Supplementary Information

Two-step photomechanical motion of a dibenzobarrelene crystal

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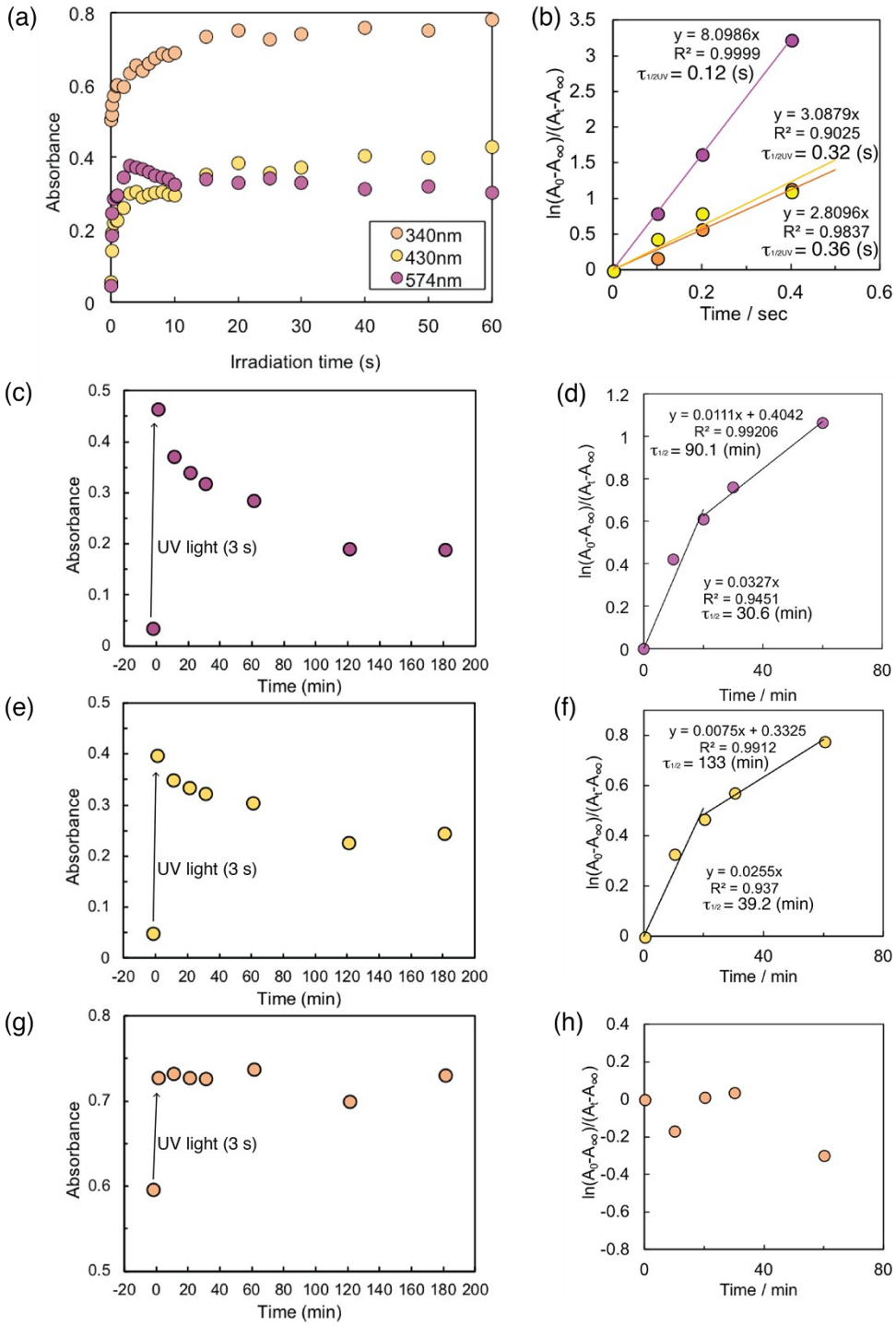

Figure S1. Time dependence of absorption peak intensities. (a) Intensity changes at 574, 430, and 340 nm upon UV light irradiation. (b) Apparent half-life calculations using initial changes at 574, 430, and 340 nm upon UV light irradiation. (c,e,g) Intensity changes at 574, 430, and 340 nm after stopping UV light exposure for 3 s. (d,f,h) Half-life calculations using initial changes at 574, 430, and 340 nm after stopping UV light exposure.

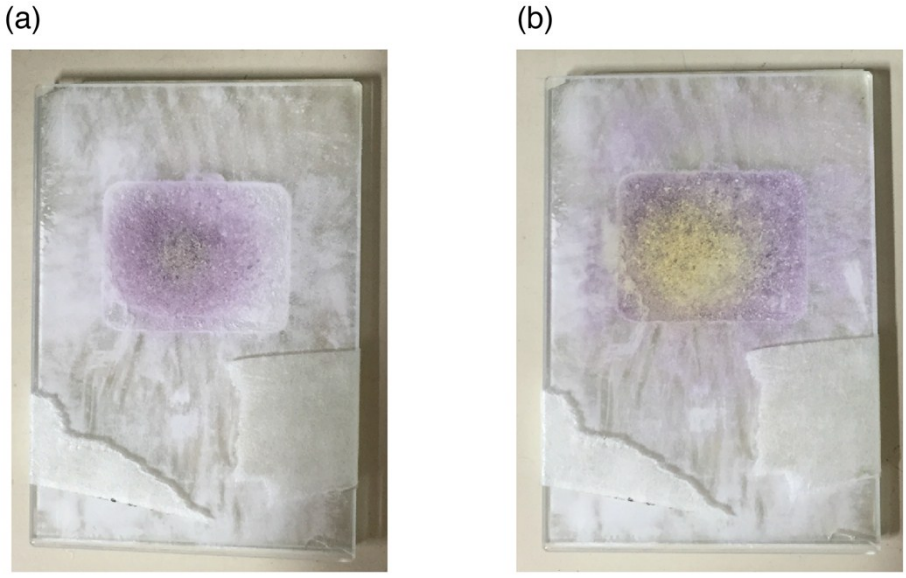

Figure S2. Colour change of a powdered sample of compound **1** upon UV light irradiation for (a) 3 s, and (b) 60 s.

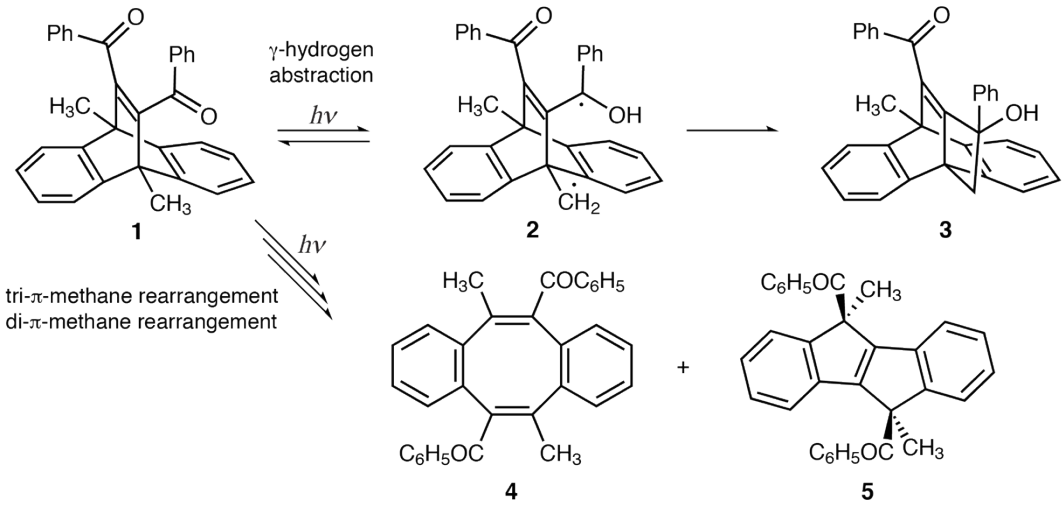

Figure S3. Possible final photoproducts formed via irreversible reactions. Biradical species **2**, which is produced by an intramolecular γ-hydrogen abstraction, can be coupled to form cyclobutanol compound **3**, as reported in benzophenone crystals.[S1–3] Molecular structures of the final photoproducts **4** and **5**, formed via a tri-π-methane rearrangement and a di-π-methane rearrangement, respectively, were determined by X-ray crystallographic analysis after UV light irradiation of a solution of compound **1** in benzene.[S4]

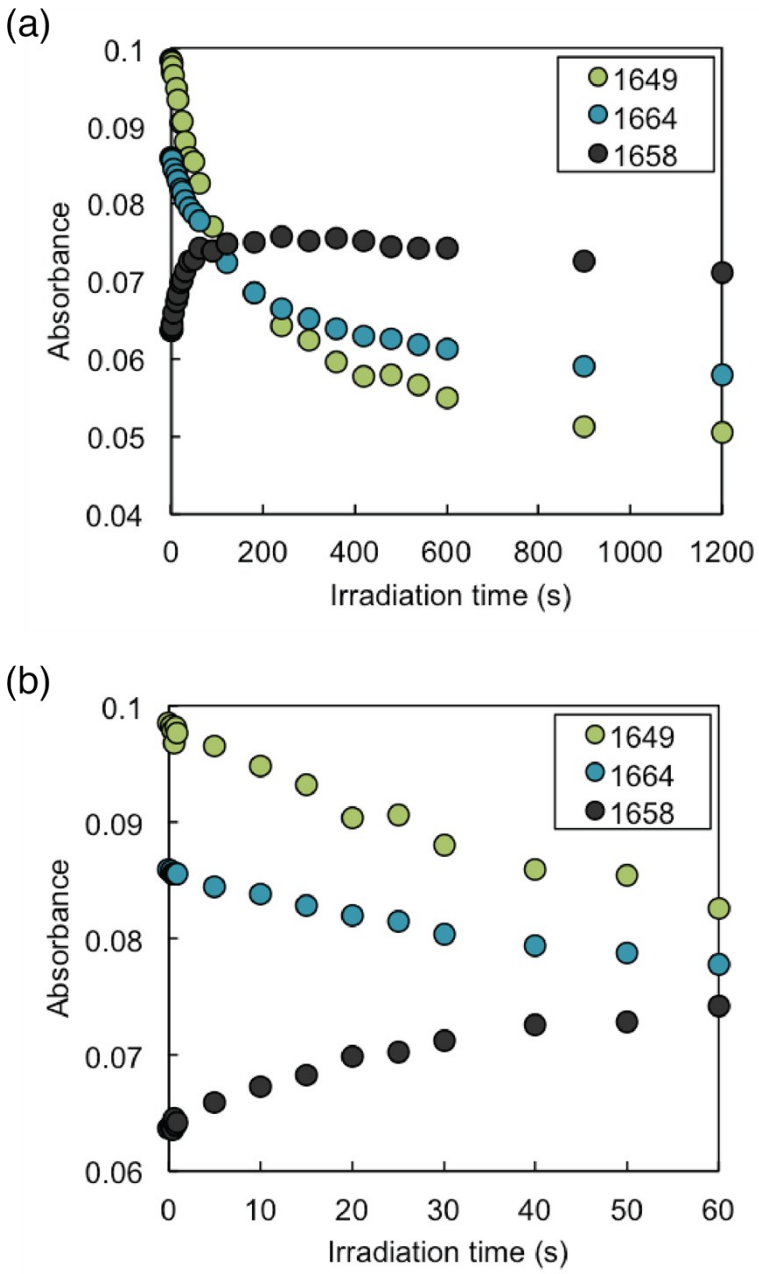

Figure S4. Temporal profiles of FT-IR peak intensities at 1,649, 1,658, and 1,664 cm^{-1}. (a) IR absorption change upon UV light irradiation. (b) Enlarged graph up to 60 s.

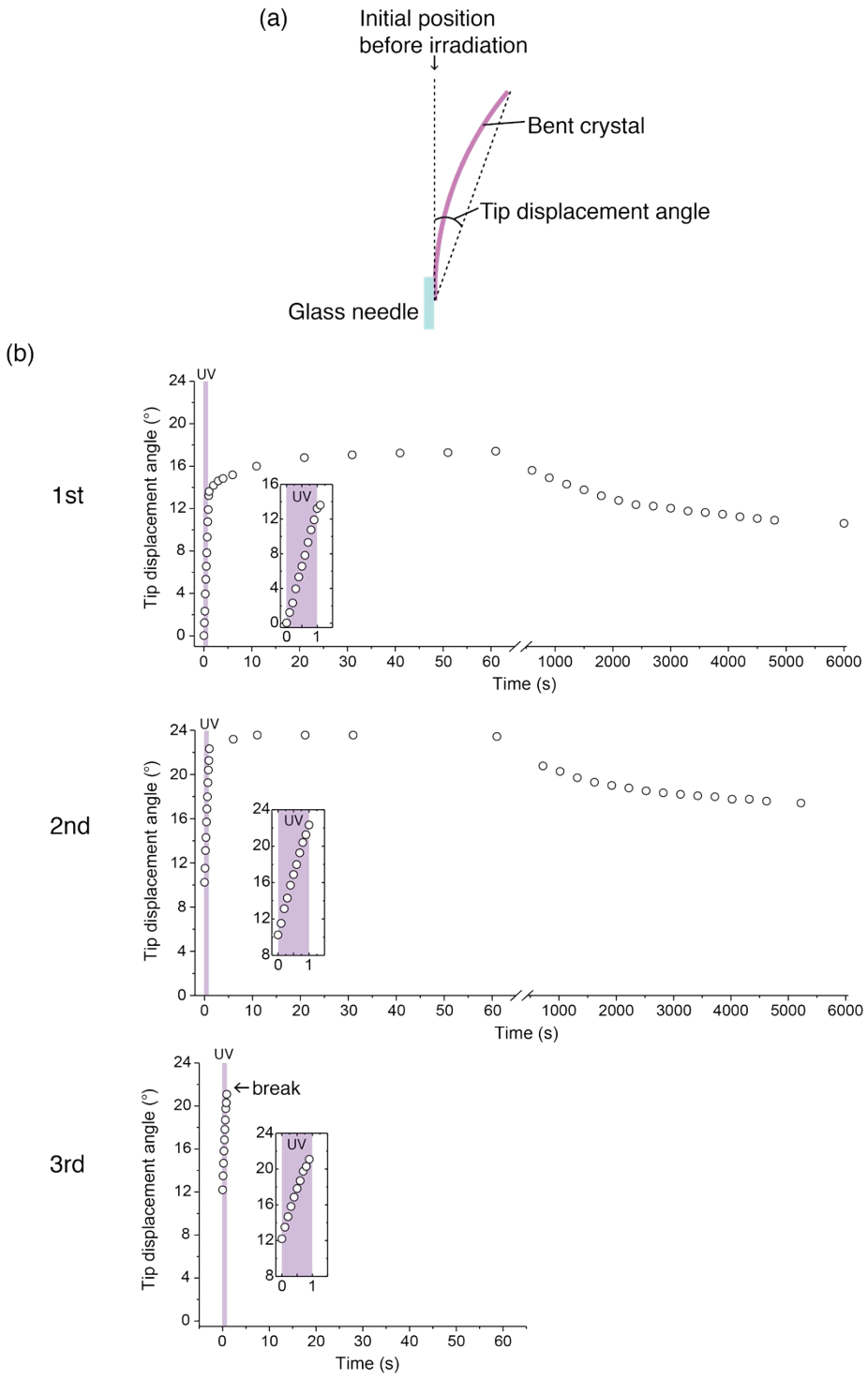

Figure S5. Time dependence of the tip displacement angle. (a) Definition of the tip displacement angle. (b) Time dependence of the tip displacement angle during bending stages 1–3 and relaxation. The crystal was irradiated by UV light (365 nm, 40 mW/cm^2) for 1 s. Insets show enlarged graphs in 1 s during UV irradiation.

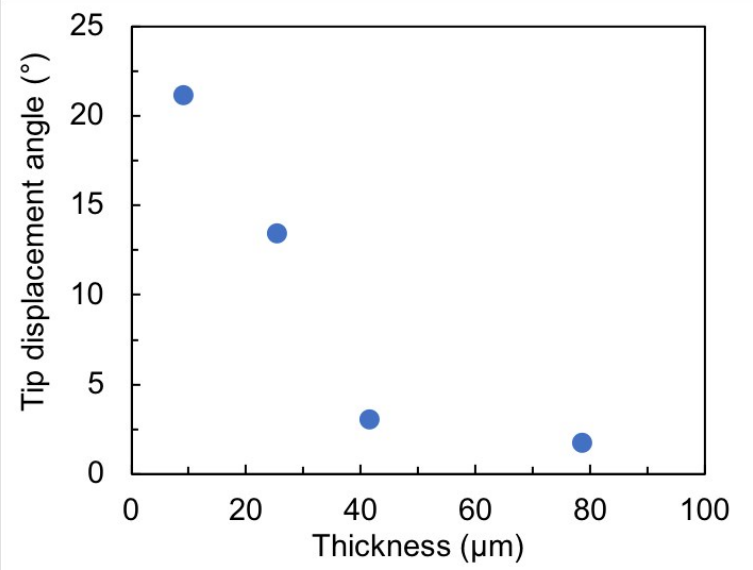

Figure S6. Relationship between tip displacement angle and crystal thickness. Tip displacement angle was calculated at the maximum bending position upon UV irradiation for 1 s. The sizes (length × width × thickness) of crystal are 4335 × 274 ×25 μm^3, 525 × 134 × 8.6 μm^3, 1334 × 126 × 78 μm^3, and 2955 × 95 × 41 μm^3, respectively.

Table S1. Crystallographic parameters of single crystal of compound **1** before and after UV light irradiation.

	Before UV	Before UV	After UV for several seconds	Relative difference (%)
Temperature (K)	293	223	223	
Empirical formula	$C_{32}H_{24}O_2$	$C_{32}H_{24}O_2$	$C_{32}H_{24}O_2$	
Formula weight	440.51	440.51	440.51	
Crystal system	Triclinic	Triclinic	Triclinic	
Space group	*P*-1	*P*-1	*P*-1	
a (Å)	9.2639(3)	9.2215(10)	9.2358(7)	+0.15
b (Å)	10.1820(4)	10.1283(10)	10.1367(9)	+0.08
c (Å)	14.3848(5)	14.3122(16)	14.2857(13)	-0.19
α (°)	102.8842(19)	102.715(6)	102.730(3)	
β (°)	99.249(2)	99.297(8)	99.234(3)	
γ (°)	112.0041(19)	111.851(6)	111.955(2)	
V (Å^3)	1180.70(8)	1165.69	1165.54	
Z	2	2	2	
ρ_{calc} (g·cm^{-3})	1.239	1.255	1.255	
R_1 [$I > 2\sigma(I)$]	0.0595	0.0575	0.0382	
wR_2 [$I > 2\sigma(I)$]	0.1517	0.1234	0.0955	
GOF	1.052	1.107	1.116	
CCDC	1860420	1860421	1860422	

Supplementary Movies

Movie S1.

First step bending of a plate-like crystal of compound **1** (4335 × 274 × 25 μm^3) upon UV light irradiation 1–3, each of 1 s.

Movie S2.

Two-step bending motion of a plate-like crystal of compound **1** (525 × 134 × 8.6 μm^3) upon prolonged UV light irradiation for 60 s.

References

S1 H. Koshima, A. Maeda, N. Masuda, T. Matsuura, K. Hirotsu, K. Okada, H. Mizutani, Y. Ito, T. Y. Fu, J. R. Scheffer, J. Trotter, *Tetrahedron: Asymmetry*, 1994, **5**, 1415–1418.

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S3 H. Koshima, M. Fukano, N. Ojima, K. Johmoto, H. Uekusa, *J. Org. Chem*., 2014, **79**, 3088–3093.

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