Electronic Supplementary Information

Turn-on mode fluorescence photoswitching of diarylethene single crystals

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Polarized absorption spectra of single crystals were measured using a polarizing microscope (Leica, DM2500P) connected with a CCD-based PMA-11 photodetector (Hamamatsu Photonics, C7473). Fig. S1 shows the instrumental setup. A 100 W halogen lamp in the microscope was used as a light source. A polarizer and an analyzer were set in parallel to each other. The intensity of the light which transmitted through the colourless crystal (I_0) was measured with the photodetector. After the colouration of the crystal by UV irradiation, the intensity of the light which transmitted through the coloured crystal (I) was measured. On the basis of the Lambert-Beer's law ($A = \log(I_0/I)$), absorption spectra of the photogenerated closed-ring isomer in the crystal were calculated. Polar plots of the absorbance were carried out by measuring the polarized absorption spectra on rotating a sample stage of the microscope. UV and visible irradiation to the crystals was carried out with a UV-LED irradiation system (Keyence, UV-400 and UV-50H) and a 300 W xenon lamp (Asahi spectra, MAX-303). Polarized fluorescence spectra were also measured with the same polarizing microscope and photodetector. Fluorescence spectra of the crystals under excitation with 450 nm or 480 nm light were measured through the analyzer.

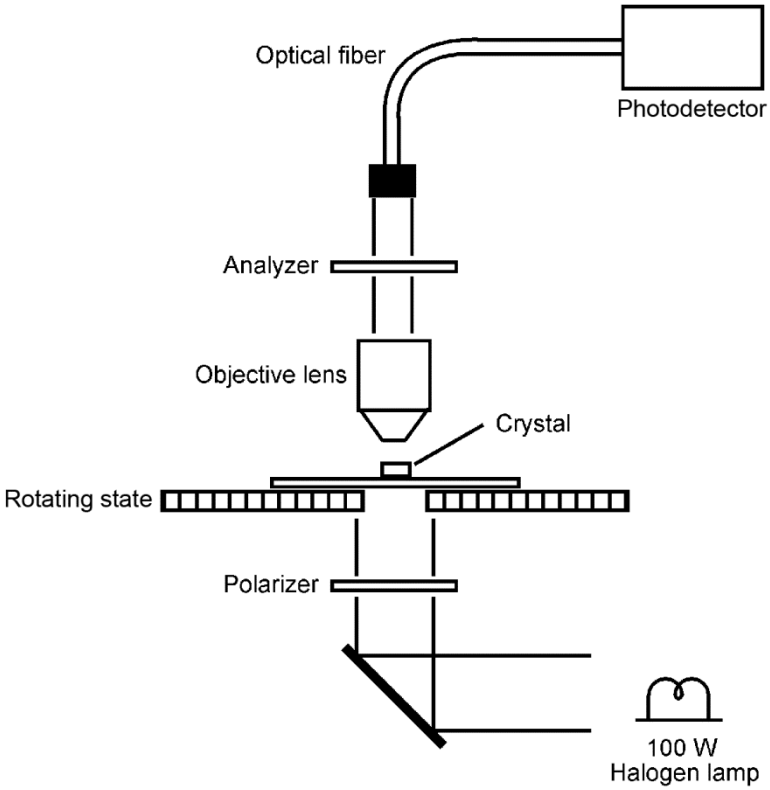


Fig. S1 Instrumental setup for polarized absorption and fluorescence spectral measurement.

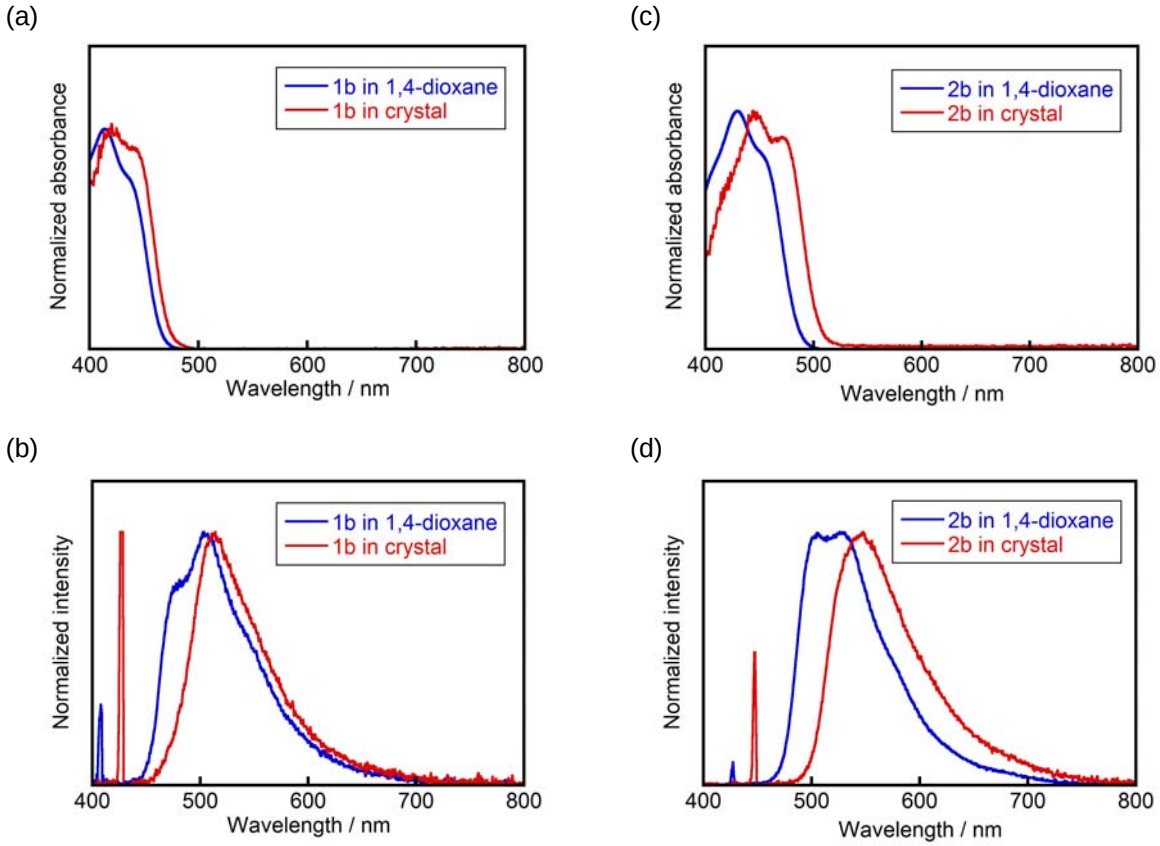


Fig. S2 (a) Absorption and (b) fluorescence spectra of **1b** in 1,4-dioxane and in the single-crystalline phase. (c) Absorption and (d) fluorescence spectra of **2b** in 1,4-dioxane and in the single-crystalline phase.

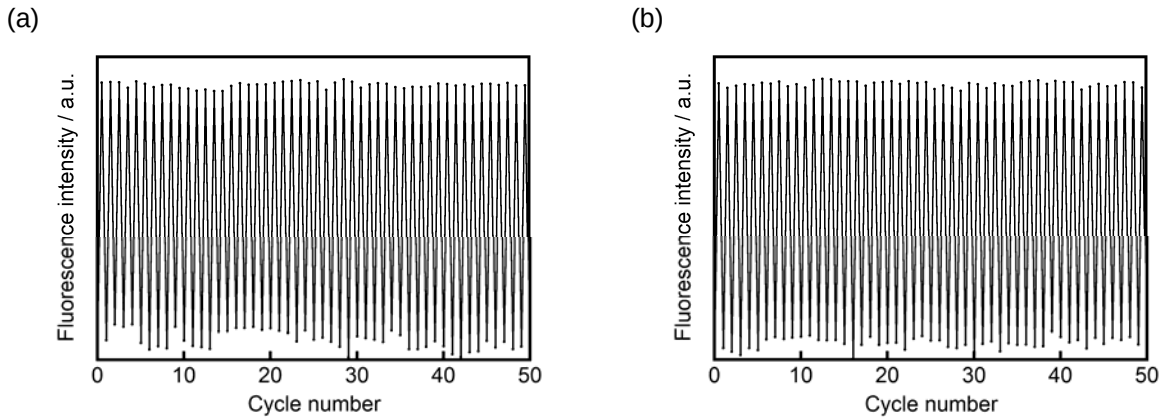


Fig. S3 Repeated fluorescence photoswitching of (a) crystal **1a** and (b) crystal **2a** by alternate irradiation with UV (λ = 365 nm) and visible (λ > 460 nm) light.

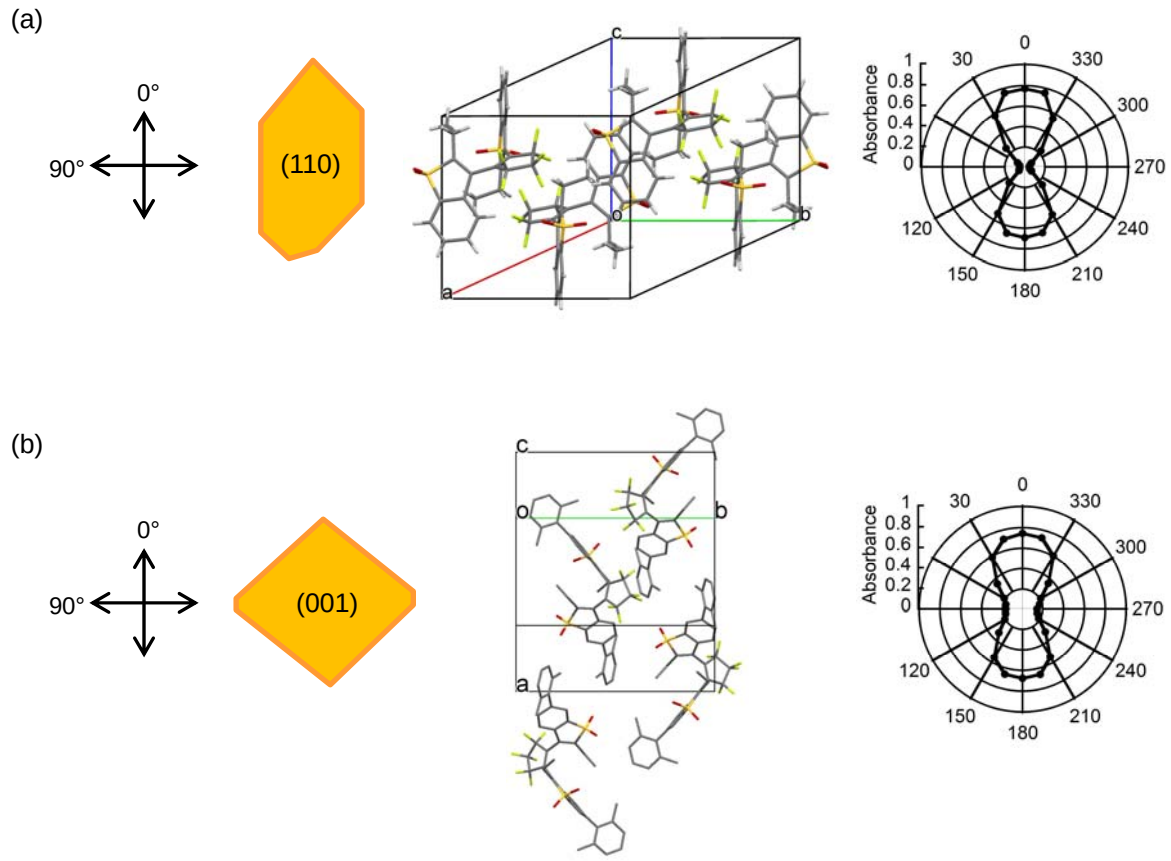


Fig. S4 Relationship between molecular packing and polarized absorption anisotropy for (a) crystal **1a** and (b) crystal **2a**.

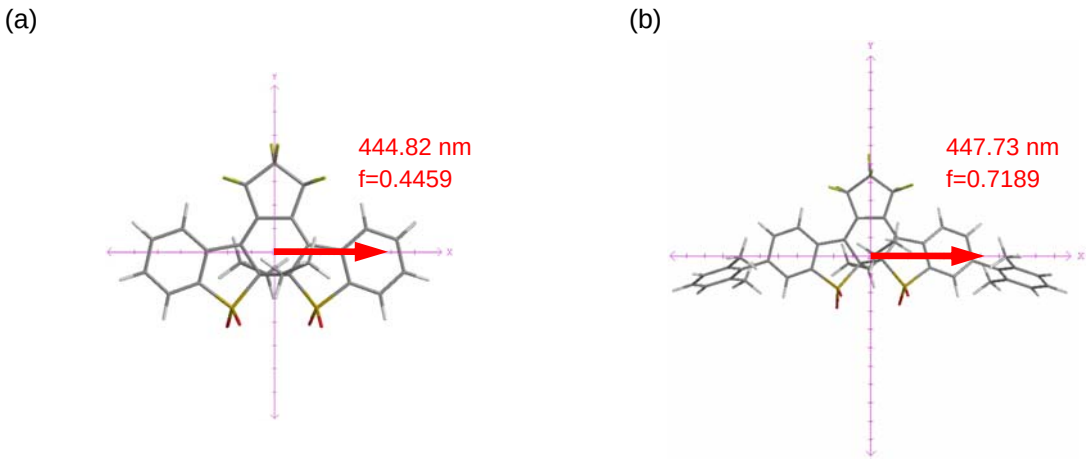
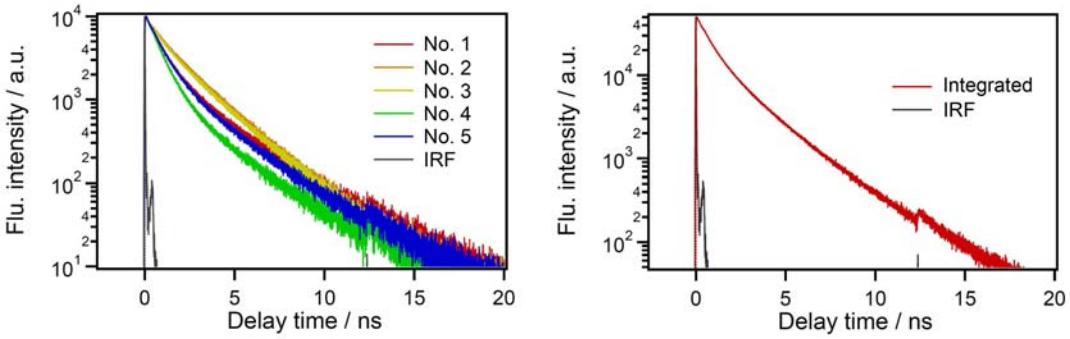


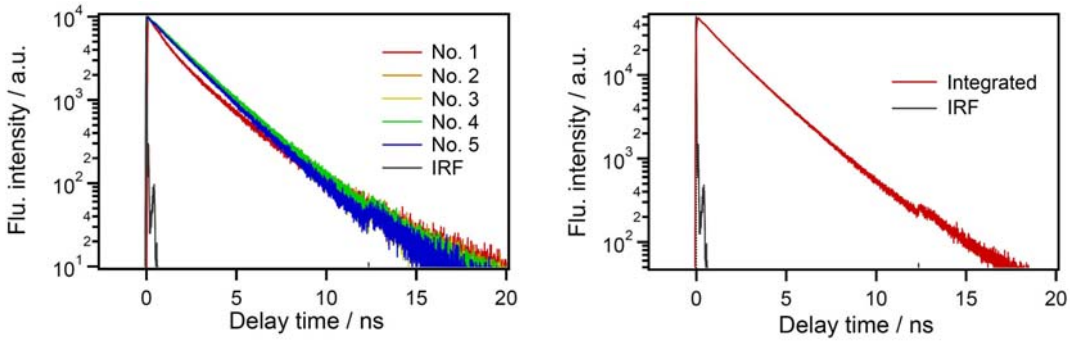
Fig. S5 Electronic transition moments for the lowest-energy excitations of (a) **1b** and (b) **2b** calculated with TD-B3LYP/6-31G(d).

(a)



	τ_1	τ_2	τ_3
No. 1	0.55 ns (50%)	0.92 ns (39%)	2.9 ns (11%)
No. 2	0.37 ns (22%)	1.3 ns (36%)	2.5 ns (42%)
No. 3	0.28 ns (17%)	0.96 ns (37%)	2.4 ns (47%)
No. 4	0.53 ns (44%)	0.87 ns (45%)	2.9 ns (11%)
No. 5	0.43 ns (33%)	0.99 ns (50%)	3.0 ns (17%)
Ave.	0.47 ns (37%)	1.2 ns (41%)	2.8 ns (22%)

(b)



	τ_1	τ_2	τ_3
No. 1	0.53 ns (32%)	1.5 ns (43%)	3.0 ns (24%)
No. 2	0.18 ns (9%)	1.4 ns (29%)	2.4 ns (62%)
No. 3	0.093 ns (9%)	1.2 ns (21%)	2.3 ns (69%)
No. 4	0.13 ns (7%)	1.3 ns (23%)	2.3 ns (70%)
No. 5	0.26 ns (8%)	1.7 ns (54%)	2.5 ns (38%)
Ave.	0.36 ns (11%)	1.6 ns (50%)	2.6 ns (39%)

Fig. S6 Fluorescence decay curves of (a) **1b** and (b) **2b** in the single-crystalline phase. The excitation wavelength was 450 nm. The fluorescence decay was monitored at 510 nm and 540 nm for **1b** and **2b**, respectively. The decay curves gave slightly different values of fluorescence lifetime depending on arbitrarily selected points (Nos. 1-5) in the crystal samples. The average values of fluorescence lifetime were determined from typical decay curves that were obtained by integrating the five decay curves.