Supplementary Information

Mechanical motion of molecular crystals induced by [4 + 4] photodimerisation

Hideko Koshima,*a Hidetaka Uchimoto,^b Takuya Taniguchi,^c Jun Nakamura,^b Tsuyoshi Asahi^b and Toru Asahi^{a,c}

- **1.** Fig. S1. (a) Narrow plate-like microcrystals of *trans*-1 and grown on a glass plate by sublimation and (b) the X-ray diffraction (XRD) profile.
- Fig. S2. (a) Relationship between the thickness of the plate-like *trans*-1 crystals and the bending angle upon UV irradiation at 365 nm. (b) Original data of the graph (a).
- **3.** Fig. S3. (a) Elongation of a narrow plate-like microcrystal of *trans*-1 (426 μ m long × 5.1 μ m wide × 0.5 μ m thick) before and after UV irradiation at 365 nm.
- **4.** Fig. S4. ¹H NMR spectra of (a) *trans*-1, (b) *cis*-1, and (c) the powdered *trans*-1 crystals irradiated at 365 nm for 4 h.
- 5. Fig. S5. (a) UV-vis absorption spectra of (a) *trans*-1 (3.1×10^{-5} M) in acetonitrile before and after UV irradiation at 365 nm for 2 min. (b) UV-vis absorption spectrum of *cis*-1 (1.7×10^{-5} M) in acetonitrile.
- **6. Fig. S6.** Relative changes in the unit cell lengths of the *trans*-1 single crystal measured under UV irradiation at 365 nm.
- 7. Movie S1. Bending of the narrow plate-like *trans*-1 microcrystal ($511 \times 4.5 \times 0.5 \mu m^3$) upon UV (365 nm) irradiation from the light. The movie is played in 20 times speed.



Fig. S1. (a) Narrow plate-like microcrystals of *trans*-1 and grown on a glass plate by sublimation and (b) the X-ray diffraction (XRD) profile.



Fig. S2. (a) Relationship between the thickness of the plate-like *trans*-1 crystals and the bending angle upon UV irradiation at 365 nm. (b) Original data of the graph (a).

The logarithm of the bending angle was inversely and linearly proportional to the logarithm of the crystal thickness.



Fig. S3. (a) Elongation of a narrow plate-like microcrystal of *trans*-1 (426.3 μ m long × 5.1 μ m wide × 0.5 μ m thick) before and after UV irradiation at 365 nm.

After UV irradiation was performed alternately from the right and the left for total 15 min, the length of the crystal increased by 0.5%.



Fig. S4. ¹H NMR spectra of (a) *trans*-**1**, (b) *cis*-**1**, and (c) the powdered *trans*-**1** crystals irradiated at 365 nm for 4 h.

In the spectrum (c), appearance of the two singlet peaks at 2.84 (H^c) and 4.82 (H^d) ppm (integration ratio 2:1) and the aromatic proton signals at 6.7-7.1 ppm revealed the formation of the head-to-tail anthracene dimer **2** by [4 + 4] photodimerisation of the *trans*-**1** in the crystalline state; the yield of **2** was estimated to be 4% from the hydrogen integration 0.08 (H^c of **2**) and 2.00 (H^a of *trans*-**1**). However, almost no appearance of the peak at 4.24 ppm (H^b) derived from the *cis*-**1** showed the almost no occurrence of *trans*-to-*cis* photoisomerisation.



Fig. S5. (a) UV-vis absorption spectra of (a) *trans*-1 (3.1×10^{-5} M) in acetonitrile (—) before and (—) after UV irradiation at 365 nm for 2 min. (b) UV-vis absorption spectrum of *cis*-1 (1.7×10^{-5} M) in acetonitrile.

Most of the *trans*-1 molecules isomerised to the *cis*-1 molecules by the UV irradiation for 2 min.



Fig. S6. Relative changes in the unit cell lengths of the *trans*-1 single crystal ($130 \times 40 \times 20 \ \mu m^3$) measured under UV irradiation at 365 nm.

Movie S1. Bending of the narrow platelike *trans*-1 microcrystal ($511 \times 4.5 \times 0.5 \ \mu m^3$) upon UV (365 nm) irradiation from the light. The movie is played in 20 times speed.