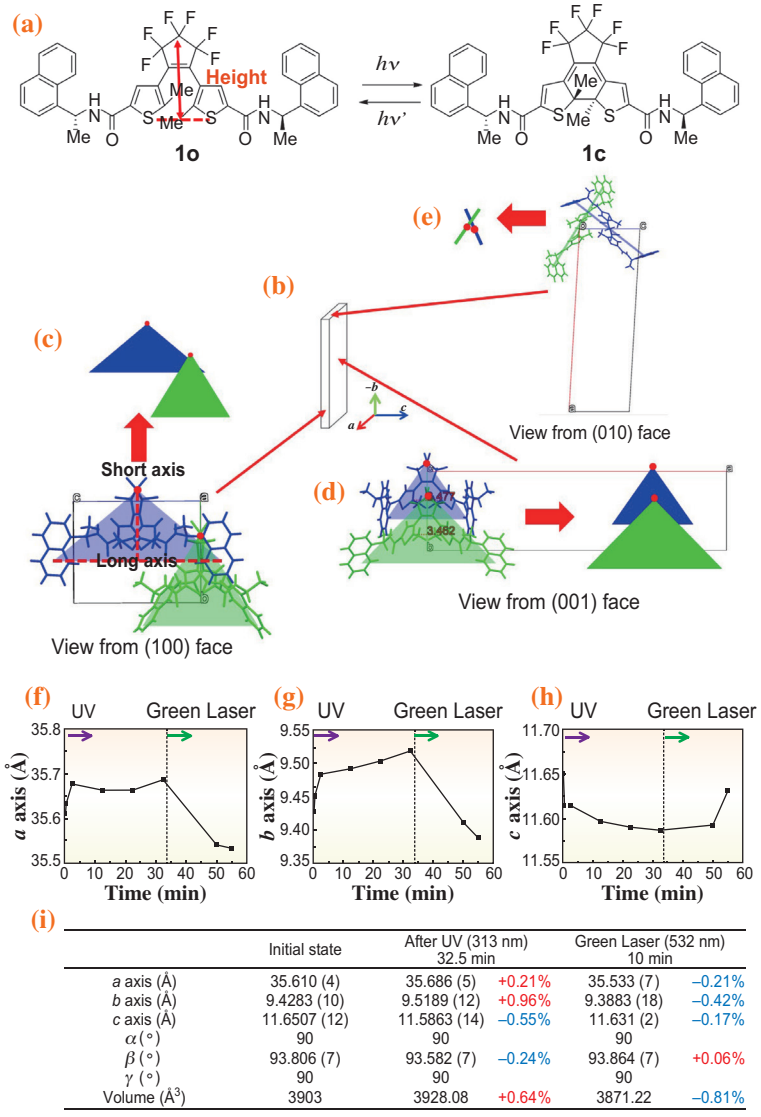
Object transport system mimicking the cilia of *Paramecium Aurelia*, making use of the light-controllable crystal bending behavior of photochromic diarylethene

Diarylethene derivatives are photochromic compounds whose colorless open-ring isomers undergo cyclization to the colored closed-ring isomers upon UV irradiation and revert to the original open-ring isomers by cycloreversion reaction upon visible light irradiation. The excellent thermal stability of both isomers, the high photochromic sensitivities and the ability to undergo reversible photochromic reactions even in the crystalline state [1] make them among the most promising photochromic molecules.

In 2007, the photoinduced bending phenomena of diarylethene crystals were reported in Nature [2]. The photoinduced microscopic movements, i.e., photoisomerization between open- and closed-ring isomers, induced the macroscopic movement of the bending behavior of the diarylethene crystals. In the paper, a crystal of diarylethene threw a ball upon UV irradiation.

We also reported the photoinduced bending behavior of other diarylethene derivatives the following year [3]. Single crystals of naphthyl-substituted derivative **1o** prepared by sublimation also showed



(i)

	Initial state	After UV (313 nm) 32.5 min		Green Laser (532 nm) 10 min	
a axis (Å)	35.610 (4)	35.686 (5)	+0.21%	35.533 (7)	–0.21%
b axis (Å)	9.4283 (10)	9.5189 (12)	+0.96%	9.3883 (18)	–0.42%
c axis (Å)	11.6507 (12)	11.5863 (14)	–0.55%	11.631 (2)	–0.17%
α (°)	90	90		90	
β (°)	93.806 (7)	93.582 (7)	–0.24%	93.864 (7)	+0.06%
γ (°)	90	90		90	
Volume (Å^3)	3903	3928.08	+0.64%	3871.22	–0.81%

Fig. 1. Molecular packing of diarylethene **1o** in the crystal prepared by sublimation, and the size changes of the unit cell upon alternate irradiation with UV and visible light. **(a)** Molecular structural changes of diarylethene **1o**, **(b-e)** molecular packing of two conformers (illustrated with green and blue triangles) of **1o** in the unit cell, (**f-i**) size changes of unit cell of **1o** upon alternate irradiation with UV and visible light.

reversible bending upon alternate irradiation with UV and visible light. However, the mechanism of the bending motion was unclear because the crystals prepared by sublimation were thin (thickness ~2 μm).

The thin platelet crystals of **1o** (Fig. 1(a)) were analyzed at SPring-8 **BL02B1** and **BL40XU** beamlines. The data obtained showed that the two conformers of **1o** are aligned along the long axis of the crystals, as shown in Figs. 1(b)–1(e). It is well known that when the short axis (height) of a diarylethene molecule in the crystal is parallel to the long axis of the crystal, the crystals exhibit bending motion away from the incident UV light [4] owing to the elongation of the height of the assumed triangular shape of the molecule (Figs. 1(b)–1(e)). Upon irradiation with UV light from the (001) surface, the *a* and *b* axes of the unit cell expand, inducing the bending of the crystal away from the incident UV light (Figs. 1(f)–1(i)). Then, upon irradiation with visible light, the crystal returned to the original straight shape because of shrinkage along the *a* and *b* axes (Figs. 1(f)–1(i)). The same bending behavior was observed when the light was irradiated onto the (100) surface. This behavior agrees with the molecular packing in the crystal.

We have designed an object-transport system made from vertically arranged diarylethene crystals (Fig. 2(a)) of **1o** [5]. The surface covered with bending crystals was fabricated in three steps. (1) By the sublimation of **1o**, only dot-shaped structures were formed on the substrate. (2) To make nucleation sites for crystal growth, magnetron sputtering with Au-Pd alloy was performed on the dot-shaped structures. (3) Using this dotted surface covered with the Au-Pd alloy as a target substrate for sublimation, we obtained thin platelet crystals of **1o** on the substrate.

We demonstrated the transport using a polystyrene bead (PB) (average diameter 1 mm) as the target object by irradiating UV and visible light from various directions. As shown in Figs. 2(b)–2(e), the motion of the PB on the thin platelet crystals was controlled at will by changing the direction of applied UV or visible light. First, UV light (λ=254 nm) was applied from the top of the screen and the PB moved downward, as a result of the cooperative bending of the crystals (Fig. 2(b)). Upon irradiation with visible light orthogonal to the surface, the PB returned upward as the bended crystals recovered to their original straight form (Fig. 2(c)). Without light irradiation, the ball did not move (Fig. 2(d)). Then UV light was irradiated from the bottom of the screen, causing the ball to move upward, indicating that the transport direction corresponded to the direction of UV incidence (Fig. 2(e)). Consequently, we succeeded in transporting the PB in any desired direction by photoirradiation. This smart surface will be applicable to remote-controlled object transport in various environments and holds potential for the development of soft robots.

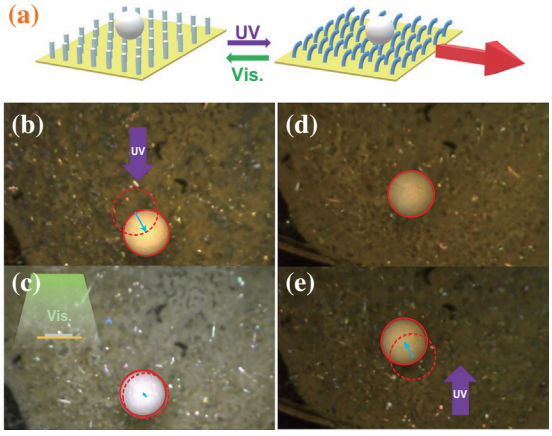


Fig. 2. **(a)** Illustration of photoinduced object transport model consisting of photoinduced bending crystals. **(b)** A polystylene bead with 1 mm diameter moved downward upon UV irradiation from the top of the screen. **(c)** Upon visible light irradiation orthogonal to the surface, the ball moved upward. **(d)** Without photoirradiation, the ball did not move. **(e)** When UV light was irradiated from below, the ball moved upward. The original position of the bead in each panel is indicated by a red dashed circle. The displacement vector is shown by a light blue arrows.

Kingo Uchida*, Ryo Nishimura and Ayako Fujimoto

Department of Materials Chemistry, Ryukoku University

*Email: uchida@rins.ryukoku.ac.jp

References

[1] M. Irie *et al.*: Chem. Rev. **114** (2014) 12174.
[2] M. Irie *et al.*: Nature **446** (2007) 778.
[3] K. Uchida *et al.*: Chem. Commun. (2008) 326.
[4] M. Morimoto, M. Irie: J. Am. Chem. Soc. **132** (2010) 14172.
[5] *R. Nishimura, A. Fujimoto, N. Yasuda, M. Morimoto, T. Nagasaka, H. Sotome, S. Ito, H. Miyasaka, S. Yokojima, S. Nakamura, B.L. Feringa and K. Uchida: Angew. Chem. Int. Ed.* ***58*** *(2019) 13308.*