Photochromic hollow crystals showing scattering of crystals and dispersal of included objects mimicking *Impatiens*

Diarylethene derivatives are photochromic compounds whose colorless open-ring isomers undergo cyclization to colored closed-ring isomers upon UV irradiation and revert to the original open-ring isomers by a cycloreversion reaction upon visible light irradiation. Diarylethenes are known by their following excellent photochromic properties: 1) high thermal stability of both isomers, 2) fatigue resistance to repeated photochromic reaction cycles, 3) high sensitivity (high absorption coefficients and photochromic quantum yields), 4) photochromic reactivity even in the crystalline state. Owing to these specific properties, diarylethene derivatives have been paid much attention in the research field of molecular memories and switches [1].

In 2007, a paper on the photoinduced bending phenomena of diarylethene crystals was published in Nature [2]. The macroscopic movement due to crystal bending was induced by the sum of the changes in each molecular volume from open-ring to closed-ring isomers. The dramatic movement of crystals upon alternate irradiation with UV and visible light attracted much interest. Then a new research field to develop systems that exhibit photoinduced macroscopic events attributed to the assumption of microscopic molecular movements was started and developed.

In addition to photochromic crystalline systems, other macroscopic phenomena called salient effects have been reported [3]. Salient phenomena refer to crystals showing jumping, breaking, or scattering into small pieces upon heating or photoirradiation. Salient phenomena induced by heating are called "thermosalient" phenomenon and those induced by photoirradiation are called "photosalient" phenomenon. Salient phenomena are much more dramatic than the photoinduced bending of crystals, i.e., in the bending the crystal lattice is maintained, while in salient phenomena the lattice is broken. When breaking the lattice, all the strained energy is released and transferred into kinetic energy. Therefore, the crystals jump or are scattered at a high speed.

Although the phenomena are dramatic and interesting to observe, they do not undergo any functions, and only breaking or jumping in unexpected directions occurs. The photoinduced bending of crystals is much slower, but some of them can be used for actual functions such as rolling gears or switching electronic devices.

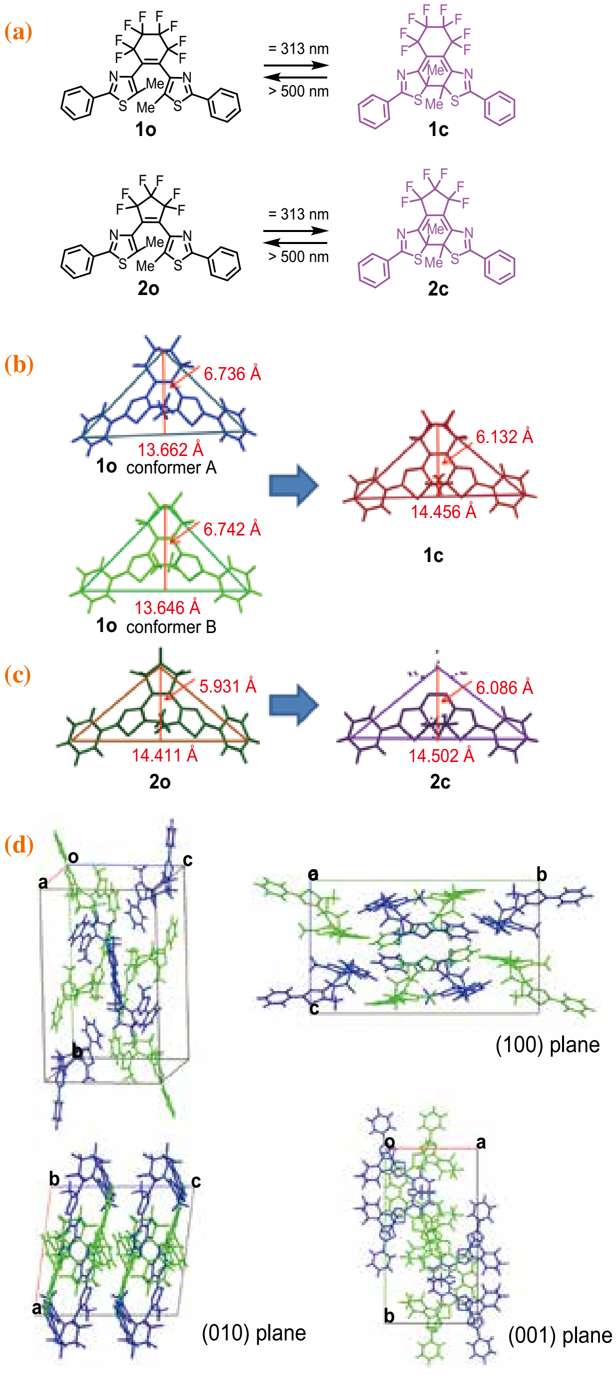

Fig. 1. Molecular movement of diarylethenes in the crystals. **(a)** Molecular structural changes of diarylethenes (1) and (2), **(b, c)** changes in structure size during the reaction from open-ring (**1o, 2o**) to closed-ring (**1c, 2c**) isomers, **(d)** molecular packing of two conformers (A and B) of **1o** in the unit cell.

We have studied the synthesis of new diarylethene derivatives to search for new photofunctions. We prepared a new derivative **1o** having a six-membered perfluorocyclohexene ring at the ethene moiety instead of the five-membered perfluorocyclopentene ring of the previously prepared derivative (**2o**) (Fig. 1(a)); derivative **2o** is the compound whose single crystal showed photoinduced bending [2]. The crystal of **1o** showed the photosalient phenomena of jumping and scattering into small pieces upon UV irradiation. The reason for this was clarified by X-ray analysis. In a unit cell of the crystal of **1o**, there are two conformers (depicted in blue (conformer A) and green (conformer B)). Upon UV irradiation, they undergo a cyclization reaction to form the closed-ring isomer **1c**. Comparing the sizes of **1o** and **1c**, the height of the molecules decreased by 9.0% for both conformers, while the widths of the molecules increased by 5.8 and 5.9% for conformers A and B, respectively (Fig. 1(b)). These changes are almost three times larger than those for the conversion from **2o** to **2c** (0.6% increase in width and 2.6% increase in height) (Fig. 1(c)). These larger structural changes induced stress in the crystal upon UV irradiation, leading to photoinduced salient phenomena [4].

Unexpectedly, **1o** formed crystals with hollow structure by sublimation on a hot plate under atmospheric pressure. We analyzed the hollow crystals at SPring-8 beamlines **BL02B1** and **BL40XU**, and found that the hollow crystals have the same molecular packing as the non-hollow crystals as shown in Fig. 1(d).

This finding inspired us to devise a function for the hollow crystals. *Impatiens* (touch-me-not) are known to have a specific biofunction. The *impatiens* plant disperses its seeds over a distance as the seedpod explodes open. We attempted to mimic this function. The dimensions of the largest hollow crystal were 5 to 30 μm in width and around 100 μm in length. Upon UV irradiation, hollow crystals were deformed as in Fig. 2(a) and finally broke down in small pieces [5]. In addition, small plastic beads (1.0 μm diameter) containing a fluorescent dye were packed into the hollow (Fig. 2(b)), and UV light was irradiated to the crystal. Then the beads inside the hollow were immediately scattered along with the deformation and breaking of the walls in the manner of the seeds of natural *impatiens* (Fig. 2(c)). This phenomenon implies that the photoresponsive hollow acts as a kind of artificial *impatiens*. With the help of SPring-8, we were able to clarify the mechanism of the photosalient phenomena of hollow crystals, which led to the generation of a new photoresponsive system mimicking *impatiens*.

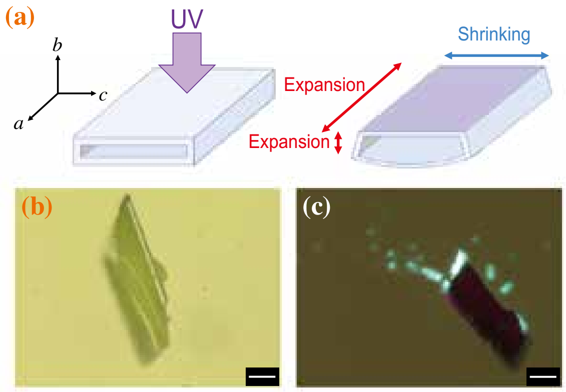

Fig. 2. **(a)** Deformation of the hollow crystal upon UV irradiation, **(b)** hollow crystal packed with fluorescent polystyrene beads with 1 μm diameter, **(c)** UV-induced scattering of fluorescent beads. Scale bars: 20 μm.

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