161.9 $\pm$ 1.5	155.3 $\pm$ 2.8
DRS 55-10-8^{*1}	159.9 $\pm$ 1.1	162.5 $\pm$ 1.9	156.6 $\pm$ 2.8
DRS 55-10-10^{*1}	160.2 $\pm$ 2.0	161.7 $\pm$ 1.5	158.7 $\pm$ 1.0

***1: DRS (the 1st annealing Temp.)-(the 2nd UV light irradiation period)-(the 3rd UV light irradiation period)**

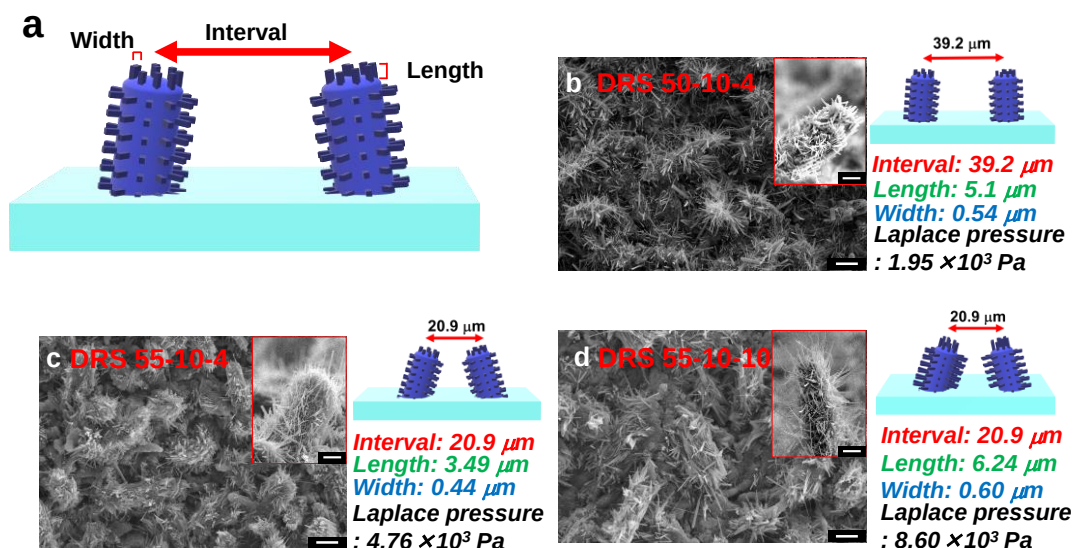


Figure 3.5 Comparison of values of Laplace pressure of double roughness surface with different sizes. a) Schematic illustration of double roughness structure. b) SEM image, crystal sizes and Laplace pressures of **DRS 50-10-4**, c) of **DRS 55-10-4**, d) of **DRS 55-10-10**. Scale bars are 10.0 μm for all SEM images, which are magnified 1000 times. Theoretical values of Laplace pressures of each surface for ideal case were shown in Table 3.2.

3.3.4 Water-droplet bouncing phenomena on the double-roughness surfaces

The water repellency against a dynamic water droplet is a very important property for a surface's self-cleaning, ability to stay dry, and resistance to icing materials.¹⁹⁻²⁸ The natural lotus leaf keeps the surface of a leaf clean by bouncing the rain drop off it along with the debris on the surface of the leaf. J. C. Bird *et al.* reported that the surfaces of plants and insects that show superhydrophobicity have specific surface structures to reduce the contact time with a water drop in order to resist icing by the freezing rain on the own surface.^{19,23-28} It is possible to minimize the mass, momentum and energy between a drop and a surface by controlling the contact time of the water drop with the surface. Therefore, we carried out a dropping test for our diarylethene microcrystalline surface having DRSs. A water droplet was released from 4 mm, 5, 10 and 15 cm above the microcrystalline surface having DRSs. Then, we took photos every 1 ms using a high-speed camera (Fig. 3.6a). However, in spite of large P_L of the surface, water droplet was not bouncing on the surface when releasing from 10 and 15 cm high. Then, we found that the reason why the non-bouncing is due

to the tilt of rod-shaped crystals of DRS compared with the surface of previous one and lotus leaf from SEM observation (Fig. 3.7).¹⁶ One of the important factors to improve the bouncing phenomena we consider is the space of non-penetrating of water droplet between the DRSs. Therefore, subsequently, we tuned the length of the small needle-shaped crystals on a rod-shaped crystal by changing the period of 3rd UV irradiation.

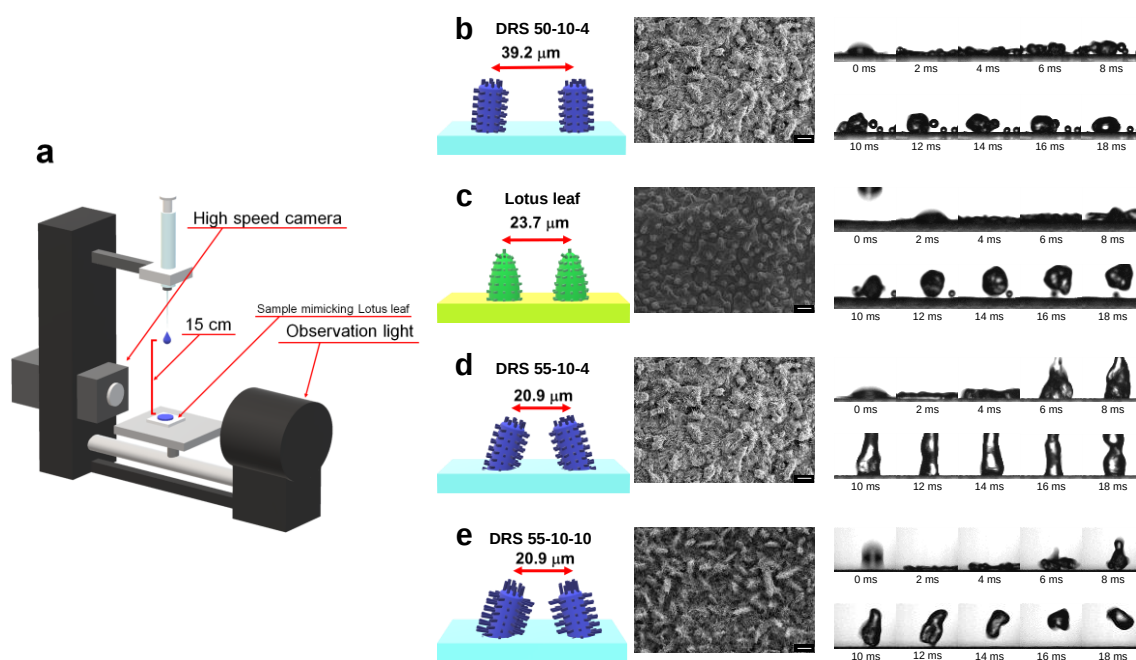


Figure 3.6 Water droplet bouncing phenomena on superhydrophobic surface. a) Schematic illustration of apparatus used to observe water droplet bouncing phenomena. b) Schematic illustration and SEM image of double roughness structures of **DRS 50-10-4**, c) lotus leaf, d) **DRS 55-10-4**, e) **DRS 55-10-10**, along with corresponding bouncing phenomena of a water droplet releasing from a height of 15 cm. Scale bars are 20.0 μm for all SEM images, which are magnified 500 times.

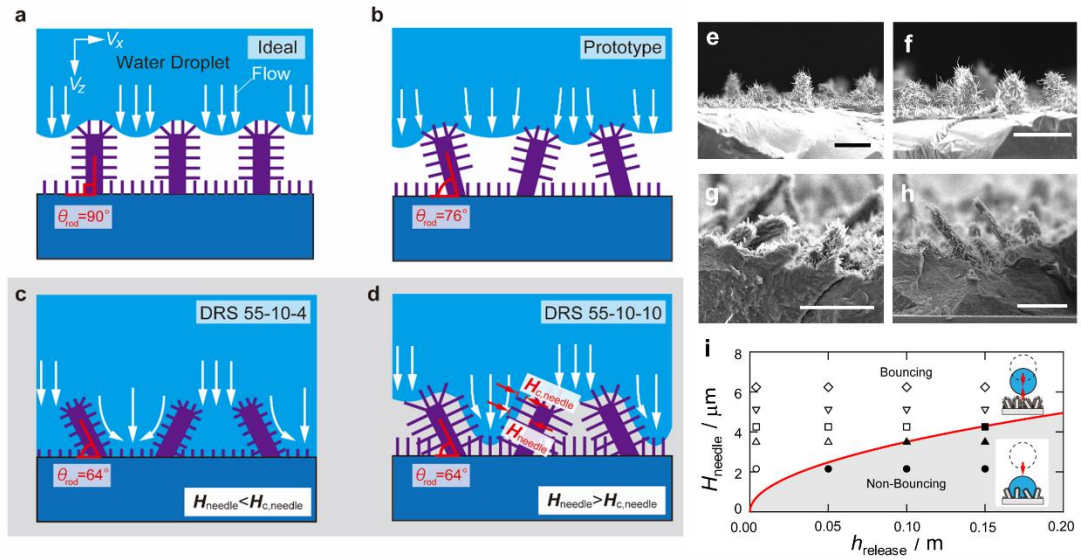


Figure 3.7 Schematic representations of bouncing droplets on DRS surfaces. a) An ideal DRS surface with rod-shaped crystal standing perpendicular to surface (tilting angle of rod-shaped crystals θ_{rod} is 90°). b) The DRS surface of the prototype with slightly tilting rod-shaped crystals of prototype (average $\theta_{rod} = 76^\circ$). This value is obtained from our previous studies.¹⁶ c, d) DRS surfaces with short and long needle-shaped crystals on tilting rod-shaped crystals (average $\theta_{rod} = 64^\circ$), where this is evaluated in this study. Flow of fluid in (a) and (b) is almost along z-axis), while the flow in (c) and (d) is along the tilting rod-shaped crystals. In (c) and (d), the magnitude relationships between $H_{c,needle}$ and H_{needle} is opposite. e, f) Side-view SEM images of **DRS 50-10-4** corresponding to (a) and (b). g, h) Side-view SEM images of **DRS 55-10-10** corresponding to (c) and (d). Scale bars are $33.3 \mu\text{m}$, which are magnified 300 times. i) Phase diagram of bouncing and non-bouncing droplets ($5.4 \mu\text{L}$) on actual DRS surfaces. DRS surfaces are **DRS 55-10-2** (circles), **DRS 55-10-4** (triangles), **DRS 55-10-6** (squares), **DRS 55-10-8** (inverted triangles) and **DRS 55-10-10** (rhombuses). The open and closed symbols mean bouncing and non-bouncing, respectively. The red curve is the theoretical phase-border line by eq. (1). The insets show schematic representations of a bouncing droplet on DRS surfaces with long needle-shaped crystals (upper) and a non-bouncing droplet on DRS surfaces with short needle-shaped crystals (lower).

Table 3.2 Obtained values of average interval p_{av} and ideal average Laplace pressure $P_{L,av}$ of lotus leaf and diarylethene surfaces.

Surface	p_{av} (rod) / μm^*	H (needle) / μm^*	D (needle) / μm^*	$P_{L,av} \times 10^3$ / Pa	Comparison with lotus leaf in $P_{L,av}$
Lotus	23.7	1.7	0.03	2.50	-
DRS 50-10-4	39.2	5.1	0.54	1.95	Smaller
DRS 55-10-2	20.9	2.15	0.38	2.92	Larger
DRS 55-10-4		6.49	0.44	4.76	Larger
DRS 55-10-6		4.25	0.59	5.86	Larger
DRS 55-10-8		5.13	0.58	7.06	Larger
DRS 55-10-10		6.24	0.60	8.60	Larger

*: All average interval between the crystals and sizes of the crystals were obtained from SEM images.

3.3.5 Preparation of double roughness structures (4): Controlling the growth and size of needle-shaped crystals; 3rd UV irradiation and 3rd annealing

This irradiation was carried out by changing the UV irradiation at several periods (2, 4, 6, 8 and 10 min) to control the length and width of the needle-shaped crystals on the pillars, followed by heating the surfaces at 50 °C for 60 min to form DRSs. The surfaces showed superhydrophobicity with CA of a water droplet around 160° (Table 3.1). The H (height or length) of the needle-shaped crystals became larger in proportion to the period of the 3rd UV irradiation (Table 3.2). The Laplace pressure of these surfaces are summarized in Table 3.2.

Laplace pressure P_L becomes larger with increasing height of the needle-shaped crystals (Fig. 3.5). We summarize the numerical parameters of the crystal size and Laplace pressures of five types of DRS surfaces with SEM images in Fig. 3.5. The largest Laplace pressure among the four surfaces in Fig. 3.5 was obtained with the temperature of the 1st Annealing at 55 °C and the period of the 3rd UV at 10 min. This value was even higher than that of a natural lotus leaf.

From the above discussions, the preparation conditions to fabricate the DRSs were optimized to improve the superhydrophobicity as well as water-bouncing ability. We prepared a microcrystalline surface having DRSs by adopting the above conditions (Fig. 3.5, Table 3.3). To estimate the water repellency quantitatively, the Laplace pressure of the surface structures was the critical index. As discussed below, we calculated the Laplace pressure of the surface of the natural lotus leaf and

photogenerated double-roughness structures by using the size parameter obtained from SEM images. The value of the Laplace pressure of the optimized DRS surface became ca. 3.4 times larger than that of a natural lotus leaf. Therefore, we succeeded in increasing the Laplace pressure by controlling the surface structures.

We compared the bouncing phenomena of a water droplet on the four surfaces having DRS. On surfaces **DRS 55-10-2, 4, 6, 8, 10**, when a water droplet (5.4 μL) released from heights of 4 mm and 5 cm, all of the surfaces showed the bouncing ability of a water droplet. However, when we released water droplets from a height of 10 cm, the surface of **DRS 55-10-2** and **4** showed non bouncing of a water droplet. Furthermore, we released a droplet from a height of 15 cm, the surface of **DRS 55-10-6** showed non bouncing phenomena. On the other hand, the surfaces of **DRS 55-10-8, 10** showed bouncing of water droplet (Fig. 3.6e). The bouncing ability thus seems to be superior to that of a natural lotus leaf. This may be due to the increment of the Laplace pressure and of non-penetrating spaces achieved by controlling the surface morphology (Fig. 3.6b-d). Actually, it was observed that the droplet completely bounced off without splitting at the surface of **DRS 55-10-10** (Fig. 3.6e), in contrast with that on a lotus leaf (Fig. 3.6c). From the perspective of the bouncing phenomena, we found that the surface having optimized intervals between the DRSs, the thickness of rod-shaped pillars, and the length of needle-shaped crystals on the rod-shaped pillars worked effectively for the bouncing ability of the surface. The results led us to understand the structures of natural hydrophobic surfaces, including that of a lotus leaf.

Finally, we optimized all conditions to prepare the surfaces. From the viewpoint of the interval between the rod-shaped crystals (Fig. 3.2a), the intervals were increased by increasing the temperature of the 1st annealing, so a surface obtained by heating at 60, 65 or 70 °C as the 1st annealing offers the possibility of showing a higher Laplace pressure compared with a surface obtained by heating at 55 °C as the 1st annealing. Therefore, we prepared DRS surfaces of the **DRS 60** series by repeating the conditions of the 2nd UV and the 2nd annealing to fatten the rod-shaped crystals in order to prevent their melting after visible light irradiation. However, no bouncing phenomena of a water droplet was observed due to the wider interval between the larger projection compared with the **DRS 55** series. The reason for the wide interval in the **DRS60** series

was due to the smaller sizes of the rod-shaped crystals compared with the size of the rod-shaped crystals at 55 °C. Since the size of the rod-shaped crystals generated at 60 °C as the 1st annealing was small, some small crystals were melted by visible light irradiation, resulting in a wider interval. Consequently, the condition of the 1st annealing at 55 °C was the optimum temperature to prepare the double-roughness structures showing superhydrophobicity and larger Laplace pressure than a lotus leaf.

Table 3.3 Preparation conditions of double roughness surfaces of **DRS 55-10-2~10**.

Surface	1 st UV irr.	1 st Anneal	2 nd UV irr.	2 nd Anneal	1 st Vis. irr.	3 rd UV irr.	3 rd Anneal	Figures
DRS 50-10-4	For 10 min at RT	24h at 50 °C	For 10 min at RT	For 3 h at 70 °C	For 4 h at RT	For 4 min at RT	For 1 h at 50 °C	Fig. 3.5b
DRS 55-10-2		20 h at 55 °C				For 2 min at RT		-
DRS 55-10-4						For 4 min at RT		Fig. 3.5c
DRS 55-10-6						For 6 min at RT		-
DRS 55-10-8						For 8 min at RT		-
DRS 55-10-10						For 10 min at RT		Fig. 3.5d

3.3.6 Theoretical understanding of DRS surface and CGT based on viscous friction in bouncing droplets

Here, we roughly discuss the mechanics. As a result, following two conditions must be satisfied to bounce. The first condition is that Laplace pressure P_L due to DRS surface is larger than dynamic pressure by impacting droplets P_d , where $P_L = 16\gamma H/(\sqrt{2}p - D)^2$ (γ : surface tension, H : height of surface structure, p : interval of surface structures, and D : diameter of the surface structures) and $P_d = (1/2 \rho V^2) = \rho gh$ (ρ : density of droplet, V : fall velocity, g : gravitational acceleration, and h : release height). Under the condition of $P_L > P_d$, droplets bounce on DRS surface. This is valid when the surface structures stand perpendicular to the surface and the needle-shaped crystals are long enough. The second condition is that the needle-shaped crystals on DRS surface must be longer than the penetration depth of water into the space between the needle-shaped crystals.

Using the needle-shaped crystals in H_{needle} and D_{needle} and the average interval between the rod-shaped crystals p_{rod} , P_L is calculated and summarized in Table 3.2. P_d is 1.47×10^3 Pa ($h = 15$ cm). In this study, a larger $P_L > P_d$ range is maintained in **DRS 50-10-4**, **DRS 55-10-4**, **DRS 55-10-6**, **DRS 55-10-8** and **DRS 55-10-10**, but

water droplets do not bounce on **DRS 55-10-4** ($h = 10, 15$ cm) and **DRS 55-10-6** ($h = 15$ cm), which contradicts the criterion of $P_L > P_d$. Actually, this criterion is valid when the surface structures stand perpendicular to the surface as shown in Fig. 3.7a, where the angle of rod-shaped crystals from surface, θ_{rod} , is 90° (ideal) and the edges of needle-shaped crystals on the top of rod-shaped crystals suppress the advances of the contact lines by pinning effect. On the prototype,¹⁶ the rod-shaped crystals were slightly tilted and their θ_{rod} was 76° as shown in Fig. 3.7b. In this study, the rod-shaped crystals are tilted as observed in Fig. 3.7g, h, and their θ_{rod} is 64° as shown in Fig. 3.7c and d. In these cases, the pinning effect is weak and the contact line advances. To investigate the advancing length of the contact line along the needle-shaped crystals, the relationship between H_{needle} and release height $h_{release}$ is shown in terms of bounding behaviors as shown in Fig. 3.7i, where the advancing length is corresponding to the critical length of needle-shaped crystals $H_{c,needle}$ to penetrate into the space between the needle-shaped crystals fully. Based on the experimental results, $H_{c,needle}$ seems to be nonlinear ($\propto (h_{release})^\alpha, 0 < \alpha < 1$). Assuming that water droplets is a Maxwell model of viscoelastic body and slightly penetrate, $H_{c,needle}$ can be described to be

$$H_{c,needle} \sim \eta \sqrt{2gh_{release}} / E_{drop}^Y, \quad (1)$$

where η : viscosity of water, g : gravitational acceleration, E_{drop}^Y : Young modulus of droplets. Eq. 1 describes the experimental results very well and the importance of the length of needle-shaped crystals. When the needle-shaped crystals are shorter than $H_{c,needle}$, water penetrates fully and non-bouncing occurs (Fig. 3.7c). In contrast, when the needle-shaped crystals are longer than $H_{c,needle}$, incomplete penetration occurs and water droplets bounce (Fig. 3.7d). The length of needle-shaped crystals is thus one of the important factors in CGT to design bouncing phenomena. In other words, long needle-shaped crystals generate large apparent Laplace pressure in CGT.

3.4 Conclusion

In summary, we succeeded in optimizing surfaces having double-roughness structures to achieve high superhydrophobicity and high Laplace pressure through controlling the CGT of photochromic diarylethene **1**. By adjusting the condition of photo-irradiation and heating processes, we optimized the intervals and height of a surface's microstructure. Then, we successfully increased the Laplace pressure of the solid surface to attain the ability to bounce a water droplet off it, a performance comparable to that of a natural lotus leaf. In fact, it is better to grow the crystals more vertically, however, we solved the issue by elongating the length of small needle-shaped crystals. In the future, we try to grow the crystals vertically by using kind of epitaxial growth technique. Furthermore, we also explained the bouncing phenomena on a surface theoretically from the perspective of the microstructure of a superhydrophobic surface. As mentioned in the Fig. 3.6c, the DRSs of the natural lotus leaf were the most suitable structure for a self-cleaning surface with reversibility.⁸ Therefore, our CGT is the most suitable one for controlling such very complex crystal growth, and no other existing system can be so readily controlled by procedures based on the reversibility of surface structures.¹⁶ Such a topological control technique is applicable to the control of wettability on solid surfaces and for the non-contact creation of functional materials such as photonic crystals.

3.5 References

- 1) F. Xia, L. Jiang, *Adv. Mater.* **2008**, *20*, 2842–2858.
- 2) K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, R. J. Full, *Nature* **2000**, *405*, 681–685.
- 3) M. D. Bartlett, A. B. Croll, D. R. King, B. M. Paret, D. J. Irschick, A. J. Crosby, *Adv. Mater.* **2012**, *24*, 1078–1083.
- 4) P. Vukusic, J. R. Sambles, C. R. Lawrence, *Nature* **2000**, *404*, 457.
- 5) Y. Zhao, Z. Xie, H. Gu, C. Zhu, Z. Gu, *Chem. Soc. Rev.* **2012**, *41*, 3297–3317.
- 6) W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1–8.
- 7) C. Neinhuis, W. Barthlott, *Ann. Bot.* **1997**, *79*, 667.
- 8) M. Yamamoto, N. Nishikawa, H. Mayama, Y. Nonomura, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2015**, *31*, 7355–7363.
- 9) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.
- 10) 39. M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.
- 11) K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura, M. Irie, *Angew. Chem. Int. Ed.* **2006**, *45*, 6470–6473; *Angew. Chem.* **2006**, *118*, 6620–6623.
- 12) N. Nishikawa, H. Kiyohara, S. Sakiyama, S. Yamazoe, H. Mayama, T. Tsujioka, Y. Kojima, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2012**, *28*, 17817–17824.
- 13) N. Fujinaga, N. Nishikawa, R. Nishimura, K. Hyodo, S. Yamazoe, Y. Kojima, K. Yamamoto, T. Tsujioka, M. Morimoto, S. Yokojima, S. Nakamura, K. Uchida, *CrystEngComm* **2016**, *18*, 7229–7235.
- 14) K. Uchida, N. Nishikawa, N. Izumi, S. Yamazoe, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii, M. Irie, *Angew. Chem. Int. Ed.* **2010**, *49*, 5942–5944; *Angew. Chem.* **2010**, *122*, 6078–6080.
- 15) N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2013**, *29*, 8164–8169.
- 16) R. Nishimura, K. Hyodo, H. Sawaguchi, Y. Yamamoto, Y. Nonomura, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *J. Am. Chem. Soc.* **2016**, *138*, 10299–10303.
- 17) K. Takase, K. Hyodo, M. Morimoto, Y. Kojima, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Commun.* **2016**, *52*, 6885–6887.

- 18) K. Uchida, R. Nishimura, E. Hatano, H. Mayama, S. Yokojima, *Chem. Eur. J.* **2018**, *24*, 8491–8506.
- 19) Y. C. Jung, B. Bhushan, *Langmuir* **2008**, *24*, 6262–6269.
- 20) S. A. Wainwright, F. Vosburgh, J. H. Hebrank, *Science* **1996**, *202*, 747–749.
- 21) P. Ball, *Nature* **1999**, *400*, 507–509.
- 22) G. D. Bixler, B. Bhushan, *Adv. Funct. Mater.* **2013**, *23*, 4507–4528.
- 23) J. C. Bird, R. Dhiman, H.-M. Kwon, K. K. Varanasi, *Nature* **2013**, *503*, 385–388.
- 24) Liu, L. Moevis, X. Xu, T. Qian, J. M. Yeomans, Z. Wang, *Nature Phys.* **2014**, *10*, 515–519.
- 25) J. Lee, H. M. Kim, Y. S. Song, J. R. Youn, *ACS Nano* **2012**, *6*, 7656–7664.
- 26) K. Lee, W. B. Jung, S. R. Nagel, T. W. Odom, *Nano Lett.* **2016**, *16*, 3774–3779.
- 27) J. Nine, T. T. Tung, F. Alotaibi, D. N. H. Tran, D. Losic, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8393–8402.
- 28) M. Song, J. Ju, S. Luo, Y. Han, Z. Dong, Y. Wang, Z. Gu, L. Zhang, R. Hao, L. Jiang, *Sci. Adv.* **2017**, *3*, e1602188.

Chapter 4

Dual wettability on diarylethene microcrystalline surface mimicking a termite wing

4.1 Introductions

In nature, many plants and insects have specifically structured surfaces that show specific surface properties. The unique micro- and nano-structures on such surfaces can be seen in the self-cleaning effect of lotus leaves ¹, the superhydrophobic forces exerted by a water strider's leg ², the attachment mechanism of geckos ³, the structure colours of the peacock ⁴, or morpho butterfly ^{5,6}, and many other natural phenomena ⁷⁻¹². These structures have received much attention, and artificial systems have been fabricated by mimicking such natural surfaces. Water repellence supports the performance of self-cleaning materials, and it has been studied in both natural and artificial systems ¹². Historically, the most important finding is the “lotus effect” of Barthlott and Neinhuis ¹³. The super-water-repellent and self-cleaning effects of the lotus leaf have been attributed to the double-roughness structure of surfaces with micro- and nanostructures (trichomes, cuticular folds, and wax crystals), as well as to the hydrophobic properties of the epicuticular wax ¹⁴.

Recently, it was reported that many terrestrial insects use non-wetting surfaces to reduce the risks of living in environments with much rain and other water surfaces that the insect may encounter ¹⁵⁻²⁰. G. S. Watson *et al.* reported that the complex structure of the termite's wing surface shows specific wettability (Fig. 4.1) ^{18,19}. The termite is one of the social insects, and it is known that high humidity is important for their breeding. One of the termites *Nasutitermes sp.* and *Microcerotermes sp.* fly during the rain period to avoid attacks by predators, while water is essential for building nests and soil tunnels, i.e., moist soil is necessary for burrowing ^{18,19}. Accordingly, they have delicate structures, or “dual wettability”, on their wings, and these specific structures work to minimize interaction with water bodies at various length scales to effectively reduce the body mass ^{18,19}. The termite's wing surface is covered with two types of projections of different sizes (Fig. 4.1). One is a hair-like

projection (macrotrichia) that is about 50 μm long and 1 μm wide, while the other is a star-shaped projection (micrasters) of 5-6 μm in height and width. These hairs protect the wing membrane from the contact with large water droplets, while the small projections work to keep the small droplets on the surface of the wing^{18,19}. The small droplets gather to build up large ones and are finally removed via the hair arrays. Furthermore, the approximation of body weight after wetting suggested the importance of collection ability by micrafter. The estimated additional body weight relation to the total body weight of *Nasutitermes sp.* and *Microcerotermes sp.* are several %. In fact, larger droplets were repelled by hair like structures, while small droplets were collected by star-shaped structures¹⁸. G. S. Watson et al. argued the *Nasutitermes sp.* and *Microcerotermes sp.* have water collecting ability, and owing to the ability, they can control their flight¹⁸. Interestingly, the termites which fly during rainy period have hair structures on their wings, but other termites have no hair shaped structures on their wings (Fig. 4.1). Owing to these functions, the termite can minimize interaction with micro-sized water droplets while flying in rain or even storm.

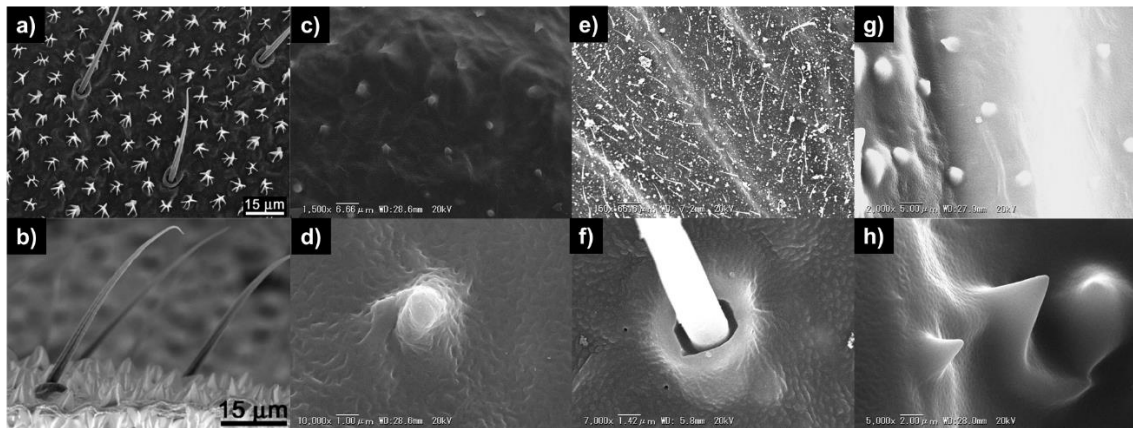


Figure 4.1 SEM images of termite wings. a, b) SEM images of *Nasutitermes sp.*, which fly during rain periods, c, d) *Reticulitermes speratus*, which fly before rain periods, e, f) *Coptotermes formosanus*, which fly during rain periods, g, h) *Incisitermes minor (Hagen)*, which fly after rain periods.

Consequently, termite wings have a structure that forms the foundation of their survival strategy. Increasingly, sustainability is also important in human society and the management of water, particularly regarding the important issues of the environment and energy. We believe that better understanding the structure of termite

wings would provide great hints for material design as an essential component of humidity management in human society. And to build it is to understand. Therefore, this research attempts to fabricate functional material replicating termite wing from diarylethene.

Diarylethene derivatives are well-known compounds whose photochromic properties, such as the thermal stability of both isomers, and high photoreactivity even in the crystalline states, are excellent among the photochromes. These unique properties are indispensable to the current research, and we applied them to the design of photoinduced topographical control systems²¹⁻²⁷. In previous papers, we showed that surface topography could be structured by using a crystal growth technique (CGT)²⁷ of photogenerated closed-ring isomer **1c** of thermally stable photochromic diarylethene **1** (Fig. 4.2)²¹. Upon UV irradiation to the microcrystalline film of **1o** (Fig. 4.2), the needle-shaped crystals of **1c** grew on the surface. Then, a superhydrophobic property was observed. Moreover, we can switch this property by melting these crystals by irradiation with visible light, thus causing the superhydrophobicity to disappear. In the next step, we mimicked the double-roughness structured surface of the lotus leaf and reproduced it on the microcrystalline surface of **1o**. Consequently, we succeeded in demonstrating the water droplet bouncing phenomena as observed for the lotus leaf in nature²⁵. The photoinduced topographical changes of **2o** were similar to those of **1o**, while the size of the needle-shaped crystal of **2c** was much smaller than that of **1c**, when they grew at 30 °C^{23,24}. We took advantage of this difference in the current study.

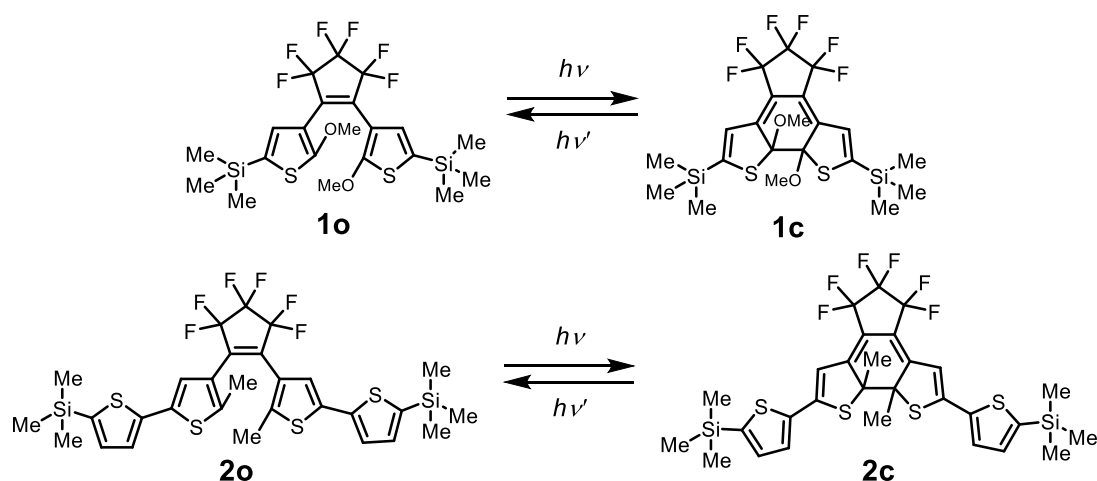


Figure 4.2 Molecular structures of diarylethenes. Molecular structures and photoisomerization of diarylethenes **1** and **2**.

Here, we prepare a photo-responsive superhydrophobic surface using a mixture of diarylethenes **1o** and **2o**. The mixture of two types of diarylethenes may produce the surface with the sum of two different characteristics or completely different characteristics. The obtained photogenerated rough surface consisting of the two different sized needle-shaped crystals **1c** and **2c** shows specific bouncing ability mimicking a termite wing as we have intended. Then, we analyse the surface structures and clarified the relation between the wettability by monitoring the different sizes of water droplet on the surfaces.

4.2 Experimental section

4.2.1 General information

A scanning electron microscope (SEM)(KEYENCE VE-8800) was used to observe the microcrystalline surfaces of diarylethenes. A Xe lamp (Ushio 500-W) was used to irradiate the visible light with an optical cut-off filter (Toshiba color filter Y48; $\lambda > 480$ nm). A hand lamp (Topcon UV lamp PU-21 (main $\lambda = 254$ nm, 23 W) and Spectroline Hand-Held UV lamp, E-series ($\lambda = 313$ nm, 8 W)) were used for UV light irradiation. The measurements of statistic and dynamic contact angles of the water droplets was monitored on Drop master 500 from Kyowa Interface Science Co., Ltd. by use of distilled water. The volume of water droplets was 1.5 μL . A micro slide glass

plate from Matsunami Glass (Thickness 1.0~1.2 mm) was used for the subphase of diarylethene microcrystalline films.

4.2.2 Preparation and characterization of the film

The microcrystalline films were prepared by coating chloroform solutions containing **1o** (640 mg mL⁻¹), **2o** (540 mg mL⁻¹) and a mixture of **1o** and **2o** (540 mg mL⁻¹, with both compounds mixed in equimolar amount (**1o**: 243 mg; 4.46×10⁻⁴ mol and **2o**: 297 mg; 4.38×10⁻⁴ mol)) onto glass substrates, and the solvent was evaporated *in vacuo*. A scanning electron microscope (KEYENCE VK-8800) was used to observe the microstructure of the surfaces. The film thickness was approximately 20 μm from the SEM images taken from a side view of the microcrystalline film. Static contact angles (CAs) and sliding angles (SAs) of the water droplets were measured with an optical contact angle meter (Kyowa Interface Science Co., Ltd., Drop Master 500). Visible light ($\lambda > 500$ nm) irradiation was carried out using an Ushio 500-W xenon lamp with a cutoff filter (Toshiba color filter Y-50), and UV light irradiation was carried out with a Spectroline Hand-Held UV lamp, E-series ($\lambda = 254$ nm, 820 mW/cm² (distance: 15 cm)). Photoirradiation experiments at the eutectic temperature were carried out using a thermo-controller (FP82HT hot stage). The crystal data were already reported in a previous paper ². For the fractal analysis, microcrystalline film samples on the glass substrate were set on the electron microscope's stage with conductive carbon tape, and the Au-Pd alloy was evaporated onto the sample surface. The cross-section was observed using a sample that was cracked together with the cover glass and set perpendicularly on the stage.

4.3 Results and discussion

4.3.1 Preparation of crystalline films mimicking the termite wing

To examine whether the surface of the mixture of **1o** and **2o** possess the properties of termite wing as we have expected, we first investigated its properties. A solution containing equimolar amount of **1o** and **2o** was coated onto a glass plate. After the solvent was evaporated *in vacuo*, the surface of the microcrystalline film was covered with plate-like crystals (Fig. 4.3a).

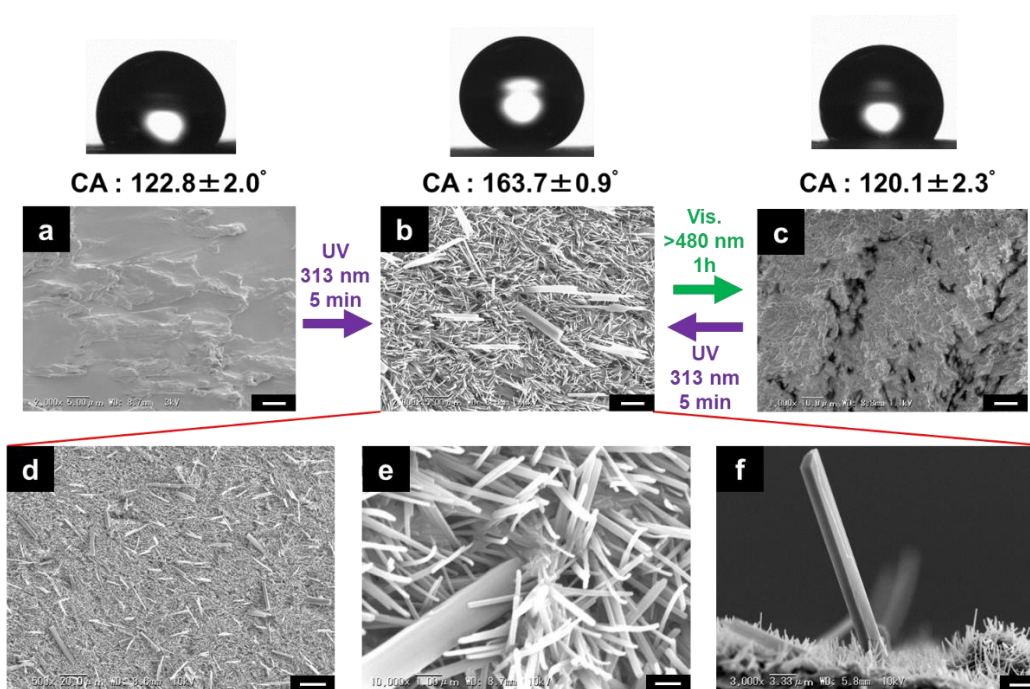


Figure 4.3 Wettability and reversible crystal growths on the surface. Images of a water droplet (Volume: 1.5 μL) on rough surfaces and SEM images (a-f) of topographical changes of microcrystalline films made from a mixture of **1o** and **2o** (molecular ratio, **1o:2o** = 1:1) by alternating irradiation with UV and visible light. a) Before UV irradiation; b) surface UV (313 nm) light irradiation for 5 min followed by storage at 30 $^{\circ}\text{C}$ in the dark for 9 days; c) visible ($\lambda > 480$ nm) light irradiation for 1 h while kept at 80 $^{\circ}\text{C}$. Scale bars: 5.00 μm for (a-c); 20.0 μm for (d); 1.00 μm for (e), 3.33 μm for (f).

On the initial surface, the contact angle (CA) of a water droplet was only 123 $^{\circ}$. Then, the surface was irradiated for 5 min with 313-nm light followed by storage at 30 $^{\circ}\text{C}$, which is higher than the T_g of both **1o** and **2o** crystals, since crystal growths of

1c and **2c** were observed on a softened surface above T_g ²⁶. After 9 days' storage at this temperature in the dark, the surface was covered with two types of needle-shaped crystals of **1c** and **2c** (**Surf_{1c+2c}**, Fig. 4.3b). SEM images at different scales of angles are shown in Fig. 4.3d-f. By comparing the SEM images of three types of surfaces, the larger needle-shaped crystals grown on the mixed microcrystalline surface are crystals of **1c**, and their lengths and widths are about 16 and 1.5 μm , respectively, while the smaller ones are crystals of **2c** with lengths and widths of about 1.9 and 0.2 μm , respectively. The intervals between the crystals were estimated from SEM images. We estimate the number of crystals per unit area as 12.6 mm^{-2} and $5.00 \times 10^6 \text{ mm}^{-2}$ for **1c** and **2c**, respectively. These sizes are quite consistent with those observed for homo-microcrystalline surfaces (Fig. 4.4). The activation energies of the crystal growth were measured independently in the previous work (**1c**: 143 kJ/mol, **2c**: 58 kJ/mol). Low activation energy of **2c** compared with **1c** probably reflect the low crystallinity of **2c**, resulting the bulky molecular structure. The surface was prepared with good reproducibility. Upon visible ($\lambda > 480 \text{ nm}$) light irradiation for 1 h at 80 °C, the needle-shaped crystals were melted (Fig. 4.3c). The formed structures were very similar, in spite of the difference in the ratio, indicating that the crystal growth of the needle-shaped crystals of **1c** and **2c** did not affect each other. To confirm this, we attempted to prepare such surfaces by changing the ratio of **1o** and **2o**; in fact, the surface topography is not so sensitive to the molecular ratio of **1o** and **2o**. The CA of a water droplet changed with the surface topographies. On the initial surface (Fig. 4.3a), the CA was only 123°. Due to the needle-shaped crystal growth of **1c** and **2c** on the surface, CA increased to 164° upon irradiation with UV light to **Surf_{1c+2c}**. The dynamic CAs of a water droplet were also observed. The advancing and receding contact angles (CA_{ad} and CA_{rec}) were $164.2 \pm 1.2^\circ$ and $159.6 \pm 0.6^\circ$, respectively, and sliding angle (SA) was 2°. Upon visible light irradiation at 80 °C, CA decreased to 120°. By alternate irradiation with UV and visible light, the surface topography, along with CA, changed reversibly at least three times (Fig. 4.5).

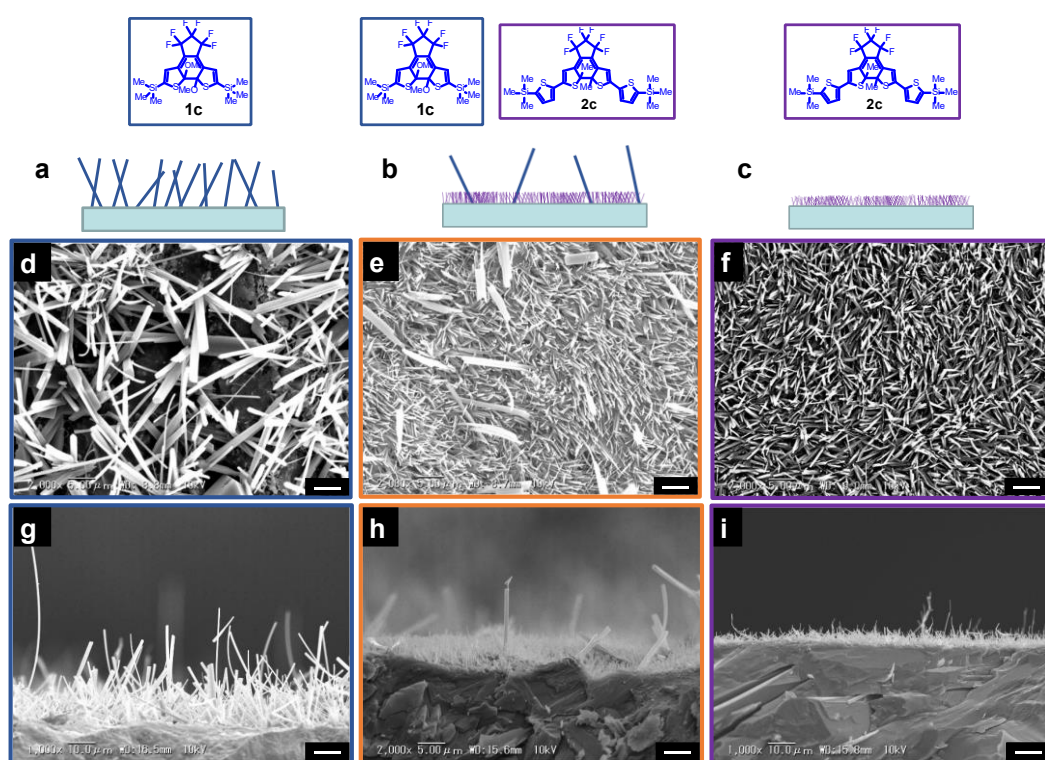


Figure 4.4 Comparison of the photoinduced surface topologies. a) **Surf_{1c}**, b) **Surf_{1c+2c}**, and c) **Surf_{2c}**: pale blue substrate and dark blue crystals correspond to crystals of open- and closed-ring isomers, respectively. SEM images of d, g) surface with needle-shaped crystals of **1c** and **2c**, e, h) surface with needle-shaped crystals of **1c** and **2c**, f, i) surface with needle-shaped crystals of **2c**. Scale bars: 5 μm for (d-f) and (h) images, which are magnified 2000 times; 10 μm for (g) and (i) images, which are magnified 1000 times.

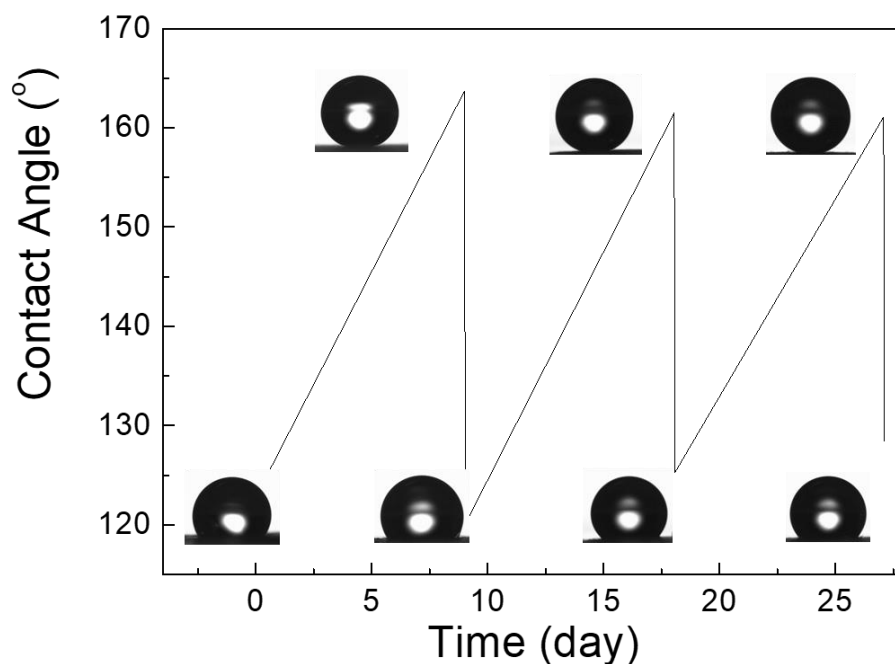


Figure 4.5 Reversible CA changes of a water droplet. By alternate irradiation with UV and visible light, the surface topography, along with CA, changed reversibly at least three times.

As we reported in previous papers, the larger crystals (approximately 5–10 μm in diameter and 20–30 μm in length) of **1c** grown by Ostwald ripening were apt to show water-adhesive properties²², while the smaller sub-micro meter crystals (0.2–0.3 μm in diameter and 2.2–2.5 μm in length) of **2c** showed super-water-repellence^{23,24}.

4.3.2 Water dropping test

In the current case, the microcrystalline surface consists of only **1o** forming a rough surface of larger needle-shaped crystals with water-adhesive properties (**Surf_{1c}**, Fig. 4.6e), while the microcrystalline surface consists of only **2o** forming a rough surface of smaller needle-shaped crystals with water-bouncing properties (**Surf_{2c}**, Fig. 4.6f). The essential point of the current study is to simultaneously grow the two types of crystals of different sizes. Consequently, we could achieve water-adhesive and -bouncing properties on the same surface.

Unlike static CAs and SAs, the dynamic surface properties are different from those of natural superhydrophobic surfaces (e.g. the surface of a lotus leaf). Water-droplet-bouncing experiments were performed by releasing water from a height of 10 cm above the three types of superhydrophobic surfaces (**Surf_{1c}**, **Surf_{2c}** and **Surf_{1c+2c}**) (Fig. 4.6). We released a water droplet to **Surf_{1c+2c}** from a height of 10 cm, and a small portion of water remained on the surface (Fig. 4.6d). On this surface, either needle shaped crystals worked to provide either water adhesion or repellence. Then, we released water droplets onto **Surf_{1c}** and **Surf_{2c}**. On **Surf_{1c}**, water droplets were adsorbed onto the surface (Fig. 4.6e), while on **Surf_{2c}**, water droplets bounced (Fig. 4.6f). These results indicated that on **Surf_{1c+2c}**, the longer needle-shaped crystal of **1c** achieved water- capturing capability, while the smaller needle-shaped crystals of **2c** achieved water-repelling capability.

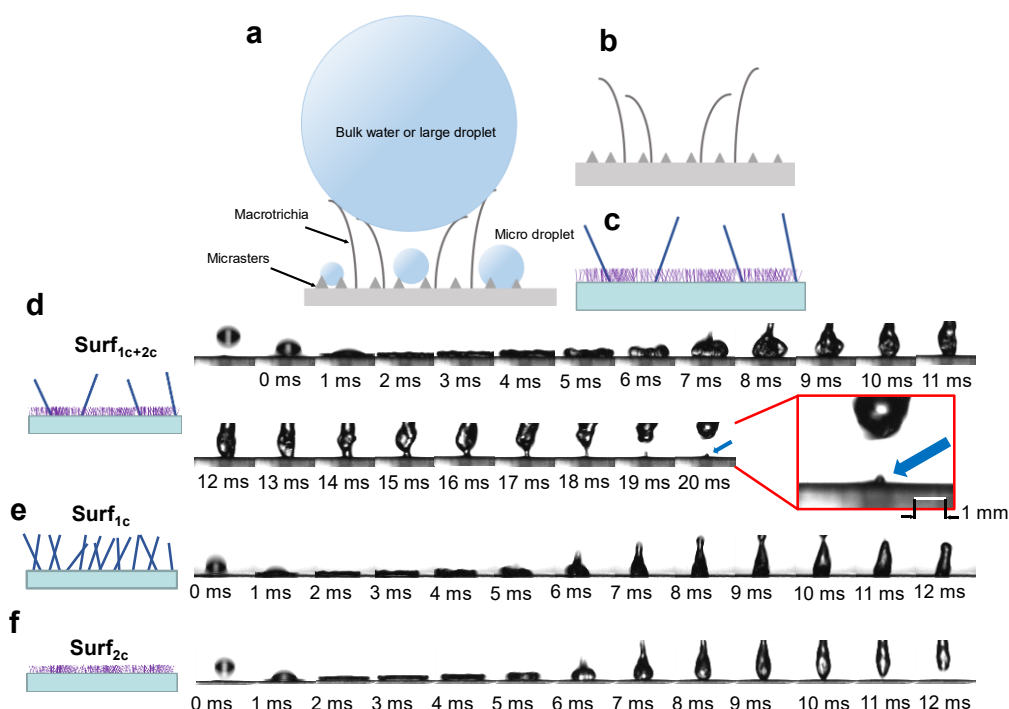


Figure 4.6 Illustration of the surface structures and bouncing phenomena. a) Schematic illustration of water droplet on the termite wing. b) Schematic illustration of surface structures of the termite wing. c) Schematic illustration of the surface structures mimicking the surface structures of the termite wing. Water-droplets ($7.6 \pm 0.6 \mu\text{L}$) were poured from a height of 10 cm onto the surfaces for monitoring the bouncing phenomena. d) Optical images of a bouncing droplet on **Surf_{1c+2c}**. A small droplet remained on the surface (blue arrow). e) Optical images of a non-bouncing droplet on **Surf_{1c}**. f) Optical images of a bouncing droplet on **Surf_{2c}**. Scale bar of expanded image is 1 mm.

4.3.3 Water spraying test

From the above discussion, **Surf_{1c+2c}** thus has the dual capabilities of capturing and repelling water owing to the presence of the two types of needle-shaped crystals of different sizes. This kind of wettability is the same as that of a termite wing, even though the small (large) needle-shaped crystals repel (capture) a droplet, unlike the role of the hairs and micrasters of termite wings, where the small micrasters capture droplets but the large hairs repel them. On the surface of termite wing, by spraying the microdroplet (20-150 μm), small-sized droplets (<100 μm) were maintained on the wing surface¹⁸. In order to regenerate the functions of the termite wing, we also sprayed microdroplet (20-640 μm) onto **Surf_{1c}**, **Surf_{2c}** and **Surf_{1c+2c}**. In fact, we could

observe microdroplets bouncing on the surfaces. We monitored the bouncing phenomena with a high-speed camera. Consequently, we could observe two cases: microdroplets showing bouncing and non-bouncing phenomena (Fig. 4.7).

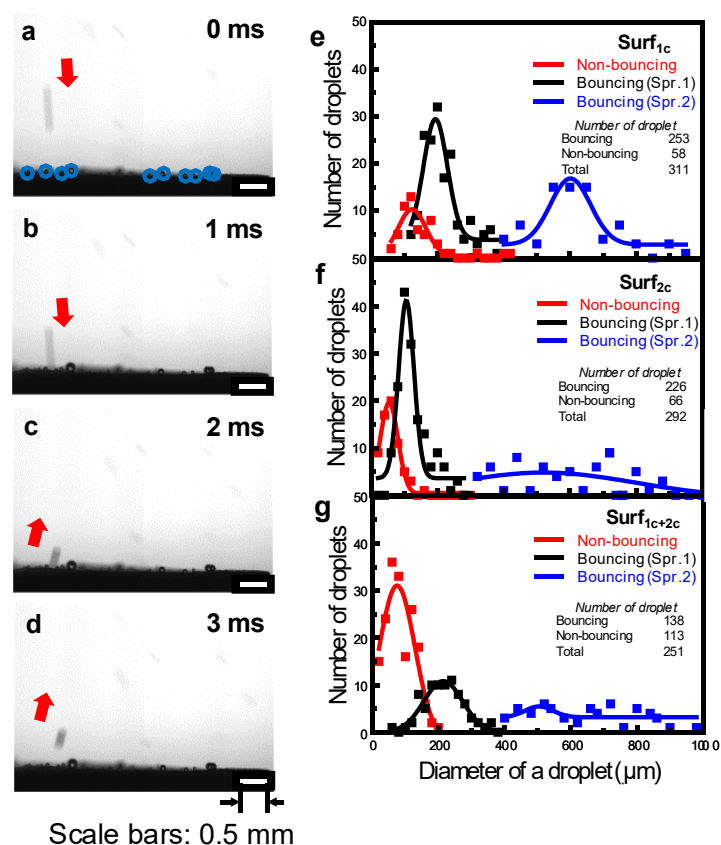


Figure 4.7 Optical images of a microdroplet and size distributions. a-d) Optical afterimages of the movement of a water droplet during bouncing on **Surff_{1c+2c}** in 3 ms. Red arrows indicate direction of droplet's movement. Blue circle marks are droplets adsorbing on the surface. e-g) Distributions of diameters of water droplets contacted with **Surff_{1c}**, **Surff_{2c}** and **Surff_{1c+2c}**. e) Distribution of diameters of water droplets contacted **Surff_{1c}**, f) contacting **Surff_{2c}**, and g) contacting **Surff_{1c+2c}**. In the graphs (e-g), the red dots show diameter distribution of non-bouncing droplets and black dots show diameter distribution of bouncing droplets generated by sprayer 1 (Spr. 1: Generating the microdroplet of 40-400 μm in diameter). The blue dots show diameter distribution of bouncing droplets generated by sprayer 2 (Spr. 2: Generating the microdroplets of 400-1000 μm in diameter). Number of droplets used for preparation of distribution is indicated inside the graphs (e-g). Scale bars for all optical images are 0.5 mm.

We measured the sizes of all droplets contacting the surfaces and summarized the results as a distribution. By comparing the distributions based on the size of the droplets, the bouncing and non-bouncing ranges are separated by mixing the two diarylethenes. For these distributions, the values of average droplet diameters are summarized in Table 1. On the surfaces of **Surf_{1c}** and **Surf_{2c}**, the difference between the average size of a droplet showing bouncing and one showing non-bouncing behaviour is relatively narrow, at 76.2 and 66.8 μm , respectively. On the other hand, this difference for **Surf_{1c+2c}** was rather larger (155.1 μm). These results indicate that by mixing the two diarylethene derivatives, the difference between bouncing and non-bouncing water droplets became dramatically separated; in other words, the dependence on the size of water droplets could be clearly distinguished for both types of wettability.

Table 1. Average diameter and standard deviation of water droplets at collision on surfaces.

	Average diameter of bouncing droplets (μm)	Average diameter of non-bouncing droplets (μm)
Surf_{1c}	222.1 $\pm$ 74.7	145.9 $\pm$ 68.5
Surf_{2c}	126.8 $\pm$ 48.9	60 $\pm$ 28.7
Surf_{1c+2c}	238.8 $\pm$ 99.3	83.7 $\pm$ 40.5

Furthermore, in order to clarify the significance of the size of droplets showing either the bouncing or non-bouncing phenomena, we fitted the sizes of real fog, drizzle and rain to the diameter distribution of water droplet contacting **Surf_{1c+2c}**. In 2017, S. Glienke and co-worker reported the quantification of the sizes of a cloud droplet (i.e. a fog droplet), a drizzle droplet, and a rain droplet with reference to a previous report and a meteorological definition (Fig. 4.8a) (American Meteorological Society, Glossary of Meteorology. “Drizzle”, (2016) [Available online at <http://glossary.ametsoc.org/wiki/Drizzle>.])²⁸⁻²⁹. The water droplet classified as rain is generated by repeating the collision and coalescence of the cloud droplet in the raincloud. Consequently, it is classified differently depending on the size. A droplet of 40-100 μm in diameter is classified as a “cloud (fog) droplet”. By surveying the literature, the definition of the size of a drizzle droplet usually sets the lower limit at

the diameter to about 100 μm . Furthermore, the American Meteorological Society defined the size of drizzle as a type of precipitation consisting of water droplets less than 500 μm in diameter but larger than 100 μm , with droplets larger than 500 μm considered raindrops. Therefore, a droplet with a 100-500 μm diameter is classified as a “drizzle droplet”, and a droplet with a diameter larger than 500 μm is classified as a “rain droplet”. Following the above guidelines, we fitted the distribution results to the sizes of rain (Fig. 4.8b). Consequently, the region of non-bouncing droplets was fitted to the region of fog droplet, while the region of bouncing droplets was fitted to the region of drizzle and rain droplet regions. These results indicate that a surface mimicking the structures of the termite wing can collect fog-sized droplets and repel droplets as large as drizzle- and rain-sized droplets selectively (Fig. 4.8c). Additionally, this distribution was related to the impacting velocity of a water droplet (Fig. 4.8d). The non-bouncing droplets collide with the surface with relatively low speed, on the other hand, the bouncing one collide with the surface with relatively high speed. This dual wettability showed by **Surf_{1c+2c}** very closely reproduces the function of a termite wing. Therefore, we succeeded in regenerating the function of termite wings by mimicking their structure by using our CGT to the microcrystalline surface of a mixture of diarylethene **1o** and **2o**.

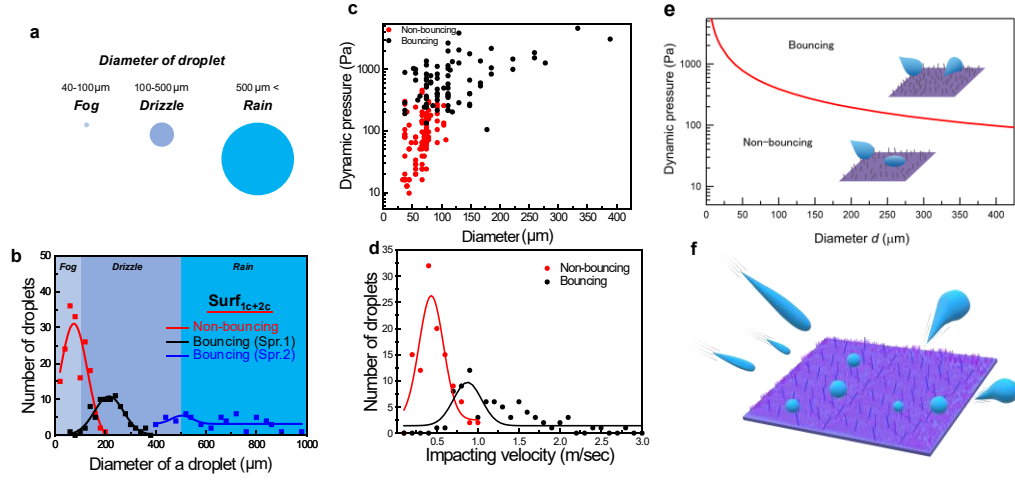


Figure 4.8 Classification and mechanical analysis of water droplets. a) Classification by droplet's diameter. b) Diameter distribution of bouncing (black) and non-bouncing (red) droplets matched to size regions of three types of rain. c) Diameter-versus-Dynamic pressure distribution of sprayed droplet. d) The distribution of Impacting velocity of water droplets-versus-Number of droplets. e) Theoretical phase diagram of bouncing/non-bouncing behavior. Phase border is described by eq. (3) under the conditions of $f = 0.088$, $e = 0.62$, $\theta_{flat} = 122.8^\circ$, and $\theta_{CB} = 163.7^\circ$, where these values are obtained from the experimental results using **Surf_{1c+2c}**. In particular, e was determined from the experimental results of velocities before and after collision of water droplets with different diameters. f) Schematic illustration of bouncing and non-bouncing of microdroplets depending on droplet size.

4.3.4 Theoretical explanation of dual wettability

To explain the phenomena theoretically, we measured the velocity at the time of collision onto the surface and the mass of all microdroplets from the optical images taken with a high-speed camera. We then calculated the dynamic pressures of impacting droplets, and compared these values with the Laplace pressure on the surface. We characterized collision velocity and mass and calculate the dynamic pressure for all droplet individually and then plotted the data to a graph (Fig. 4.8). The values of dynamic pressure P_d were evaluated by Equation 1,

$$P_d = \frac{1}{2} \rho V^2 \quad (1)$$

where ρ is the density of water and V is the collision velocity of a water droplet. In Fig. 4.8, the results of the non-bouncing droplets are represented by red dots, while those of the bouncing droplets are represented by black dots. According to the

distribution, the two different phenomena were nearly switched at around 200-300 Pa. This result suggests that a threshold of dynamic pressure for bouncing phenomena exists on **Surf_{1c+2c}**.

To understand the threshold of dynamic pressure P_d^{th} , a simple theory is provided. Considering that the kinetic energy of a droplet after bouncing is equal to actual adhesion energy, P_d^{th} can be formulated as

$$P_d^{th} = \frac{5.1\gamma_L(1+\cos\theta_{flat})f}{e^2d} \quad (2)$$

where the factor of 5.1 is obtained from the apparent contact area of the droplet, γ is surface tension of liquid (water), e is the restitution coefficient, θ_{flat} is the equilibrium contact angle on a flat surface, f is the area fraction of a solid surface in the Cassie-Baxter wetting state, and d is the diameter of a droplet. Fig. 4.8e shows the theoretically obtained results of P_d^{th} , which explain well Fig. 4.8c. The importance of adhesion energy to the bouncing ability of microdroplets is thus confirmed theoretically. Actually, f , e and the state of the surfaces (**Surf_{1c}**, **Surf_{2c}** and **Surf_{1c+2c}**) are strongly related to each other.

To understand the correlation between f , e and the typical surface scales, we tried to describe e of **Surf_{1c}**, **Surf_{2c}** and **Surf_{1c+2c}** in terms of V , average interval between needle-shaped crystals and diameter. To discuss e , it is necessary to consider dissipation energy in bouncing droplets. Considering dissipation energy in volume and interfacial parts of microdroplets as shown in Fig. 4.9, residual energy of microdroplets after bouncing on **Surf_{1c}** and **Surf_{2c}** E_{res} is

$$E_{res} = \frac{1}{2}mv^2 = \frac{1}{2}mV^2 - \frac{4\pi\eta r_0^2 V}{3} \left[1 + \frac{4r_0^2 V'}{w^2 V} \right] - \frac{\alpha\pi^2\eta r_0^2 h^2 V}{p^2} \left[1 + \frac{V'}{V} \right] - \alpha\pi r_0^2 \gamma_L (1 + \cos\theta_{flat}) \left(f + \frac{4Dh}{p^2} \right) \quad (3)$$

where $(1/2)mv^2$ is kinetic energy corresponding to the residual energy after bouncing, m is mass of microdroplets, η is viscosity of water, w is the width of wetting area as shown in Fig. 4.9b, α is the ratio of wetting area in comparison with πr_0^2 , V' is recoil velocity ($(V')^2 = V^2 - 2\eta V/(r_0\rho) - 3\alpha\pi\eta Vh^2/(2r_0\rho p^2)$, ρ : density of water), p is the average interval between needle-shaped crystals and h is penetration depth ($h = \eta r_0 V/(6\gamma_L)$). Surface structures are reflected in the third and

last terms of Equation 3. Since squared restitution coefficient e^2 corresponds to $(v/V)^2$, e can be obtained from Equation 3.

$$e = \left(1 - \frac{2\eta}{r_0\rho V} \left[1 + \frac{4r_0^2 V'}{w^2 V} \right] - \frac{3\alpha\pi\eta}{2r_0\rho p^2 V} h^2 \left[1 + \frac{V'}{V} \right] - \frac{3\alpha\gamma_L(1+\cos\theta_{flat})}{2r_0\rho V^2} \left(f + \frac{4Dh}{p^2} \right) \right)^{1/2} \quad (4)$$

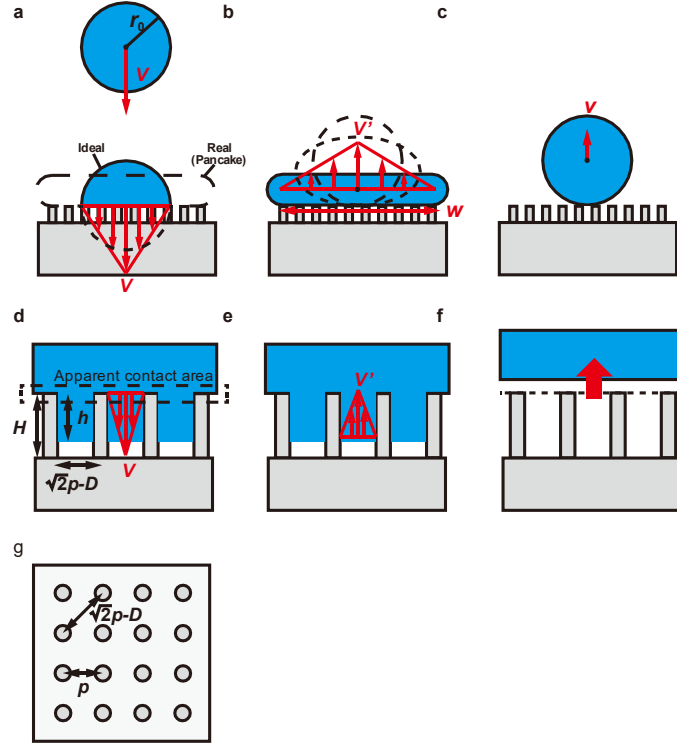


Figure 4.9 Schematic representation of process of dissipation energy. a-c) Dissipation energy in volume part, d-f) dissipation energy in the interfacial part, g) geometry of surface structure (top view).

From the condition that E_{res} is required to be larger than energy to pull water droplets off the surface, e should be larger than threshold of restitution coefficient e_{th} . The conditions of e to bounce of water droplets with radius r_0 is

$$e \geq e_{th} = \left(\frac{3\alpha\gamma(1+\cos\theta_{flat})}{2r_0\rho V^2} \left(f + \frac{4Dh}{p^2} \right) \right)^{1/2}. \quad (5)$$

Computational results of the dependence of e on d ($2r_0$) for **Surf_{1c}** and **Surf_{2c}** are shown in Fig. 4.10a-c. The calculation conditions are $\eta = 10^{-3} \text{Pa} \cdot \text{s}$, $\rho = 10^3 \text{kg m}^{-3}$, $V = 1.00 \text{m s}^{-1}$, $\alpha = 3.40$, $\theta_{flat} = 130.8^\circ$ and 129.5° , $f = 0.249$ and 0.0816 for **Surf_{1c}** and **Surf_{2c}**, respectively. Theoretically, water droplets bounce in

the conditions between the curves of e and e_{th} . Obviously, the calculation results show that the diameter of the bouncing droplets on **Surf_{1c}** is larger than that on **Surf_{2c}**. Next, let us discuss dual wettability on **Surf_{1c+2c}**. Since **Surf_{1c+2c}** is consisted of **Surf_{1c}** and **Surf_{2c}**, dissipation energies on **Surf_{1c}** and **Surf_{2c}** should be considered to understand the bouncing droplets on **Surf_{1c+2c}**. Considering the possibility that water droplets bounce on both the needle-shaped crystals of **1c** and **2c** for very short time or at the same time, then its dissipation energy is the sum of the dissipation energies on **Surf_{1c}** and **Surf_{2c}**. Then, residual energy on **Surf_{1c+2c}** $E_{res, Surf_{1c+2c}}$ is obtained by subtracting dissipation energies of **Surf_{1c}** and **Surf_{2c}** from $(1/2)mV^2$.

$$E_{res, Surf_{1c+2c}} = \frac{1}{2}mv^2 = \frac{1}{2}mV^2 - \left[\frac{4\pi\eta r_0^2 V}{3} \left(1 + \frac{4r_0^2 V'}{w^2 V} \right) + \frac{\alpha\pi^2 \eta r_0^2 h^2 V}{p^2} \left(1 + \frac{V'}{V} \right) + \alpha\gamma_L (1 + \cos \theta_{flat}) \pi r_0^2 \left(f + \frac{4Dh}{p^2} \right) \right]_{Surf_{1c}} - \left[\frac{4\pi\eta r_0^2 V}{3} \left(1 + \frac{4r_0^2 V'}{w^2 V} \right) + \frac{\alpha\pi^2 \eta r_0^2 h^2 V}{p^2} \left(1 + \frac{V'}{V} \right) + \alpha\gamma_L (1 + \cos \theta_{flat}) \pi r_0^2 \left(f + \frac{4Dh}{p^2} \right) \right]_{Surf_{2c}} \quad (6)$$

Squared restitution coefficient of **Surf_{1c+2c}** $e_{Surf_{1c+2c}}^2$ is

$$e_{Surf_{1c+2c}}^2 = 1 - \left[\frac{2\eta}{r_0 \rho V} \left(1 + \frac{4r_0^2 V'}{w^2 V} \right) + \frac{3\alpha\pi\eta}{2r_0 \rho p^2 V} h^2 \left(1 + \frac{V'}{V} \right) + \frac{3\alpha\gamma_L (1 + \cos \theta_{flat})}{2r_0 \rho V^2} \left(f + \frac{4Dh}{p^2} \right) \right]_{Surf_{1c}} - \left[\frac{2\eta}{r_0 \rho V} \left(1 + \frac{4r_0^2 V'}{w^2 V} \right) + \frac{3\alpha\pi\eta}{2r_0 \rho p^2 V} h^2 \left(1 + \frac{V'}{V} \right) + \frac{3\alpha\gamma_L (1 + \cos \theta_{flat})}{2r_0 \rho V^2} \left(f + \frac{4Dh}{p^2} \right) \right]_{Surf_{2c}} \quad (7)$$

The conditions to bounce on **Surf_{1c+2c}** is

$$e \geq e_{th} = \left(\left[\frac{3\alpha\gamma_L (1 + \cos \theta_{flat})}{2r_0 \rho V^2} \left(f + \frac{4Dh}{p^2} \right) \right]_{Surf_{1c}} + \left[\frac{3\alpha\gamma_L (1 + \cos \theta_{flat})}{2r_0 \rho V^2} \left(f + \frac{4Dh}{p^2} \right) \right]_{Surf_{2c}} \right)^{1/2} \quad (8)$$

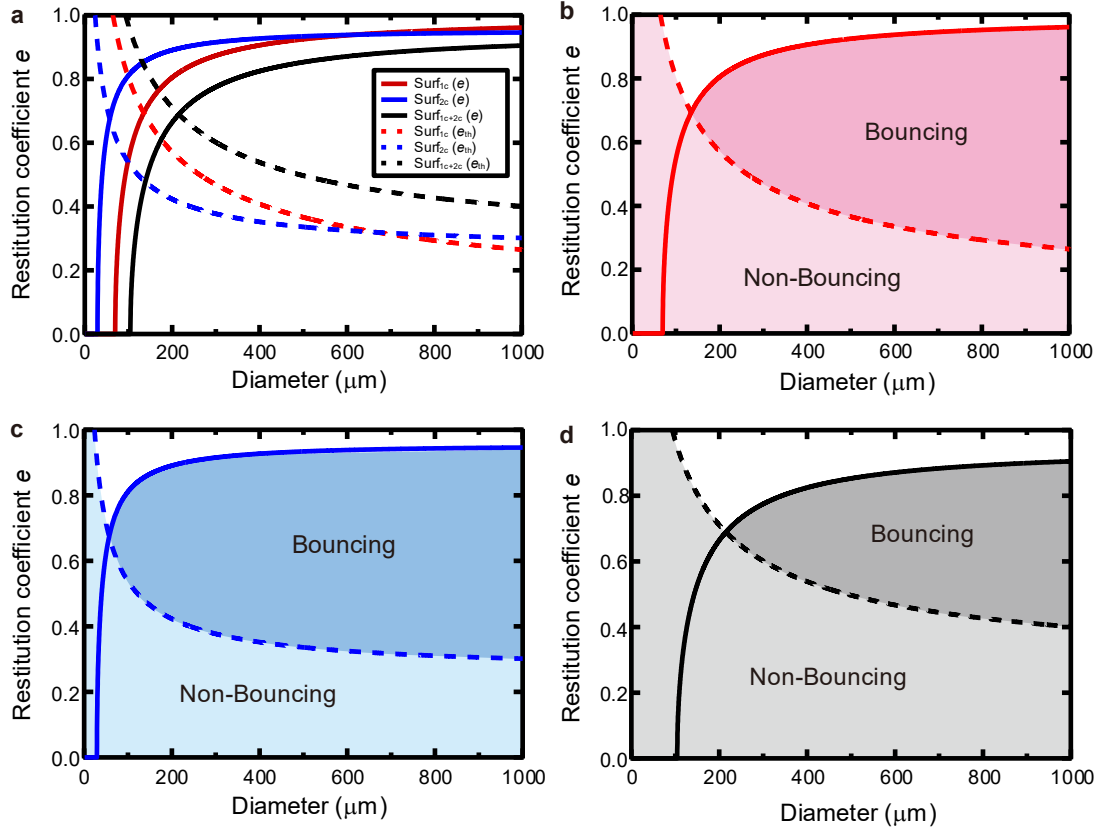


Figure 4.10 Theoretical diagrams of bouncing/non-bouncing behaviors. a) Dependences of restitution coefficients of Surf_{1c} , Surf_{2c} and Surf_{1c+2c} on diameter. b-d) The phase diagrams of Surf_{1c} , Surf_{2c} and Surf_{1c+2c} , respectively. The solid curves in (a-d) are restitution coefficient e , while the dotted curves are the thresholds of restitution coefficients e_{th} . The areas highlighted by deep and light colors in (b-d) mean the theoretical conditions of bouncing and non-bouncing, respectively. The conditions of calculations are shown in text.

Computational result of the dependence of e on r_0 for Surf_{1c+2c} is shown in Fig. 4.10a and 8d. The computational result shows that the diameter of the bouncing microdroplets on Surf_{1c+2c} is larger than that of Surf_{1c} . The computational results in Fig. 4.10 thus reproduced the distributions of bouncing and non-bouncing droplets in Fig. 4.7e-g. Actually, a small droplet remains on Surf_{1c+2c} as shown in Fig. 4d. This is not included in the theory, but it is caused by very long needle-shaped crystals of **1c**; an example of such a very long needle-shaped crystal is observed in the left side of Fig. 4.4g. Fig. 4.11 shows the schematic representations of bouncing and non-bouncing droplets based on Fig. 4.10 and it explains the reason why the obtained distribution of non-bouncing droplets is enhanced on Surf_{1c+2c} than that on Surf_{2c} and

Surf_{1c}. On **Surf_{1c+2c}**, smaller droplets with bouncing size on **Surf_{2c}** are collected onto **Surf_{1c}** efficiently. In addition, kinetic energy in bouncing larger droplets is dissipated, the residual energy decreases and the conditions of non-bouncing is amplified. Surface structure thus determines dissipation energy and bouncing behaviors of water droplets.

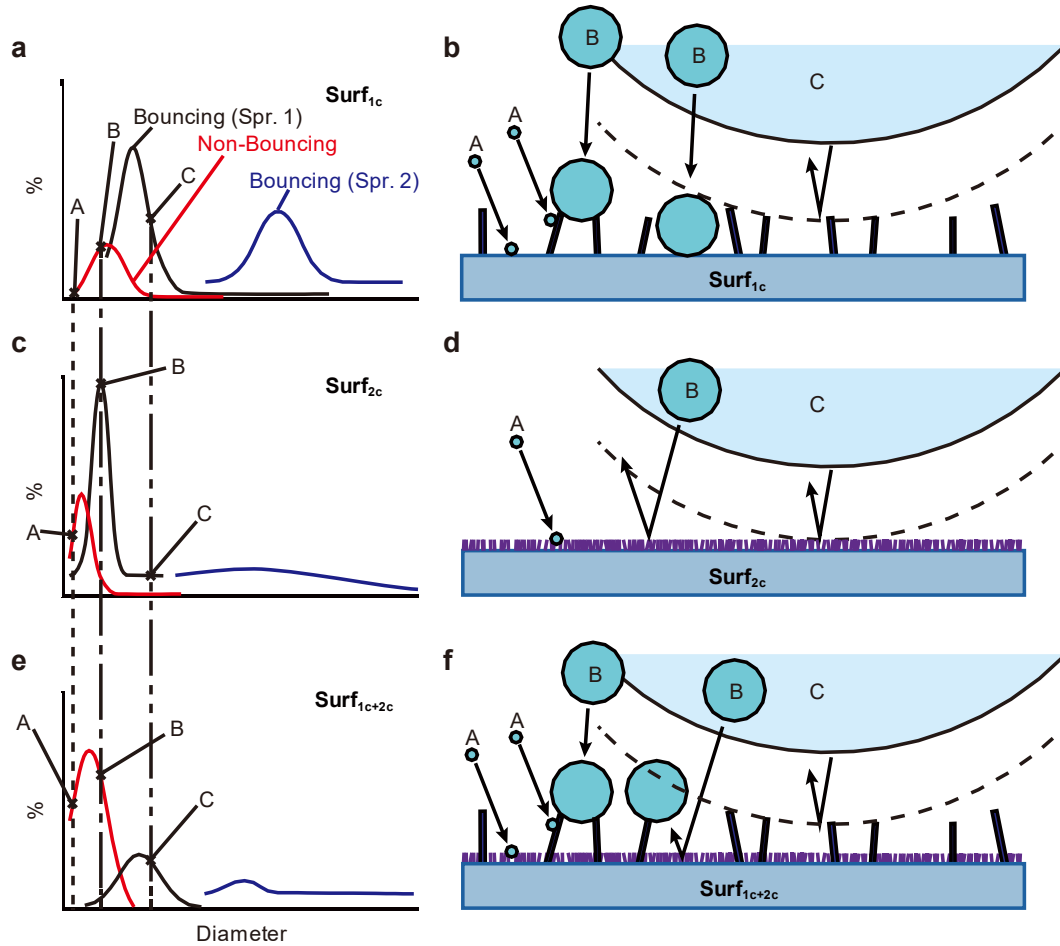


Figure 4.11 Theoretical situation of bouncing droplet. a, c, e) Schematic representations of the obtained distributions of bouncing and non-bouncing droplets of **Surf_{1c}**, **Surf_{2c}** and **Surf_{1c+2c}**. b, d, f) Schematic representations of bouncing/non-bouncing behaviors suggested by theory. a, b) Non-bouncing microdroplets (A) and bouncing microdroplets (B and C) shown by the crosses (×) in the distributions of bouncing and non-bouncing on **Surf_{1c}** in (a) are illustrated in (b). c, d) The same on **Surf_{2c}** and (e, f) on **Surf_{1c+2c}**.

4.4 Conclusion

In conclusion, microcrystalline films consisting of the mixtures of diarylethenes **1o** and **2o** were prepared as a first attempt to mimic the surface structure of a termite wing. The mixed microcrystalline film formed needle-shaped crystals of both **1c** and **2c** upon UV irradiation followed by storage above T_g in the dark. On **Surf_{1c}**, consisting of only larger needle-shaped crystals of **1c**, water did not show bouncing phenomena, while on **Surf_{2c}** consisting of only smaller needle-shaped crystals of **2c**, clear bouncing behaviour was observed. By mixing these two different sizes of needle-shaped crystals, *simultaneous water-adhesive and water-bouncing phenomena* were observed. These results indicate that larger crystals work well for adhesive force on the surface, while smaller-sized crystals work well for bouncing behaviour. Furthermore, **Surf_{1c+2c}** demonstrated its ability to both capture fog-sized droplets and repel rain-sized droplets, which is determined by the size of droplet. Consequently, we succeeded in regenerating the surface function of the termite wing by using the photoinduced CGT for diarylethenes, and the dual wettability observed on **Surf_{1c+2c}** was consistent with those on the wing surfaces of *Nasutitermes sp.* and *Microcerotermes sp.* Dual wettability of **Surf_{1c+2c}** was explained theoretically by dissipation energy in bouncing microdroplets and adhesion energy between microdroplets and **Surf_{1c+2c}**. Such surface functions inspired by nature will lead to novel advanced materials, such as self-cleaning surfaces and parts for water collection and conservation systems. This study represents one of the research efforts made toward understanding how the surface of the termite wing, in nature, has effectively achieved the ability to apply both key properties of wetting.

4.5 References

1. L. Feng, S. Li, Y. Li, H. Li, L. Zhang, L. Zhai, Y. Song, B. Li, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, *14*, 1857–1860.
2. F. Shi, J. Niu, J. Liu, F. Liu, Z. Wang, X.-Q. Feng, X. Zhang, *Adv. Mater.* **2007**, *19*, 2257–2261.
3. H. Lee, B. P. Lee, P. B. Messersmith, *Nature* **2007**, *448*, 338–341.
4. J. Zi, X. Yu, Y. Li, X. Hu, C. Xu, X. Wang, X. Liu, R. Fu, *Proc. Natl. Acad. Sci. USA* **2000**, *100*, 12576–12578.
5. D. Xu, H. Yu, Q. Xu, G. Xu, K. Wang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 8750–8756.
6. A. D. Pris, Y. Utturkar, C. Surman, W. G. Morris, A. Vert, S. Zalyubovskiy, T. Deng, H. T. Ghiradella, R. A. Potyrailo, *Nat. Photonics* **2012**, *6*, 195–200.
7. X.-M. Li, D. Reinhoudt, M. C. Calama, *Chem. Soc. Rev.* **2007**, *36*, 1350–1368.
8. X. Zhang, F. Shi, J. Niu, Y. Jiang, Z. Wang, *J. Mater. Chem.* **2008**, *18*, 621–633.
9. Y. Lee, S.-H. Park, K.-B. Kim, J.-K. Lee, *Adv. Mater.* **2007**, *19*, 2330–2335.
10. A. R. Parker, H. E. Townley, *Nat. Nanotechnol.* **2007**, *2*, 347–353.
11. B. L. Zhou, *Mater. Sci. Eng. C* **2000**, *11*, 13–18.
12. F. Xia, L. Jiang, *Adv. Mater.* **2008**, *20*, 2842–2858.
13. W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1–8.
14. C. Neinhuis, W. Barthlott, *Ann. Bot.* **1997**, *79*, 667–677.
15. Y. Tian, B. Su, L. Jiang, *Adv. Mater.* **2014**, *26*, 6872–6897.
16. M. W. Holdgate, *J. Exp. Biol.* **1995**, *32*, 591–617.
17. P. Wagner, C. Neinhuis, W. Barthlott, *Acta Zoologica* **1996**, *77*, 213–225.
18. G. S. Watson, B. W. Cribb, J. A. Watson, *ACS Nano* **2010**, *4*, 129–136.
19. G. S. Watson, B. W. Cribb, J. A. Watson, *PLoS ONE* **2011**, *6*, e124368.
20. M. J. Pearce, *Termites biology and pest management*; CAB International: **1997**, UK p 172.
21. K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura, M. Irie, *Angew. Chem. Int. Ed.* **2006**, *45*, 6470–6473; *Angew. Chem.* **2006**, *118*, 6620–6623.
22. K. Uchida, N. Nishikawa, N. Izumi, S. Yamazoe, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii, M. Irie, *Angew. Chem. Int. Ed.* **2010**, *49*, 5942–5944.

23. N. Nishikawa, H. Kiyohara, S. Sakiyama, S. Yamazoe, H. Mayama, T. Tsujioka, Y. Kojima, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2012**, *28*, 17817–17824.
24. N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2013**, *29*, 8164–8169.
25. R. Nishimura, K. Hyodo, H. Sawaguchi, Y. Yamamoto, Y. Nonomura, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *J. Am. Chem. Soc.* **2016**, *138*, 10299–10303.
26. N. Fujinaga, N. Nishikawa, R. Nishimura, K. Hyodo, S. Yamazoe, Y. Kojima, K. Yamamoto, T. Tsujioka, M. Morimoto, S. Yokojima, S. Nakamura, K. Uchida, *CrystEngComm* **2016**, *18*, 7229–7235.
27. K. Uchida, R. Nishimura, E. Hatano, H. Mayama, S. Yokojima, *Chem. Eur. J.* **2018**, *24*, 8491–8506.
28. S. Glienke, A. Kostinski, J. Fugal, R. A. Shaw, S. Borrmann, and J. Stith, *Geophys. Res. Lett.* **2017**, *15*, 8002–8010.
29. T. Takahashi, *Rev. Geophys.* **1973**, *4*, 903–924.

Chapter 5

Object transportation system mimicking the cilia of paramecium aurelia making use of the light-controllable crystal bending behavior of a photochromic diarylethene

5.1 Introductions

Recently, molecular machines, in which one molecule or an assembly of responsive molecules exhibit a mechanical motion at the microscopic or nanoscale accompanied by three-dimensional structural changes due to external stimuli, have been actively studied.¹⁻⁶ In nature, many animals and plants have specific micro/nanostructures at their surfaces exhibiting various dynamic functions.⁷ In particular, the responsive structures and cooperative effects in arrays, for example, the antireflection effect of the moth eye,⁸⁻¹⁰ strong adhesion and friction forces of the gecko foot,^{11,12} and cilia of the mammal's respiratory tract,¹³⁻¹⁹ have been studied and put to practical use. The cilia's functions include the transportation of food, body fluids, body waste, and reproductive products, and the cleaning of the respiratory tract. Especially, those of *Paramecium aurelia* have attracted much attention, since the cilia's motion induces many complex movements of the body.²⁰ Mechanical functions and responsive surfaces are very attractive;²¹⁻²³ therefore, cilia-inspired functional materials have been designed.¹³⁻¹⁹ Chemo-responsive self-oscillating gels such as the artificial cilia-inspired actuator have been studied.¹³⁻¹⁵ The spontaneous mechanical oscillation of the gel is induced by the Belousov–Zhabotinsky (BZ) reaction and propagates as a wave on the gel plate. The diffusion of this chemical wave affects the dynamic behavior of neighboring BZ gels. This diffusing dynamic behavior regenerates wave of cilia. These systems operate by no external stimuli; therefore, precise control of the gel's motion is difficult. On the other hand, other systems responding to external stimuli (e.g. light or magnetic field) have also been reported.¹⁶⁻¹⁹ Jiang and co-workers reported the transportation of a microsphere by magnetically actuated fibers mimicking the cilia's

bending motion.¹⁶ The fibers consist of polydimethylsiloxane (PDMS) and cobalt magnetic particles (Co MPs). The bending motion of the fiber array was guided by a magnetic field. On the smart array, a PS microsphere was transportable by the magnetic field. In the other report, a water droplet was transported by the magnetic field.¹⁷ However, in this system, a droplet moved not only because of the magnetic field but also because of longitudinal vibrations. Photo-actuated cilia inspired materials also have been studied.^{18,19} Oosten and co-workers reported a light-driven miniature polymeric actuator mimicking the motion of natural cilia; the actuator was prepared by inkjet printing technology and self-organization of a liquid crystal network.¹⁸ They introduced two different azobenzene units in the polymer as the photo-responsive moieties. By assembling two different photo-actuated polymers to the substrate and irradiating with UV and visible light, they realized the complex asymmetric motion of cilia. The other example also realized the complex motion of cilia and transported the object by flow generated by fiber motion.¹⁹ In the above examples, the complex motions of natural cilia were achieved. However, on-demand directional transportation of an object was not achieved.

Diarylethenes, a highly promising class of thermally stable photochromic compounds, show reversible cyclization and cycloreversion reactions upon alternating irradiation with UV and visible light, even in the crystalline state.²⁴ The most commonly observed crystal behavior has been photoinduced bending, rolling, and twisting,²⁵⁻²⁹ resulting in the elegant demonstration by Irie and co-workers of an iron ball being lifted on a bending crystal.²⁶ Previously, we have shown the reversible photoinduced bending behavior of a crystal of a diarylethene **3o** that takes advantage of intermolecular hydrogen bonding (Fig. 5.1a).²⁸ The thin crystal of **3o** bent away from the incident UV light, and reverted to the original shape upon visible-light irradiation from any direction.

Herein, we report a unique surface-confined transportation system using the bending behavior of an **3o** crystal which is controlled only by photoirradiation (Fig. 5.1b). This system has the possibility to transport an object in any desired direction upon a change in the direction of incident UV light.

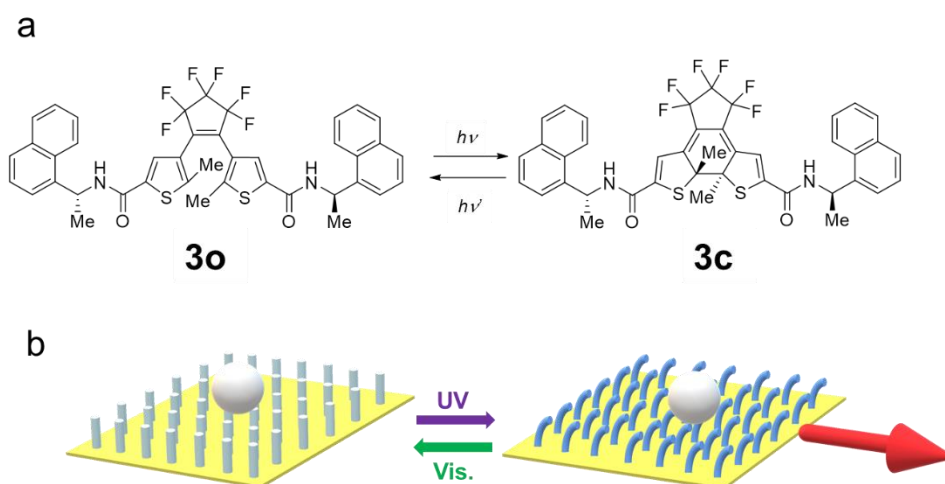


Figure 5.1 Molecular structure of the open- and closed-ring isomers of diarylethene derivative **1** a), and the concept of the photo reactive object transportation system b).

5.2 Experimental section

5.2.1 General information

Diarylethene derivative **3o** was synthesized according to a reported procedure.²⁸ For irradiation of the platelet crystals of **3o**, UV lamp TOPCON FI51S ($\lambda=254$ nm) was used. For the fabrication of the photo-actuated surface, hotplates KPI Model HP-19U300P, MODEL HP-19U300 were used. XRD pattern were measured on Rigaku RINT2500. Optical microscopy was carried out using Nikon OPTIPHOT2-POL, equipped with Shimadzu moticam 2000 2.0 M Pixel USB2.0 and KEYENCE VH-S30, VH-S1, and VH-Z450. A scanning electron microscope (KEYENCE VK-8800) was used to analyse the surface fine structure. For the sputtering of Au-Pd alloy to the dotted surface, Vacuum Device MSP-1S Magnetron Sputter was used.

5.3 Results and discussion

5.3.1 Photoinduced bending behavior of platelet crystal of **3o**

A key requirement in the design of the micro object transportation system is that the crystals bend in any direction in response to the incident UV light. Following the preparation of the platelet crystals of diarylethene derivative **3o**, we confirmed the bending behavior by irradiating with UV light from different incident directions.²⁸ At first, upon UV light ($\lambda=254$ nm) irradiation of the (001) surface (the wide face), the crystal bent away from the incident UV light (Fig. 5.2a).

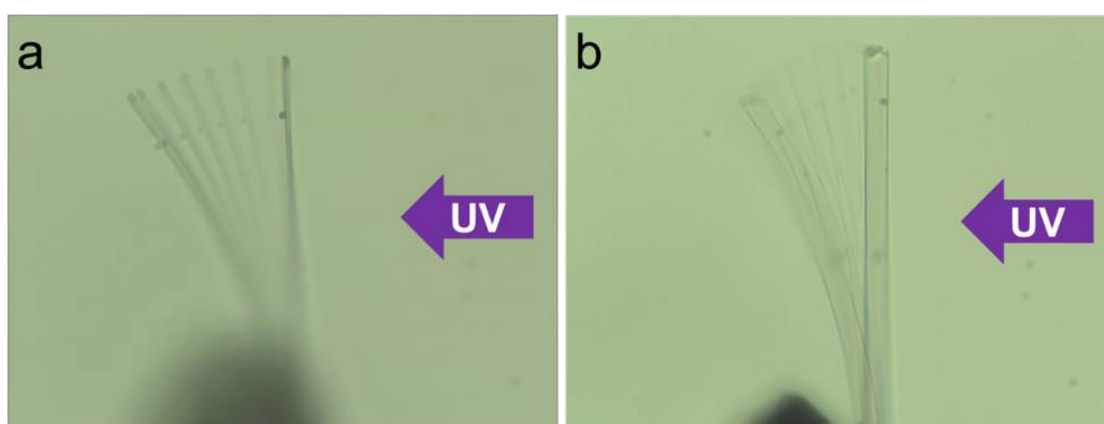


Figure 5.2 Bending behavior of the platelet crystal of **3o**. a) Graphic overlay of the bending behavior of the platelet crystal of **3o** by irradiation with UV light to the (001) face and b) (100) face from right side.

Subsequently, UV light ($\lambda=254$ nm) was applied to the (100) surface, the narrow face, and the crystal also bent slowly away from the incident light (Fig. 5.2b). Irie and co-workers reported the mechanism of the photoinduced crystal bending behavior of the photochromic diarylethene.²⁶ When the short axis (height) of a diarylethene molecule in the crystal is parallel to the long axis of the unit cell, the crystals exhibit a bending motion away from the incident UV light,²⁶ due to the elongation of the height of the assumed triangle shape of the molecule (Fig. 5.3).

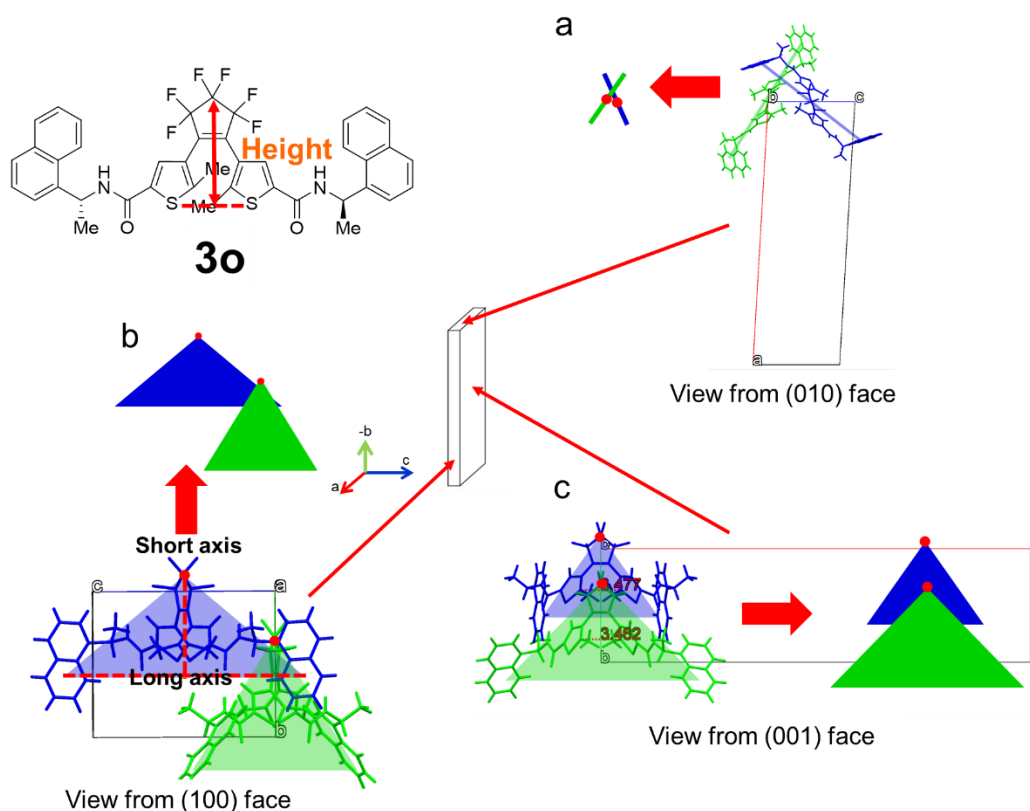
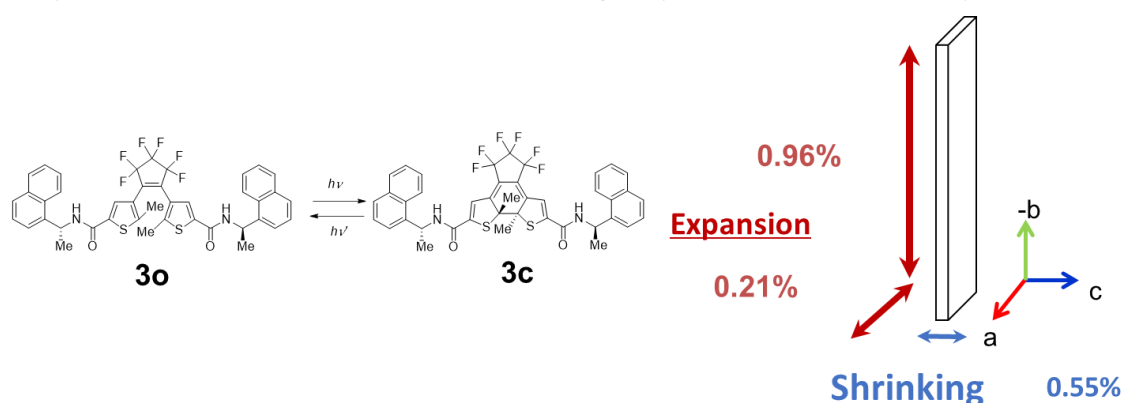


Figure 5.3 X-ray crystallographic analysis of single crystal of **3o**. a) The result of X-ray crystallographic analysis and schematic illustration of molecular packing of two conformers in the unit cell view from (010) face, b) in the unit cell view from (100) face, c) in the unit cell view from (001) face.

The X-ray crystallographic analysis of the **3o** crystal shows that two conformers exist in the unit cell. The distances between the reacting carbon atoms in the thiophene rings of two (green- and blue-colored) conformers are 3.462 and 3.477 Å, respectively, which are short enough for a photocyclization reaction to occur in the crystalline state (Fig. 5.3). Moreover, molecules of **3o** were packed so as to bend away from the incident UV light, when the crystal was irradiated from any side face of the crystal, regardless of which face was irradiated. When the crystal of **3o** was irradiated with UV light, the a and b axis of the unit cell expanded by 0.21 and 0.96%, respectively. On the other hand, the c axis of the unit cell contracted by 0.55% (Table 5.1). The irradiation of the crystal of **3o** with UV light induced the elongation of the long axis of the unit cell, because the height of the molecule increased. Therefore, the crystal of **3o** bends away from the incident UV light. Based on the above findings, the bending

motion of crystalline **3o** was suitable for our strategy to transport an object in the desired direction. Thus, we designed the photo-actuated object transportation surface consisting of many vertically aligned **3o** crystals.

Table 5.1 Crystal data before and after UV irradiation and visible light irradiation of the thin platelet crystal of **3o** obtained by sublimation, and rod-shaped crystal of **3o** prepared by recrystallization from chloroform measured at SPring-8 (synchrotron radiation facility).



	3o thin platelet crystal obtained by sublimation.	3o-UV (thin platelet crystal obtained by sublimation.) ^{a)}	3o rod-shaped crystal obtained by recrystallization.	3o-UV (rod-shaped crystal obtained by recrystallization.) ^{b)}
Formula	C ₄₁ H ₃₂ F ₆ N ₂ O ₂ S ₂	C ₄₁ H ₃₂ F ₆ N ₂ O ₂ S ₂	C ₄₁ H ₃₂ F ₆ N ₂ O ₂ S ₂	C ₄₁ H ₃₂ F ₆ N ₂ O ₂ S ₂
Formula weight	762.83	762.83	762.83	762.83
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2	C2	C2	C2
<i>a</i> / Å	35.551(7)	35.6965(30) 0.41%	35.610(4)	35.686(5) 0.21%
<i>b</i> / Å	9.4738(22)	9.5236(85) 0.53%	9.4283(10)	9.5189(12) 0.96%
<i>c</i> / Å	11.5816(25)	11.5858(97) -0.04%	11.6507(12)	11.5863(14) -0.55%
<i>a</i> / °	90	90	90	90
<i>b</i> / °	93.653(53)	93.621(51) -0.03%	93.806(7)	93.582(7) -0.24%
<i>g</i> / °	90	90	90	90
<i>V</i> / Å ³	3892.79	3930.90 0.98%	3903.00	3928.08 0.64%
<i>Z</i>	2	2	2	2
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	-	-	0.0629	0.0751
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	-	-	0.1533	0.1901
<i>R</i> ₁ (all data)	-	-	0.1	0.2003
<i>wR</i> ₂ (all data)	-	-	0.1776	0.2242
CCDC No.	-	-	1880827	1880828

a) After 313 nm light irradiation for 35 s to thin platelet crystal of **3o**. b) After 313 nm light irradiation for 32.5 min to rod-shaped crystal of **3o**.

5.3.2 Measurement of Young's modulus of the platelet crystal of **3o**

The Young's modulus of the crystal was measured by means of a manual beam-bending test.^{26,27} The beam used in the test was prepared as a cantilever by fixing one of the edges of the crystal on a glass plate with glue. A static point load was applied by hanging a weight on the beam and the bending of the beam was measured (Fig. 5.4). The Young's modulus was calculated using an equation which relates the dimension

of the crystal, the load applied, the flexure, and the modulus. The Young's modulus of the crystal of **3o** was estimated to be 5.5 GPa. (an average value of five samples). This value is much larger than those of typical polymer materials (ca. 1 GPa).³² These results suggest that the assembled surface of photo-bendable crystals can be applied for light-induced actuation to establish an object transportation system.

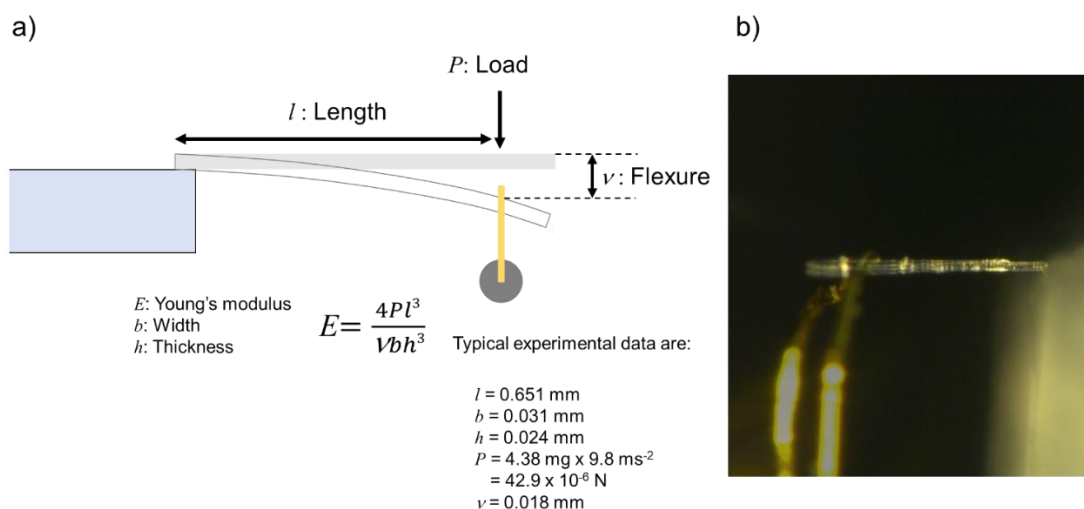


Figure 5.4 Measurement of Young's modulus by the manual beam-bending test.^{26,27} a) A schematic illustration of the experimental setup and the equation used for the measurement of Young's modulus by the manual beam-bending test. b) A typical photograph demonstrating the bending test. Two photographs of the setup before and after hanging the weight were superimposed.

5.3.3 Preparation of object transportation system

The (source) microcrystalline surface of **3o** was prepared by coating a solution onto a glass substrate. A THF solution of **3o** (600 mgmL^{-1}) was coated onto the glass substrate, the solvent evaporated at room temperature, and an amorphous film of **3o** remained. When the amorphous film was heated at $200 \text{ }^{\circ}\text{C}$ for 20 min, it crystallized. This crystallization is essential, as it was observed that the subsequent sublimation process at elevated temperatures does not proceed because of decomposition of **3o**. In the current study we tried to fabricate the photo-actuated surface by sublimating a crystalline film of **3o** onto the glass substrate. To prepare the object transportation surface, we sublimated the microcrystalline film of **3o** at $260 \text{ }^{\circ}\text{C}$ for 1.5h under ambient atmosphere onto the clean and flat target glass substrate. However, standing platelet

crystals of **3o** were not obtained on the glass substrate. Instead of the rough surface covered with standing platelet crystals, we obtained an amorphous film of **3o** with a nearly flat surface. This result suggested that the nucleus of the crystal growth was not generated on the amorphous surface. Noting the importance of surface rough structures for crystallization, we followed the strategy taken by Lin and co-workers. They reported the vertical growth of ZnO nanowires (NWs), where the surface roughness assisted the nucleation of ZnO.^{30,31} The Zn atoms from the gas phase have enough thermal energy to move freely on a smooth surface. On the other hand, the Zn atoms are stuck once they migrate into pits or craters, due to higher energy barriers for migration. Consequently, the rough surface provides nucleation sites for crystal growth. In the next attempt to prepare the crystalline film of **3o** by sublimation, we made dot-shaped microstructures consisting of **3o** generated densely on the glass substrate upon sublimation at 250 °C for 20 min under ambient atmosphere (Fig. 5.5b). We intended to use the dotted structured rough surface, which was amorphous (Fig. 5.5d), as the precursor in the nucleation process. The average diameter and height of a dotted structure were 0.30 and 0.43 μm , respectively. When the temperature was elevated by only 10 °C, the dotted structures were not obtained within the same heating period.

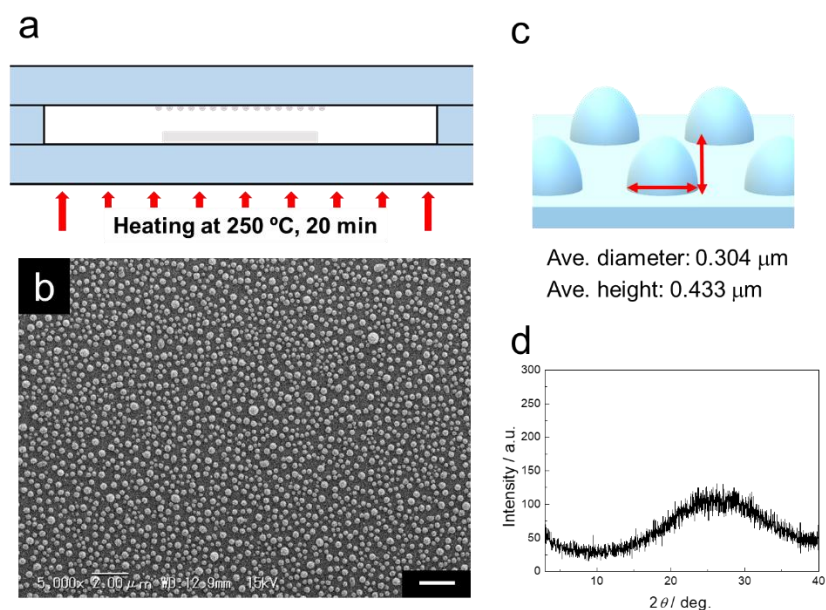


Figure 5.5 Illustrations and properties of the dotted microstructures. a) Schematic illustration of generation of amorphous dotted microstructures. b) SEM image of the dotted microstructures on the glass substrate. Scale bar: 2.0 μm , which is magnified 5000 times. c) Schematic illustration of dotted microstructures. The average diameter and height of the dotted microstructures were 0.34 and 0.43 μm , respectively. d) XRD diffraction of the surface of dotted substrate. This XRD measurement indicated that the dotted structures were amorphous.

By using the dotted structured target surface (Fig. 5.6a–c), we sublimated **3o** from the crystalline film of **3o** as the source. Still, no standing bending crystals were grown on the glass substrate; furthermore, the dotted structures were covered with newly sublimed **3o** and each grew to become a grain (Fig. 5.6d, e), according to the scanning electron microscopy (SEM) observation. Since the dotted structures do not serve as seeds for the crystallization of bending needle-like or thin platelet crystals, we attempted to change the continuous growth mode of the **3o** dots during sublimation by magnetron sputtering the dotted surface with Au-Pd alloy (Fig. 5.6f). Use of this dotted surface with the Au-Pd alloy as a target substrate resulted in the accelerated growth of thin platelet crystals of **3o** on each of the dots on the glass substrate (Fig. 5.6g, h, Fig. 5.7).

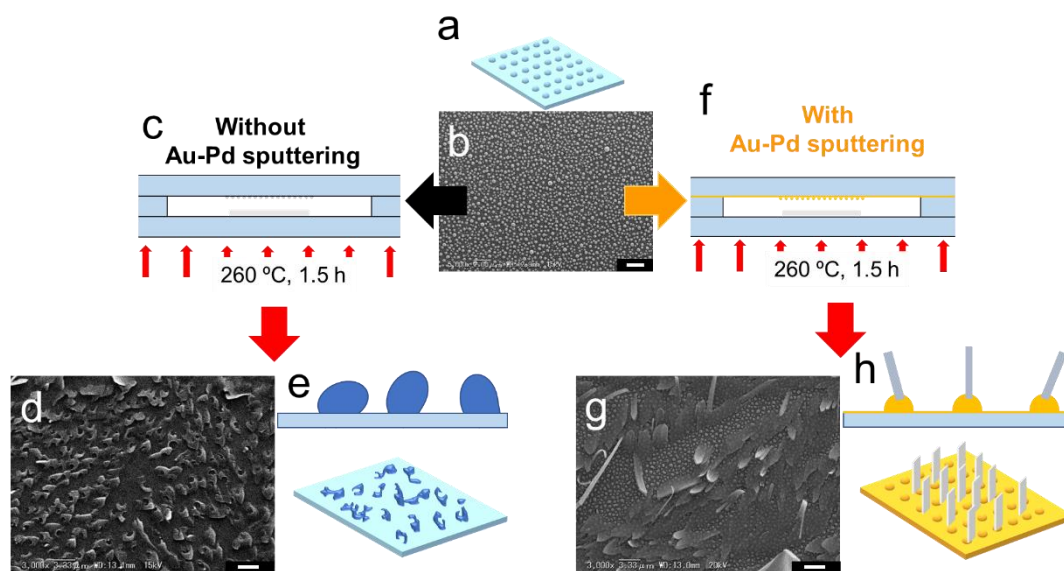


Figure 5.6 The effect of the dotted structures with Au-Pd sputtering. a) Schematic illustration of the dotted substrate. b) SEM image of the dotted microstructures. Scale bar: 2.0 μm , which is magnified 5000 times. c) Schematic illustration of the sublimation setting dotted substrate without Au-Pd sputtering. d) The SEM image of the dotted substrate after sublimation of crystalline film of **3o** to the dotted substrate without Au-Pd sputtering. Scale bar: 3.33 μm , which is magnified 3000 times. e) Schematic illustration of the surface structures on the no sputtering surface after sublimation. f) Schematic illustration of the sublimation setting dotted substrate with Au-Pd sputtering. g) The SEM image of the dotted substrate after sublimation of crystalline film of **3o** to the dotted substrate with Au-Pd sputtering. Scale bar: 3.33 μm , which is magnified 3000 times. h) Schematic illustration of the surface structures on the sputtering surface after sublimation.

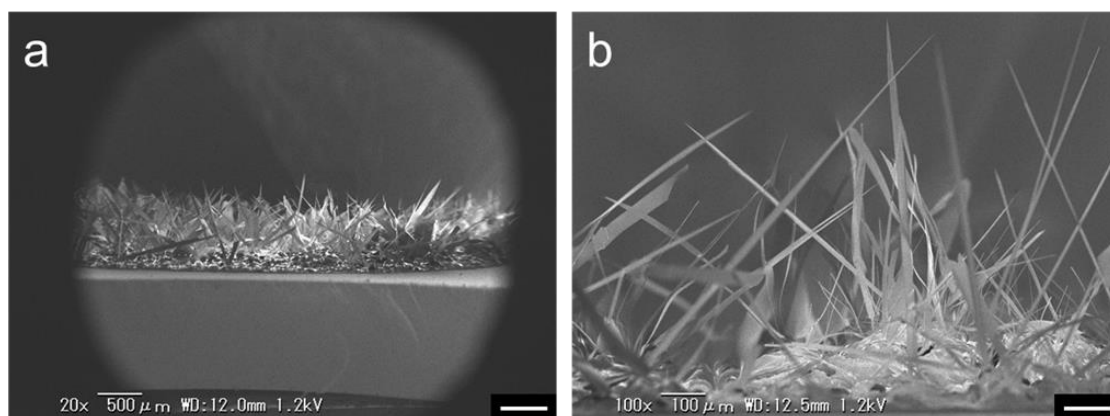


Figure 5.7 SEM images of **3o** crystals on the glass substrate. Scale bars: a) 500 μm , b) 100 μm , which are magnified 20 and 100 times, respectively.

The average length and width of the platelet crystals of the **3o** on the glass substrate was 384.5 and 10.5 μm , respectively.

5.3.4 The effect of dotted structures for crystal growth

To confirm the effect of the dotted structures, we sublimated the crystalline film of **3o** onto both the areas with dotted structures and without dotted structures (Fig. 5.8). On the surface with dotted structures, platelet crystals of **3o** were observed, while on the flat surface, no crystals were generated. Additionally, the sublimation of **3o** onto a surface with gentle irregularities that had been a magnetron sputtered with Au-Pd alloy did not generate thin platelet crystals. These results indicated that the dotted structures assist the nucleation by limiting the migration of the molecules on the substrate.

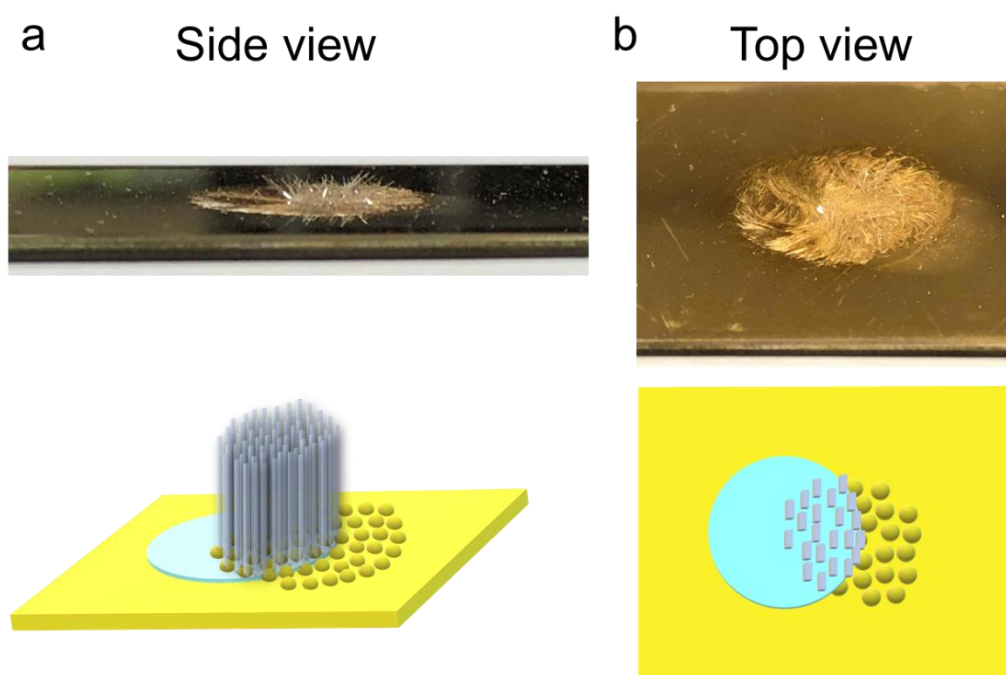


Figure 5.8 The effect of the dotted microstructures for the crystal growth of platelet crystals of **3o**. a) Side view and b) top view image and schematic illustration of the crystals on the dotted substrate.

5.3.5 Photo-actuation of the surface growing standing platelet crystal

Next, the object transportation system controlled only by photoirradiation was designed. To clarify the bending behaviour of the crystals grown on the glass substrate, we irradiated the photo-actuated surface with UV light from various directions. The bending behavior was observed by using a digital microscope (KEYENCE, 28 fps, Fig.

5.9). At first, the object transportation surface was irradiated with UV light ($\lambda=254$ nm) from the right side, and the whole crystals bent away from the light. Subsequently, the surface was irradiated with visible light applied from the top, and the crystals reverted to the original position (observation light of the digital microscope: white light). Furthermore, upon UV light irradiation from the left side, crystals bent away from the photo-incidence, and crystals also reverted to the original position upon visible-light irradiation.

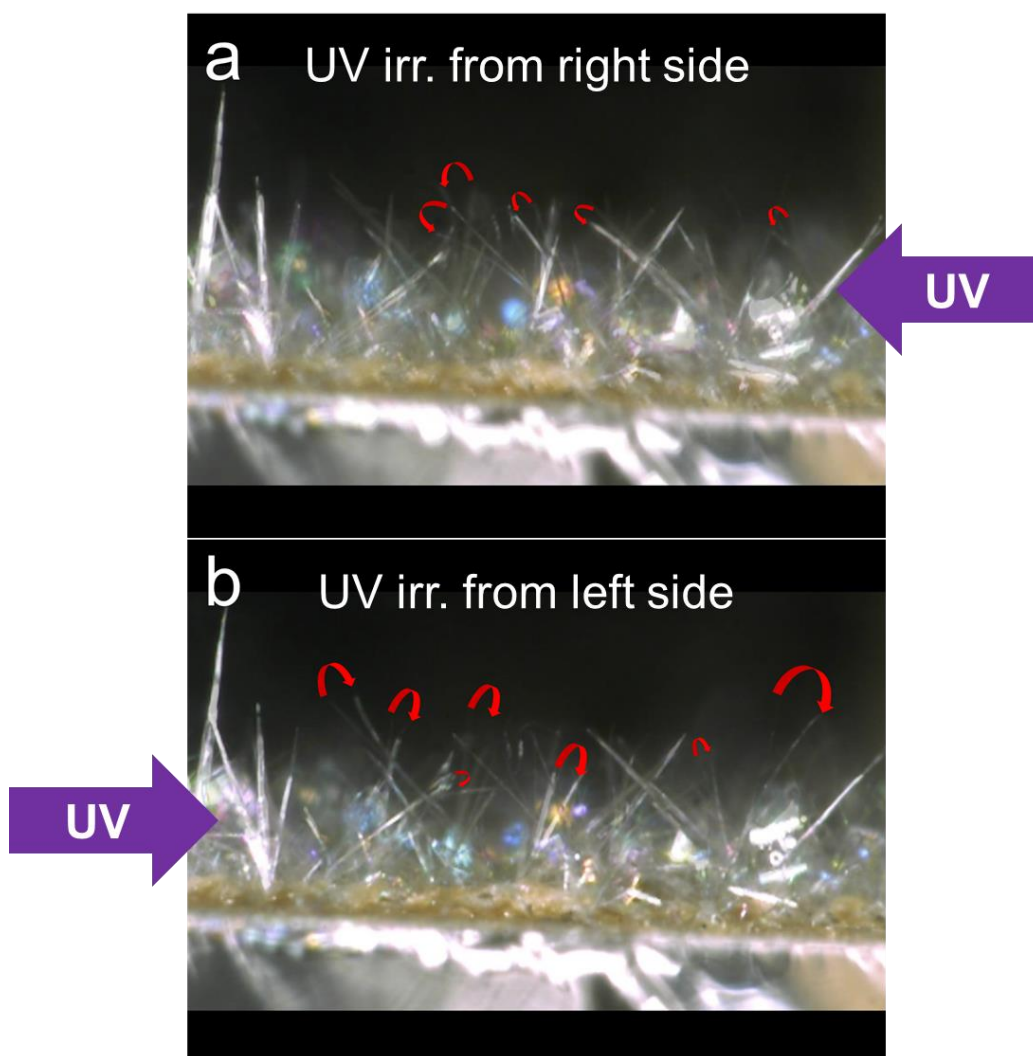


Figure 5.9 Bending behavior of platelet crystals of **3o** grown on the substrate. Both optical images are the graphic overlay before and after UV irradiation. a) Bending behavior of the crystals by irradiation with UV light from right side, b) bending behavior of the crystals by irradiation with UV light.

5.3.6 Object transportation by the light

We demonstrated the transportation by using a polystyrene bead (PB) (average diameter 1 μ m) as a target and by applying UV- and visible-light irradiation from various directions. When the PB was placed on the nanostructured surface, the motion of the PB was observed upon UV- and visible-light irradiation (Fig. 5.10). First UV light ($\lambda=254$ nm) was applied from the bottom of the screen and the PB moved upward, accompanied by the cooperative bending of the crystals. Continuing irradiation with UV light ($\lambda=254$ nm) from the right side induced the PB to move to the left side, such that the transportation direction corresponded to the direction of UV incidence. Upon irradiation with visible light orthogonal to the surface, the PB returned to the lower right, which was the original position. As shown in the Fig. 5.10, continuous irradiation with UV or visible light caused the PB to move in the direction of the bending direction of the crystals. Consequently, we succeeded in transporting the PB object exclusively by photoirradiation in any desired direction by changing the direction of the incident light.

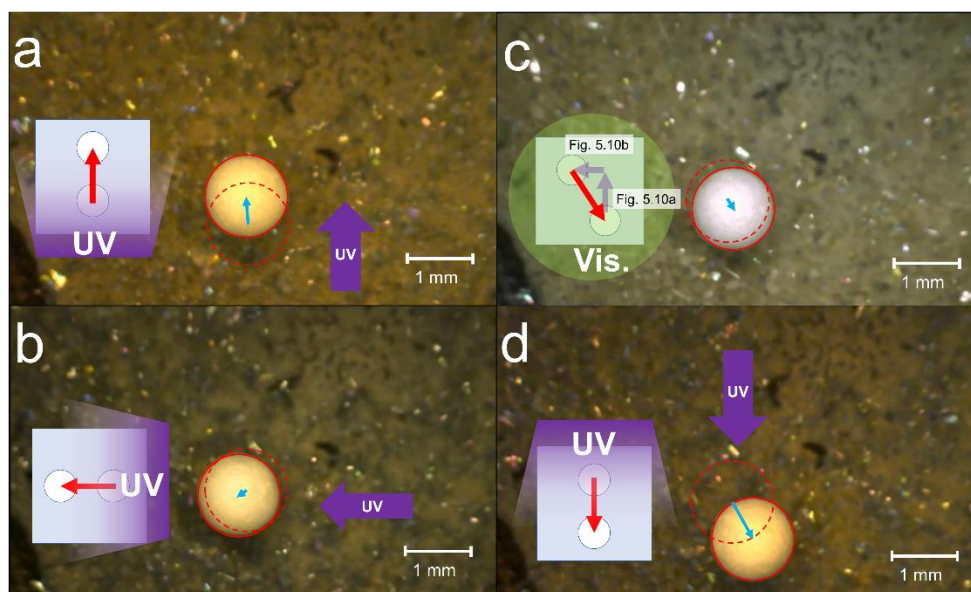


Figure 5.10 Photograph of transportation of the PB by UV and visible light irradiation. a) after UV irradiation from downward, b) after UV light irradiation from right side of the screen, c) after visible light irradiation from the top of the surface, d) after UV light irradiation from the upper direction. Scale bars: 1 mm.

5.4 Conclusion

In conclusion, we have designed an object transportation system actuated only by light irradiation using a crystalline film of **3o**. In order to prepare the photo-actuated smart surface, a glass substrate was covered with micro-structured dots of **3o** and then sputtered with Au-Pd alloy; this surface preparation plays a key role for the generation of the nuclei for crystal growth of **3o** on the target substrate. The bending behavior of the platelet crystal of **3o** was suitable to design a responsive surface, and the surface covered with **3o** crystals showed reversible cooperative crystal bending upon irradiation with UV and visible light. Finally, this photo-actuated surface can transport a PB in a controlled manner in a desired direction depending on the direction of incident light. For longer transportation of an object, we will realize local photoinduced bending on assembly by using laser light in the future. This smart surface will be applicable for remote-controlled object transportation in various environments and holds potential for the development of soft robots.

5.5 References

- 1) T. Kudernac, N. Ruangsapichat, M. Parschau, B. Maciá, N. Katsonis, S. R. Harutyunyan, K.-H. Ernst, B. L. Feringa, *Nature* **2011**, 479, 208–211.
- 2) J. Chen, F. K.-C. Leung, M. C. A. Stuart, T. Kajitani, T. Fukushima, E. van der Giessen, B. L. Feringa, *Nat. Chem.* **2018**, 10, 132–138.
- 3) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 189–192; *Angew. Chem.* **1989**, 101, 192–194.
- 4) M. C. Jimenez, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2000**, 39, 3284–3287; *Angew. Chem.* **2000**, 112, 3422–3425.
- 5) R. A. Bissell, E. Clrdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, 369, 133–137.
- 6) J. M. Spruell, A. Coskun, D. C. Friedman, R. S. Forgan, A. A. Sarjeant, A. Trabolsi, A. C. Fahrenbach, G. Barin, W. F. Paxton, S. K. Dey, M. A. Olson, D. Ben&tezt, E. Tkatchouk, M. T. Colvin, R. Carmielli, S. T. Caldwell, G. M. Rosair, S. G. Hewage, F. Duclairoir, J. L. Seymour, A. M. Z. Slawin, W. A. Goddard, M. R. Wasielewski, G. Cooke, J. F. Stoddart, *Nat. Chem.* **2010**, 2, 870–879.
- 7) F. Xia, L. Jiang, *Adv. Mater.* **2008**, 20, 2842–2858.
- 8) P. B. Clapham, M. C. Hutley, *Nature* **1973**, 244, 281–282.

- 9) K. Choi, S. H. Park, Y. M. Song, Y. T. Lee, C. K. Hwangbo, H. Yang, H. S. Lee, *Adv. Mater.* **2010**, 22, 3713–3718.
- 10) N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir* **2013**, 29, 8164–8169.
- 11) K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, R. J. Full, *Nature* **2000**, 405, 681–685.
- 12) K. Liu, J. Du, J. Wu, L. Jiang, *Nanoscale* **2012**, 4, 768–772.
- 13) O. Tabata, H. Hirose, S. Aoki, R. Yoshida, E. Kokufuta, *Sens. Actuators A* **2002**, 95, 234–238.
- 14) R. Yoshida, *Adv. Mater.* **2010**, 22, 3463–3483.
- 15) O. Kuksenok, P. Dayal, A. Bhattacharya, V. V. Yashin, D. Deb, I. C. Chen, K. J. Van Vliete, A. C. Balazs, *Chem. Soc. Rev.* **2013**, 42, 7257–7277.
- 16) S. Ben, J. Tai, H. Ma, Y. Peng, Y. Zhang, D. Tian, K. Liu, L. Jiang, *Adv. Funct. Mater.* **2018**, 28, 1706666.
- 17) Y. Lin, Z. Hu, M. Zhang, T. Xu, S. Feng, L. Jiang, Y. Zheng, *Adv. Funct. Mater.* **2018**, 28, 1800163.
- 18) C. L. van Oosten, C. M. Bastiaansen, D. J. Broer, *Nat. Mater.* **2009**, 8, 677–682.
- 19) A. H. Gelebart, M. Mc Bride, A. P. H. J. Schenning, C. N. Bowman, D. J. Broer, *Adv. Funct. Mater.* **2016**, 26, 5322–5327.
- 20) A Video showing the movement of the cilia of *Paramecium aurelia*, <https://www.youtube.com/watch?v=HXcEACQv5-8>.
- 21) Y. Naitoh, *Science* **1966**, 154, 660–662.
- 22) M. Noguchi, Y. Nakamura, K. Okamoto, *Cell Motil. Cytoskeleton* **1991**, 20, 38–46.
- 23) O. Kutomi, M. Seki, S. Nakamura, H. Kamachi, M. Noguchi, *Protoplasma* **2013**, 250, 1219–1227.
- 24) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, 114, 12174–12277.
- 25) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, 446, 778–781.
- 26) M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, 132, 14172–14178.
- 27) F. Terao, M. Morimoto, M. Irie, *Angew. Chem. Int. Ed.* **2012**, 51, 901–904; *Angew. Chem.* **2012**, 124, 925–928.
- 28) K. Uchida, S. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y.

- Kojima, S. Nakamura, J. Areephong, A. Meetsma, B. L. Feringa, *Chem. Commun.* **2008**, 326–328.
- 29) D. Kitagawa, H. Nishi, S. Kobatake, *Angew. Chem. Int. Ed.* **2013**, 52, 9320–9322; *Angew. Chem.* **2013**, 125, 9490–9492.
- 30) S.-T. Ho, K.-C. Chen, H.-A. Chen, H.-Y. Lin, C.-Y. Cheng, H.-N. Lin, *Chem. Mater.* **2007**, 19, 4083–4086.
- 31) S.-T. Ho, C.-Y. Wang, H.-L. Liu, H.-N. Lin, *Chem. Phys. Lett.* **2008**, 463, 141–144.
- 32) C. L. van Oosten, K. D. Harris, C. W. M. Bastiaansen, D. J. Broer, *Eur. Phys. J. E* **2007**, 23, 329–336.

Chapter 6

Conclusions

In this thesis, I describe the photo-reactive biomimetic functional surface consisting of photochromic diarylethenes. The goal of this research is to understand the mechanism of splendid natural functions by reproducing or mimicking the mechanism on our molecular systems. Through the photoinduced crystal growth technique and vapor deposit method of diarylethene derivatives, we succeeded to realize the photo-responsive smart surface inspired by the fine surface structures of creatures.

In Chapter 1, the researches of biomimetics have been studied long time, and it becomes important studies to realize the low environmental loading and sustainable society. The studies of fundamental researches of photochromic compounds also have been done, however, the example applied studies in real society are not many. Therefore, I developed some photo-reactive biomimetic systems showing macroscopic behaviour or motion caused by photo-isomerization of diarylethene derivatives.

In Chapter 2, the author succeeded to prepare the double roughness structures (DRS) mimicking the surface structures of lotus leaf by controlling the photoinduced crystal growth of diarylethene **1** by light irradiation and heating. The water droplet bouncing phenomena, one of the important factors for self-cleaning materials was observed only on the superhydrophobic surface with DRS, and it showed importance of DRS for the natural lotus leaf.

In Chapter 3, the author optimized the DRS to increase the Laplace pressure of the surface to solve the problem of releasing height dependence bouncing phenomena. In the study as mentioned above, the double roughness surface cannot bounce off a water droplet releasing from 15 cm high, due to the low laplace pressure compared with dynamic pressure of the released droplet. In this study, we modified the surface structures, for example length of small needle-shaped crystal, width of the larger crystals and interval between the DRS, to increase the laplace pressure by optimize the heating and photo-irradiation conditions. Along with above strategy, we succeeded to improve the bouncing ability even if I released a water droplet from more high position.

In Chapter 4, the author prepared a surface mimicking the surface structures of

the termite wing by mixing two diarylethene derivatives. On the surface mixing two derivatives, the two types of crystal, longer and shorter needle-shaped crystals, worked for water adhesion and water bouncing, respectively. Furthermore, by spraying the microdroplet to the surface mimicking the surface structures of termite wing, the smaller droplet like fog were captured onto the surface, on the other hand, the larger one like rain droplet were repelled from the surface. Consequently, we succeeded to regenerate the specific wettability of termite wing by mimicking the surface structures of that one.

In Chapter 5, the author designed the object transportation system by using the photoinduced bending behaviour of diarylethene crystals standing onto the substrate. We selected the diarylethene crystals bending away from the light source, if I irradiate from any direction. In order to prepare the transportation surface, we sublime the crystalline film of **3o** to the rough glass substrate to accelerate the generation of nucleus of crystal growth. The surface growing standing crystals of **3o** actuated by UV and visible light irradiation depending on the direction of light incidence. Finally, I succeeded to transport the polystyrene bead onto the system by UV and visible light irradiation, and succeeded to control the direction of transportation by changing the direction of UV light irradiation.

In conclusion, I have developed photo-controllable biomimetic functional surface by using the photochromic reaction of diarylethene derivatives. The studies in this thesis expanded not only the possibility of photochromic compound but also region of biomimetic materials.

List of Publications

Publications Described in This Thesis

1. Fractal Surfaces of Molecular Crystals Mimicking Lotus Leaf with Phototunable Double Roughness Structures
R. Nishimura, K. Hyodo, H. Sawaguchi, Y. Yamamoto, Y. Nonomura, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida
J. Am. Chem. Soc. **2016**, *138*, 10299–10303.
2. Crystal Growth Technique for Formation of Double Roughness Structures Mimicking Lotus Leaf
R. Nishimura, H. Mayama, Y. Nonomura, S. Yokojima, S. Nakamura, K. Uchida
Langmuir **2019**, *35*, 14124–14132 (Selected as supplementary cover).
3. Dual Wettability on Diarylethene Microcrystalline Surface Mimicking a Termite Wing
R. Nishimura, K. Hyodo, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida
Commun. Chem. **2019**, *2*, article number: 90.
4. Object Transportation System Mimicking the Cilia of Paramecium Aurelia by Using Light-Controllable Crystal Bending Behavior of a Photochromic Diarylethene
R. Nishimura, A. Fujimoto, N. Yasuda, M. Morimoto, T. Nagasaka, H. Sotome, S. Ito, H. Miyasaka, S. Yokojima, S. Nakamura, B. L. Feringa, K. Uchida
Angew. Chem. Int. Ed. **2019**, *58*, 13308–13312 (Selected as back cover).

Publications Not Described in This Thesis

5. Photoinduced Topographical Changes on Microcrystalline Surfaces of Diarylethenes
N. Fujinaga, N. Nishikawa, **R. Nishimura**, K. Hyodo, S. Yamazoe, Y. Kojima, K. Yamamoto, T. Tsujioka, M. Morimoto, S. Yokojima, S. Nakamura, K. Uchida
CrystEngComm **2016**, *18*, 7229–7235 (Selected as back cover).

6. Metal-Vapor Integration/transportation Based on Meta-Atom Desorption from Polymer Surfaces with a Low Glass-Transition Temperature
T. Tsujioka, R. Shirakawa, S. Matsumoto, **R. Nishimura**, K. Uchida
J. Vac. Sci. Technol. A **2017**, 35, 020603.
7. Photosalient Phenomena that Mimic Impatiens Are Observed in Hollow Crystals of Diarylethene with a Perfluorocyclohexene Ring
E. Hatano, M. Morimoto, T. Imai, K. Hyodo, A. Fujimoto, **R. Nishimura**, A. Sekine, N. Yasuda, S. Yokojima, S. Nakamura, K. Uchida
Angew. Chem. Int. Ed. **2017**, 56, 12576–12580.
8. In Situ Optical and Spectroscopic Imaging of Photochromic Cyclization and Crystallization of a Diarylethene Film with Optical Microscopy
K. Tawa, T. Kadoyama, **R. Nishimura**, M. Toma, K. Uchida
J. Photochem. Photobiol. A **2018**, 356, 397–402.
9. Photochromic Crystalline Systems Mimicking Bio-Functions
K. Uchida, **R. Nishimura**, E. Hatano, H. Mayama, S. Yokojima
Chem. Eur. J. **2018**, 24, 8491–8506.
10. In Situ Microscopic Imaging of Photoisomerization and Crystallization of Diarylethene Film Controlled by an Aluminum Plasmonic Chip
T. Kadoyama, **R. Nishimura**, M. Toma, K. Uchida, K. Tawa
Langmuir **2018**, 34, 4217–4223.
11. Photochromic Diarylethene with Turn-off Fluorescent Switching Property
L. Kono, Y. Nakagawa, A. Fujimoto, **R. Nishimura**, Y. Hattori, T. Mutai, N. Yasuda, K. Koizumi, S. Yokojima, S. Nakamura, K. Uchida
Beilstein J. Org. Chem. **2019**, 15, 2204–2212.

12. Theoretical Consideration of Wetting in Cassie-Baxter State on Multi-Pillar and Multi-Hole Surfaces: Thermodynamics and Laplace Pressure

H. Mayama, T. Nishino, A. Sekiguchi, **R. Nishimura**, K. Uchida, S. Yokojima, S. Nakamura, Y. Nonomura

J. Photopolym. Sci. Technol. **2019**, 32, 279–285.

Acknowledgements

This work describing on doctoral thesis was carried out at Department of Materials Chemistry, Graduate School of Science and Technology, Ryukoku University (Uchida laboratory). I would like to deepest express to Prof. Dr. Kingo Uchida for his kind guidance and encouragement throughout this work. And I am deeply grateful to him to giving me the opportunity to have wonderful experience and to meet many wonderful people in this period.

I would like to express deepest appreciation to Prof. Dr. Hiroyuki Mayama (Asahikawa Medical University) for great supporting, suggestion and discussion with his amazing dynamic theory for my studies of wettability.

I also would like to express to Dr. Shinichiro Nakamura (RIKEN) and Prof. Dr. Satoshi Yokojima (Tokyo University of Pharmacy and Life Sciences) for fruitful suggestion and discussion.

I am grateful to Prof. Dr. Yoshimune Nonomura (Yamagata University) for investigation to observe a water droplet impacting to the superhydrophobic surface.

I wish to thank to Dr. Nobuhiro Yasuda (Japan Synchrotron Radiation Research Institute) for helpful suggestion and lecture about single crystal X-ray structure analysis at the synchrotron radiation facility (SPring-8).

I would like to thank to Prof. Dr. Masakazu Morimoto (Rikkyo University) for measurement of the value of Young's modulus of the crystal.

I would like to deeply grateful to Prof. Dr. Ben. L. Feringa (University of Groningen) for his kind suggestion and discussion for object transportation system.

I am also grateful to Dr. Yohei Hattori and member of uchida laboratory in Ryukoku university for kind discussion, suggestion, collaboration, friendship and enjoyable time during course of this work.

Finally, I would like to sincerely appreciation to my family for supporting my dairy life economically and mentally.

March 2020