Supporting Information

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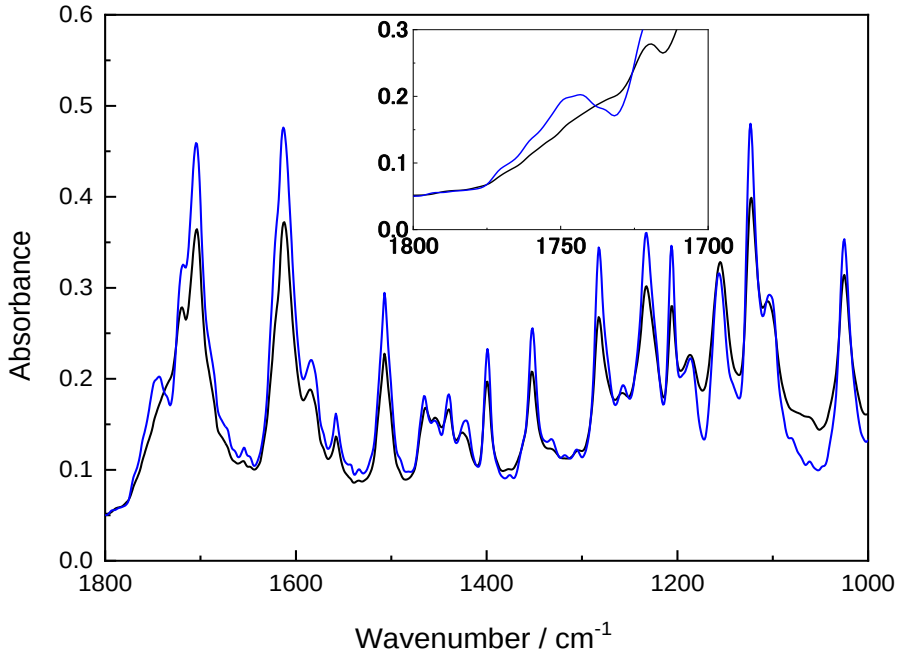

Fig. S1. Infrared spectral changes on the surface of a single crystals of **1** upon UV irradiation observed by FT-ATR (black line; before UV irradiation, blue line; after 254 nm light irradiation for 1 h).

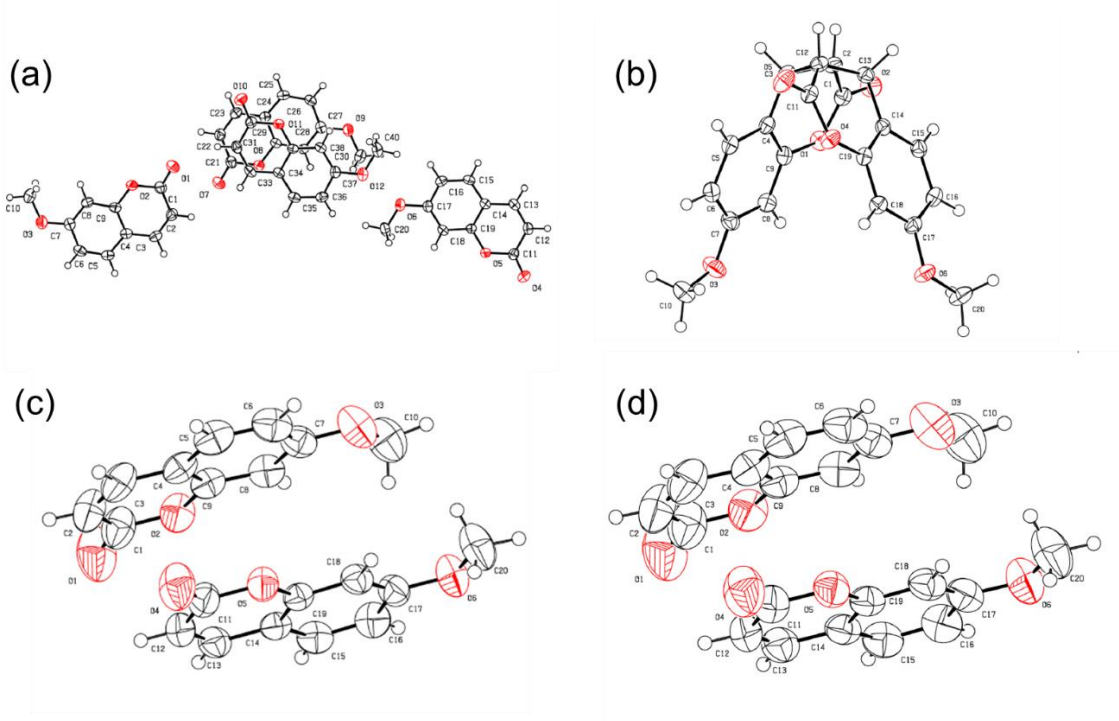

Fig. S2. ORTEP diagram of 7-methoxycoumarin (**1**) and dimer (**2**) molecules in the crystals (a) molecule **1** in Table 1, (b) molecule **2** in Table 1, (c) molecule $\mathbf{1}_{\text{before UV irr.}}$ in Table 2, (d) molecule $\mathbf{1}_{\text{400 nm 10 min}}$ in Table 2.

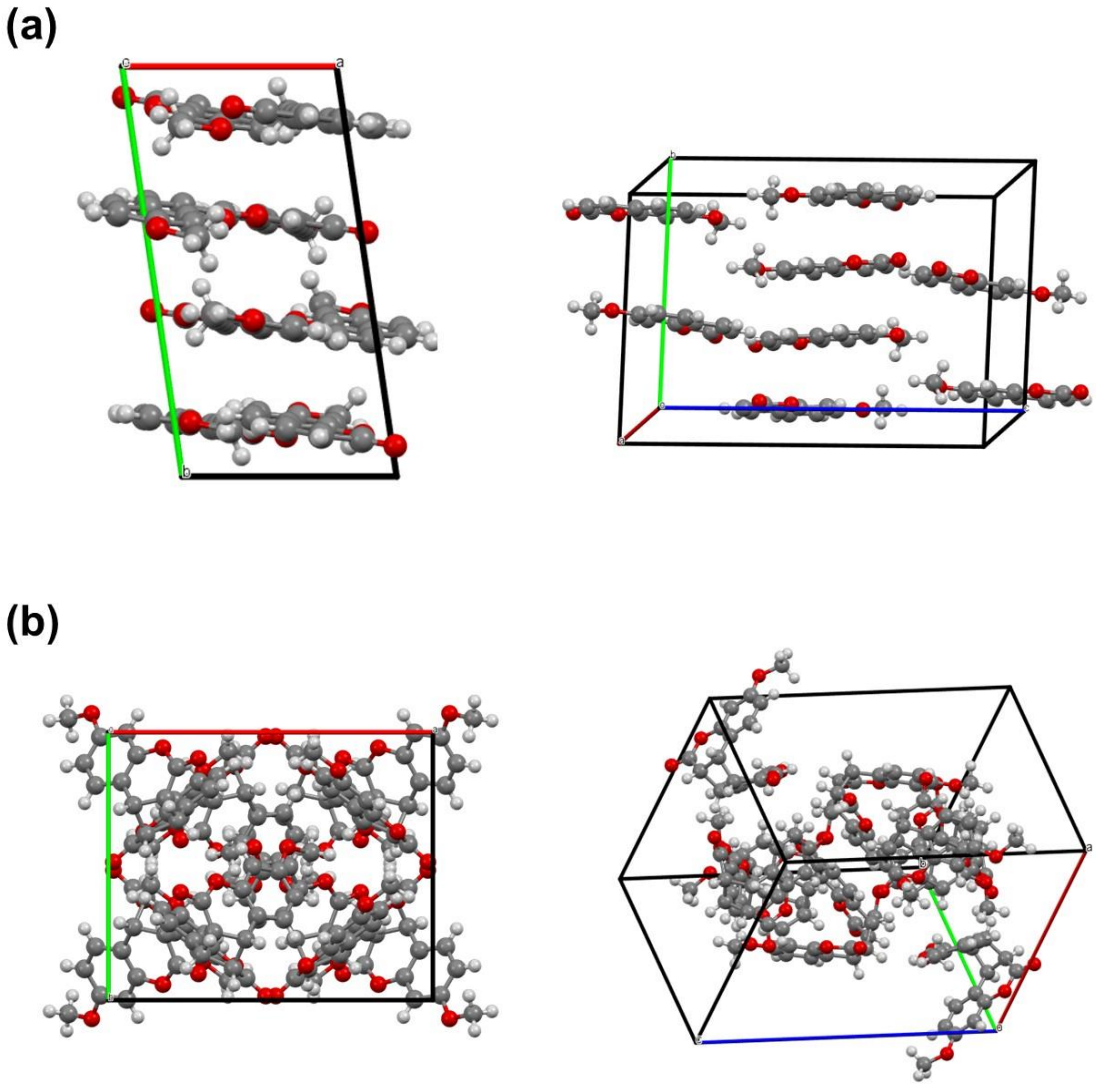

Fig. S3. Molecular packing in the crystals. (a) Molecular packing of 7-methoxycoumarin (**1**) and (b) the dimer (**2**). Left side pictures: view along c-axis. The planer molecules of **1** is aligned in layers in the crystal, while photodimer **2** does not oriented in layer.

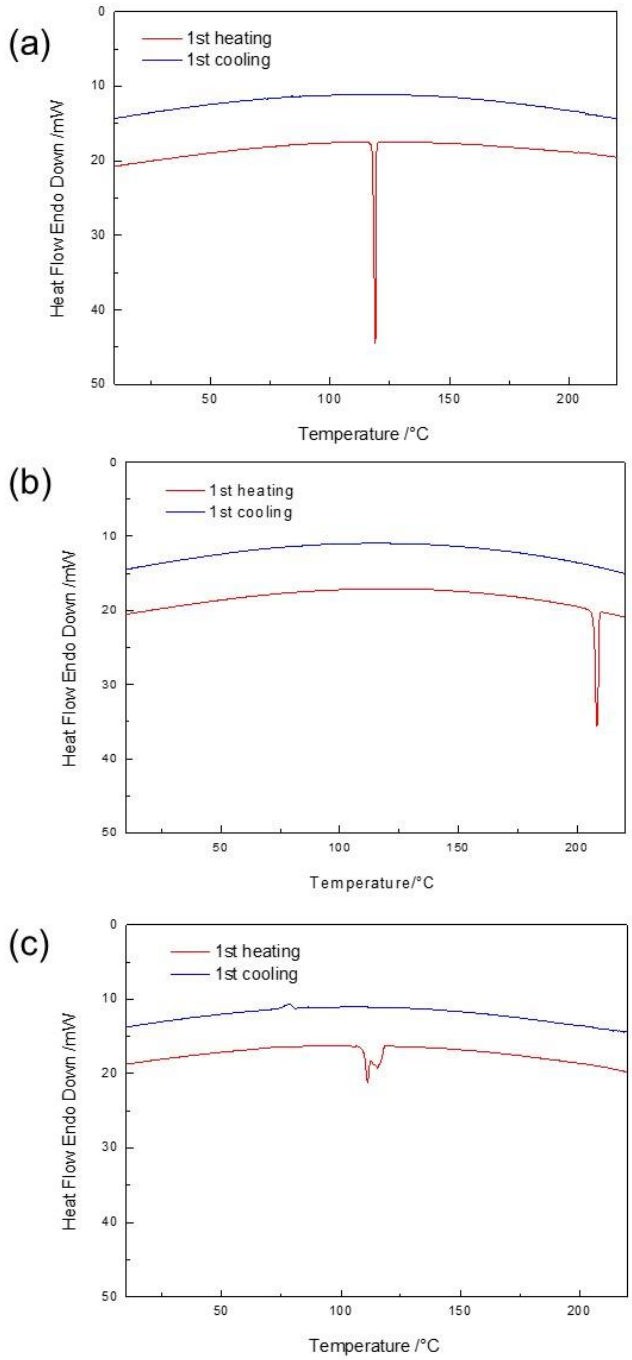

Fig. S4. DSC curves of crystals of monomer **1** (a), crystals of dimer **2** (b), and crystals of **1** after UV (365 nm 1.6 mW/cm^2) irradiation for 1 h (c). The melting points of crystals of **1** and dimer **2** were observed at 119 and 208 °C, respectively. The DSC curve of **1** after 365 nm irradiation for 1 h showed two peaks at 110 sand 115 °C during the heating process. The temperatures of new peaks are lower than those of **1** and **2**, indicating the molecular packing is different from those of the crystals of **1** and **2**.

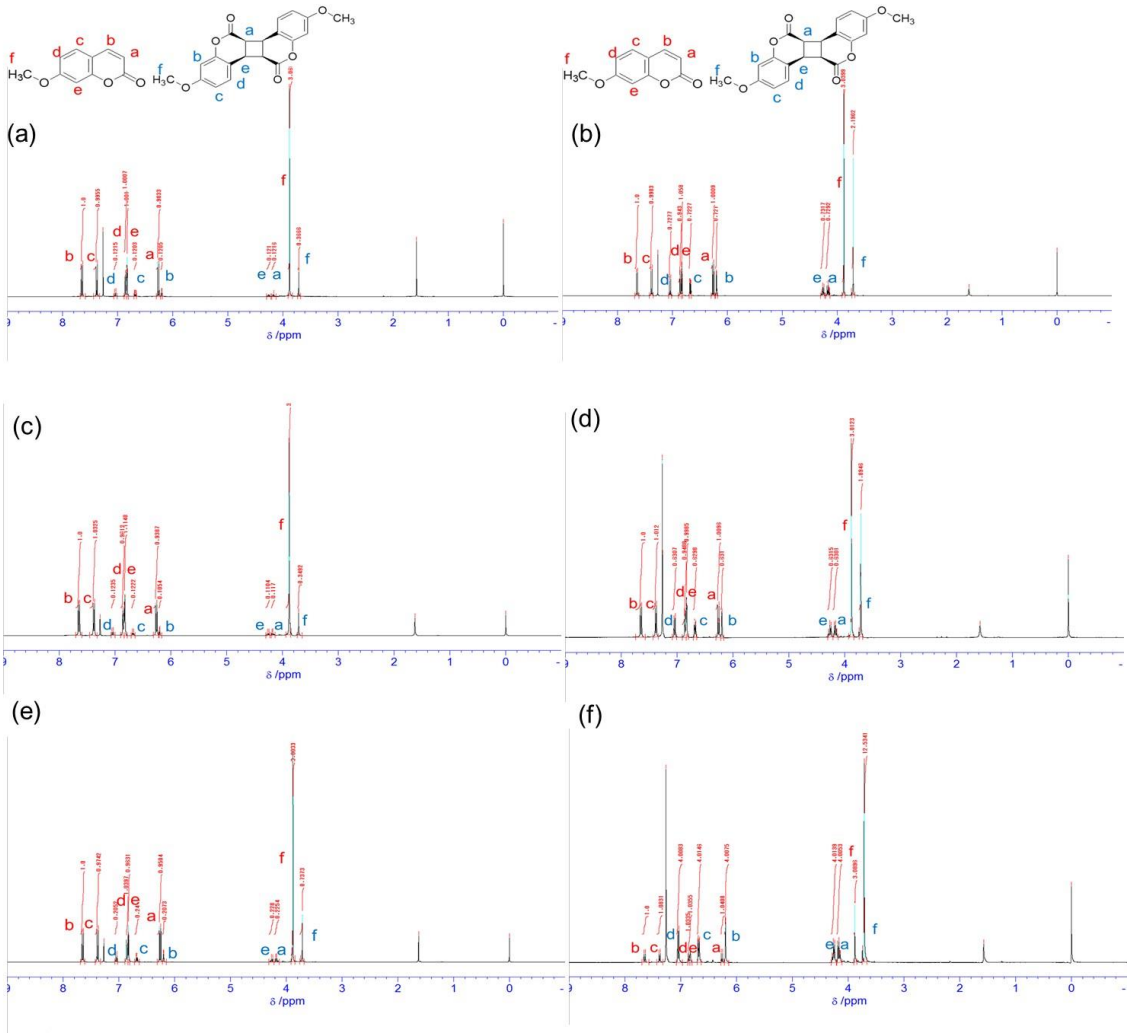

Fig. S5. ^{1}H NMR spectra of 7-methoxycoumarin crystals with different wavelength UV light for 1 and 24 h. a) UV light (PU-21 lamp: broad UV region containing 254 and 365 nm (see Fig. S6), irradiation period: 1 h)(the ratio of **1** : **2** = 89 : 11), b) UV light (irradiation with PU 21 lamp for 24 h) (the ratio of **1** : **2** = 58 : 42), c) 313 nm light for 1 h (the ratio of **1** : **2** = 89 : 11), d) 313 nm light irradiation for 24 h (the ratio of **1** : **2** = 61 : 39), e) 365 nm light irradiation for 1 h (the ratio of **1** : **2** = 83 : 17), f) 365 nm light irradiation for 24 h (the ratio of **1** : **2** = 20 : 80).

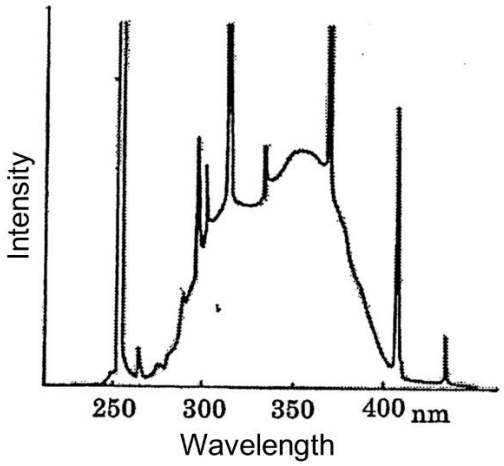

Fig. S6. Spectral characteristics of a UV lamp, PU-21

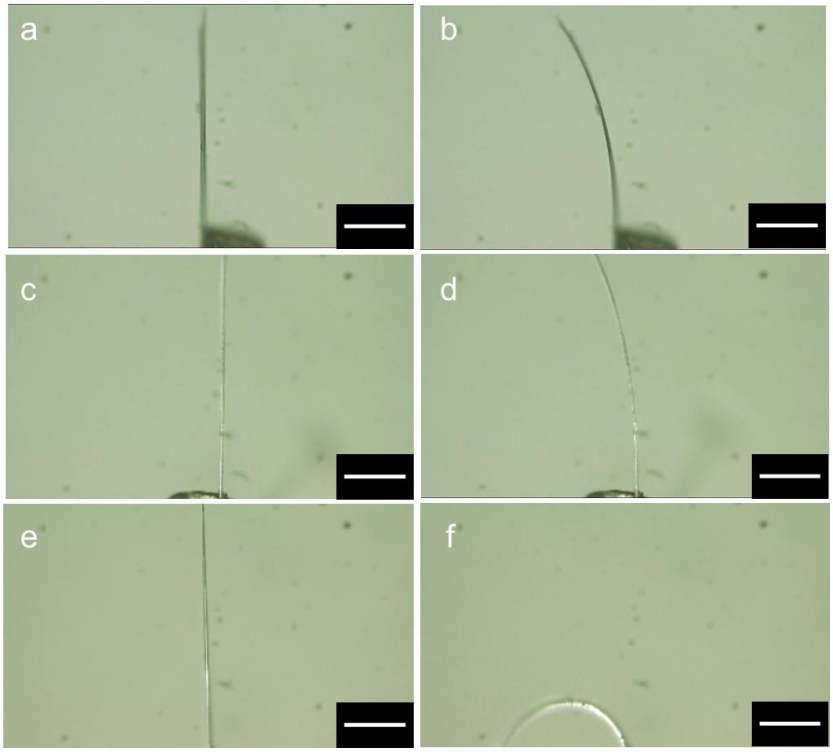

Fig. S7. Pictures during bending of thin crystal of **1** in the Movie 4.

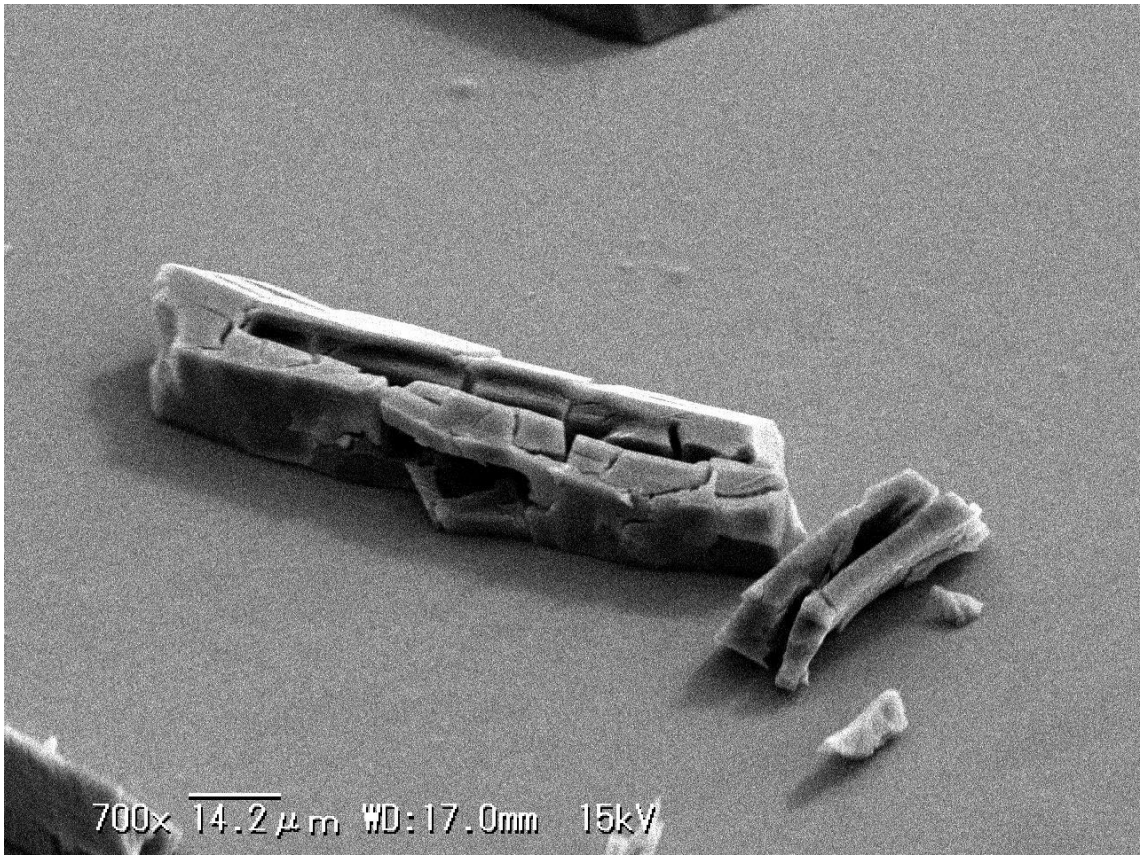

Fig. S8. Crystal capsules broken by photosalient phenomenon upon UV irradiation. The SEM image is the remained part of the crystal capsule. The centre cavity remained indicated the initial crystal had the capsule structure.

Table S1. Time profile of crystal data of **1** under 400 nm light irradiation.

	Before UV	400 nm 1 min irrad.	400 nm 3 min irrad.	400 nm 6 min irrrad.	400 nm 10 min irrad.
a / Å	6.8137(3)	6.8163(3) **+0.04%**	6.8218(3) **+0.12%**	6.8313(4) **+0.26%**	6.8504(8) **+0.54%**
b / Å	10.6684(5)	10.6743(5) **+0.06%**	10.6854(5) **+0.16%**	10.7000(6) **+0.30%**	10.7265(13) **+0.54%**
c / Å	12.4313(6)	12.4237(6) **−0.06%**	12.4055(6) **−0.21%**	12.3716(7) **−0.48%**	12.3293(15) **−0.82%**
α / °	108.1891(15)	108.1688(16)	108.1186(16)	108.0702(19)	107.962(4)
β / °	95.2297(15)	95.2529(16)	95.3130(16)	95.3960(19)	95.521(4)
γ / °	95.2045(15)	95.2278(16)	95.2767(16)	95.3435(19)	95.436(4)
V / Å^3	848.11(7)	848.40(7) **+0.03%**	848.75(7) **+0.08%**	848.71(8) **+0.07%**	850.38(18) **+0.27%**
R1	0.0627	0.0642	0.0668	0.0644	0.0708

	400 nm 15 min irrad.	400 nm 20 min irrad.	400 nm 25 min irrad.	400 nm 30 min irrad.
a / Å	6.8712(7) **+0.84%**	6.8897(12) **+1.12%**	6.896(2) **+1.21%**	6.900(2) **+1.27%**
b / Å	10.7514(12) **+0.78%**	10.7534(19) **+0.80%**	10.769(4) **+0.94%**	10.754(4) **+0.80%**
c / Å	12.2348(14) **−1.58%**	12.175(2) **−2.06%**	12.224(4) **−1.67%**	12.201(4) **−1.85%**
α / °	107.805(4)	107.690(5)	107.880(9)	107.814(11)
β / °	95.671(4)	95.714(6)	95.620(9)	95.532(11)
γ / °	95.545(4)	95.641(6)	95.601(9)	95.549(11)
V / Å^3	848.63(16) **+0.06%**	847.2(3) **−0.11%**	851.9(5) **+0.45%**	850.3(5) **+0.26%**
R1	0.0857	0.1039	0.1056	0.1120

The notes of the supplementary movies

Supplementary movie 1: A single crystal of compound **1** prepared by recrystallization was irradiated with ultraviolet light (KEYENCE UV-400 LED: 365 nm).

Supplementary movie 2: A thin crystal of **1** obtained by sublimation was irradiated with ultraviolet light (Topcon hand lamp Fi-51s: 254 nm) at an irradiation distance of 5 cm. (4x speed)

Supplementary movie 3: A thin crystal of **1** obtained by sublimation was irradiated with ultraviolet light (Topcon hand lamp Fi-5L: 365 nm) at an irradiation distance of 5 cm. (4x speed)

Supplementary movie 4: A thin crystal of **1** obtained by sublimation was irradiated with ultraviolet light (KEYENCE UV-400 LED: 365 nm) at an irradiation distance of 5 cm. (1x speed)

Supplementary movie 5: A hollow crystal of **1** obtained by sublimation was irradiated with ultraviolet light (KEYENCE UV-400 LED: 365 nm) at an irradiation distance of 5 cm.

Supplementary movie 6: The hollow crystals of **1** obtained by sublimation were irradiated with ultraviolet light (KEYENCE UV-400 LED: 365 nm) at an irradiation distance of 5 cm.

Supplementary movie 7: A crystalline capsule of **1** obtained by sublimation was irradiated with ultraviolet light (KEYENCE UV-400 LED: 365 nm) at an irradiation distance of 5 cm.