

## Molecular crystalline capsules that release their contents upon irradiation

Photosalient phenomena are well-known marked responses of organic crystals, such as jumping of crystals, or breaking or scattering of crystals into small pieces upon photoirradiation [1]. When the crystalline lattice breaks upon light irradiation, the strained energy is released and transformed into kinetic energy. Therefore, the crystals jump or scatter with high speed. Photosalient phenomena have also been observed in crystals of photochromic diarylethenes [2].

We previously created a photosalient crystal with a cavity formed during sublimation and demonstrated the scattering of 1- $\mu\text{m}$  diameter beads from inside the cavity upon UV-irradiation [3]. This was a biomimetic system mimicking the seeds of *Impatiens*, except that the closed edge of the crystal was cut and the 'seeds' were artificially implanted by capillary action by dipping the edge of the hollow crystal into a reservoir of beads dispersed in water. In addition, there was no lid for the cavity, and thus it was always open. Here, we discovered a photosalient crystalline capsule that naturally traps organic solutions during recrystallization. The capsule is sealed and can contain any solute in solvent, in principle.

### Photochromic crystals showing photosalient effect

We prepared a new diarylethene with *m*-trimethylsilylphenyl groups at both ends of the molecule (**1o**) (Fig. 1(a)). Diarylethenes are extensively studied compounds with photochromism and show a reversible transformation between open and closed forms upon photoirradiation. Diarylethene **1o** showed photochromism between **1o** and **1c** in solid and in solution. When the crystals were continuously irradiated with UV light ( $\lambda = 313 \text{ nm}$ ), they turned blue and then showed slight bending followed by fragmentation (a photosalient effect). Then, we attempted to obtain single crystals of **1o** by a common evaporation method. From a hexane solution, 7.7% of the crystals (668 out of 7967) had capsule structures. We analyzed the capsule structured crystals at SPring-8 BL02B1 and BL40XU beamlines, and found them to have the same molecular packing as the noncapsule crystals.

We observed the formation of the capsule structure by optical microscopy and captured the moment of formation of primary liquid inclusions. The mechanism of formation of the capsule is attributed to the

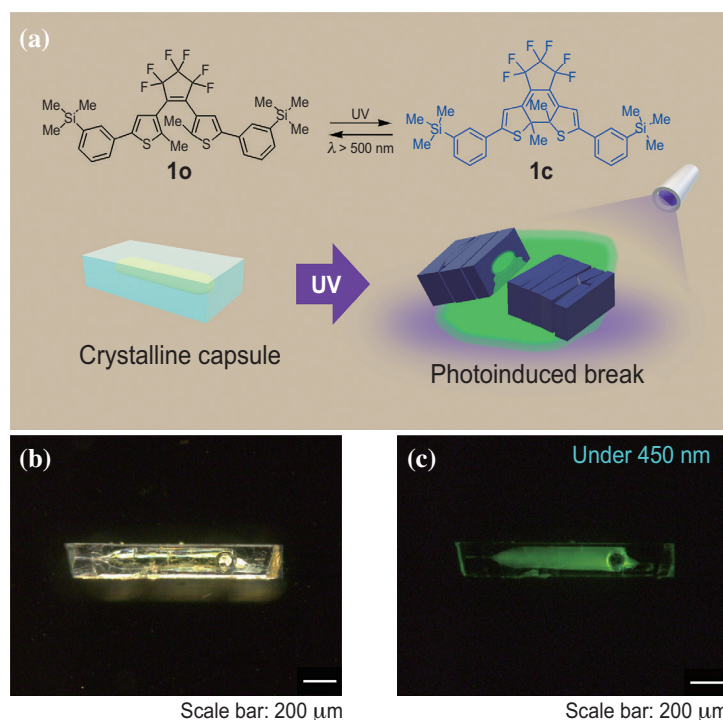


Fig. 1. Molecular crystalline capsule that releases the content, 5(6)-carboxyfluorescein (**5(6)-FAM**). (a) Molecular structures of open (**1o**) and closed-ring isomer (**1c**) and photorelease from a crystalline capsule. (b) Crystalline capsule containing **5(6)-FAM** inside under daylight. (c) Capsule under 450 nm light irradiation. **5(6)-FAM** inside emits green fluorescence.

inhomogeneous growth of crystals. The appearance of cavities due to this inhomogeneous growth of the crystals and the trapping of the solution in the cavities were observed.

To visually demonstrate the photoinduced property of a crystalline capsule of **1o**, we made crystalline capsules containing 5(6)-carboxyfluorescein (5(6)-FAM), a fluorescent dye used as a fluorescent tracer. The crystalline capsules were prepared from an acetone–methanol (3:1) solution of **1o** and 5(6)-FAM in 21% yield. The included 5(6)-FAM was ascertained by green fluorescence from the dye under 450 nm light irradiation. If a chemical can be dissolved in a solvent and can coexist with **1o** under recrystallization conditions, it is assumed that the capsule can include any such chemicals in solution.

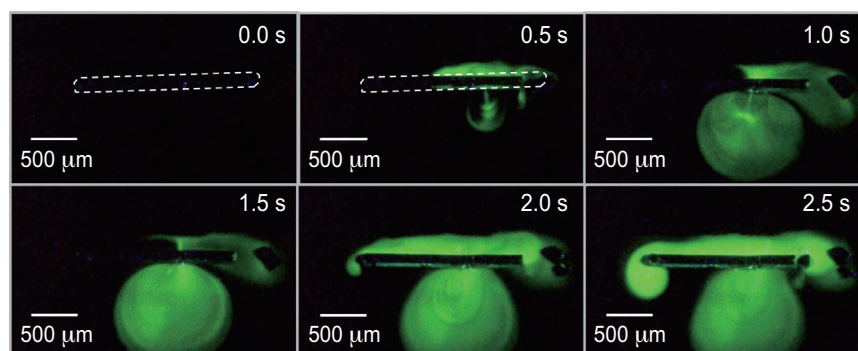
#### Photorelease of the included fluorescence dye from the crystalline capsule upon 365 nm light irradiation

A crystal was floated on an aqueous buffer droplet (pH = 9.18 at 25°C) under a microscope (Fig. 1(b)), and the green fluorescence of 5(6)-FAM was visualized by 450 nm LED light irradiation, which does not induce the photoreaction of **1o** (Fig. 1(c)). Upon UV irradiation, the green fluorescence emission from 5(6)-FAM diffused in the aqueous buffer that appeared after

the capsule was broken. The area of fluorescence of 5(6)-FAM expanded over the water surface around the crystal, indicating successful photoinduced release from the crystalline capsule (Fig. 2).

To control the crystal size, we changed the recrystallization period to obtain crystalline capsules. When the crystalline capsules containing 5(6)-FAM were prepared by recrystallization from the mixture of acetone and methanol with dissolved dye, the sizes of the obtained capsules were 2 mm in length and 300–400 μm in width for a 48 h recrystallization period. The size was reduced to less than 400 μm in length and less than 50 μm in width by shortening the recrystallization period to 12 h. The smaller capsules also released the 5(6)-FAM.

Such photorelease was also induced by multiphoton excitation with a femtosecond laser pulse at 802 nm without raising the temperature of the crystals. Additionally, the photorelease of the crystal of **1o** depends on the polarization direction of light, since all of the molecules are regularly aligned in the single crystals. A crystal whose long axis was perpendicular to the polarization direction showed coloration followed by jumping out from the field of view, whereas another crystal whose long axis was parallel to the polarization direction showed almost no change.



Under UV irradiation at 365 nm

Fig. 2. Photoinduced scattering of diarylethene capsule under 365 nm light irradiation.

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