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Supplementary Information for:

Bundle Formation of Supramolecular Fibers of Amphiphilic Diarylethene by Depletion Force

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Contents

I. Experimental Section

A. Preparation of sample

Synthesis of amphiphilic diarylethene **1** was previously reported.[S1] Methylcellulose (MC) was commercially available (Wako, Methyl Cellulose 25 (mean molecular weight, 40000; degree of polymerization, 200), Methyl Cellulose 4000 (140000; 740)).

Figs. 2 and 3: Concentrated aqueous suspensions of **1** (0.91 mg/mL) was prepared by adding pure water (5.1 mL) to a solution of **1** (5.1 mg) in acetonitrile (0.46 mL) in one portion at room temperature. A portion of the resulting suspension (ca. 5.6 mL) was diluted to 0.30 mg/mL by an appropriate amount of water: pure water (60 μL) was added to the suspension (30 μL). MC (mean molecular weight 40000) was then added to the diluted suspension (1.2 mg (1.3 wt%) or 3.8 mg (4.1 wt%)). The mixed suspension of **1** containing MC (ca. 30 μL) was placed in a glass dish (Matsunami, glass-bottom dish, thickness of the bottom glass: ca. 0.17 mm, thickness of the optical path: 1 mm) and covered by thin glass. The spherical aggregates composed of the open-ring isomer **1o** did not show clustering in the presence of MC in this condition under an optical microscope.

Figs. 5 and 6: The suspension of **1** (0.91 mg/mL) containing no MC was photoisomerized upon irradiation with UV (365 nm) light to form individual nanofibers. The purple-colored suspension of **1** (10 μL) and MC suspension (4.1 wt%, 50 μL) were mixed using a pipette and the resulting suspension (3.4 wt% of MC) was filled into the dish. Bundled fibers composed of the closed-ring isomer **1c** were observed as purple network structure.

B. Photoirradiation under microscope and observation

Optical microscopy was performed in a similar manner in our previous work.[S1] The observation of the bundled fibers was carried out using an inverted microscope (Olympus, IX73) coupled with a ZEISS AxioCam MRc CCD camera. A halogen lamp was employed for observation under transmitted path.

UV irradiation (mainly 365 nm, Figure S1a) under the microscope was performed using an epifluorescence system with a mercury lamp (Olympus, U-LH100HG with Ushio, USH-103OL, 100 W), filter set (interference filter BP360-370, dichroic mirror DM410, and interference filter BA420IF, OptoSigma), ND filters (FND-25C02-5, 5% transmittance and FND-25C02-1, 1% transmittance), polarizer (Edmund Optics, 89-602), and objective lens (Olympus, SLCPlanFI, 40×/0.55). ND filters were used to obtain the comparable intensity of light between unpolarized and polarized condition. Light intensity (I) and degree of polarization (DOP) of illuminated UV light were obtained as follows. Unpolarized light: I = 11 mW cm^{-2} and DOP = 0; x-polarized light: I = 21 mW cm^{-2} and DOP = 0.99; y-polarized light: I = 16 mW cm^{-2} and DOP = 0.96. Photoirradiation with unpolarized visible light (mainly 546 nm, I = 29 mW cm^{-2}, Figure S1b) was also carried out by

exchange a filter set (interference filter BP530-550, dichroic mirror DM570, and interference filter BA575IF, OptoSigma).

Luminescent spectra of light source for excitation were measured using a miniature fiber-optic spectrometer (Ocean Optics, S2000) with an optical fiber (diameter 600 μm). The irradiation power was measured using a laser power meter (Ophir, NOVAII) with a thermal sensor (Ophir, 3A-FS).

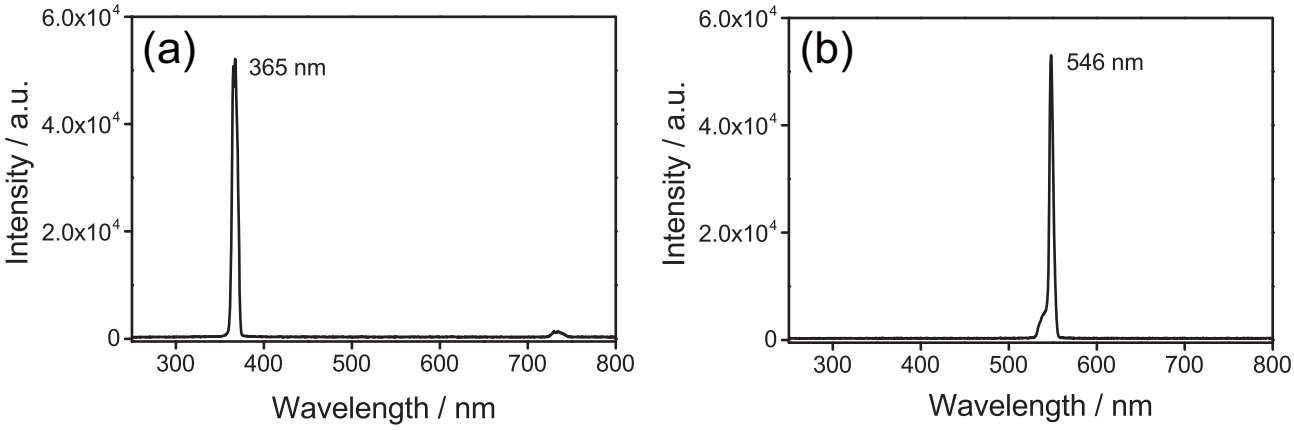

Fig. S1. Luminescent spectra of (a) UV light and (b) visible light under the optical microscope.

C. Photochromism in suspension

Photochromism of amphiphilic diarylethenes was recorded using the following instruments and conditions. UV-vis spectra were measured using a UV-vis spectrometer (Jasco, V-670). The suspension of diarylethene **1** (0.91 mg/mL, 130 μL) was added into an aqueous solution of MC (4.1 wt%, 660 μL), which was filtered in advance (Advantec, HP045AN, 0.45 μm), and the resulting suspension was added into a thin cuvette (optical path length: 1 mm) for measurement of the spectral change because the thickness of the glass cell for observation under an optical microscope was also 1 mm. For photoirradiation, a super high-pressure mercury lamp (Ushio, 500 W) was employed as a light source. The light passed through band-pass filters (ATG, UV-29 and UV360) and a monochromator (Ritsu MC-20L) was employed for irradiation with monochromatic UV (365 nm) light. Photoirradiation with visible (> 480 nm) light was carried out using filters (ATG, UV-29 and Y-48) without the monochromator.

D. DLS measurement

Particle size distributions were measured on a DLS instrument (Malvern, Zetasizer μV) equipped with a 830 nm near-infrared laser as the light source, using a fixed angle (90°) at room temperature.

Particle sizes were determined using a summation of volume-weighted size distributions. The change in viscosity caused by the photogenerated fibers and MC was not considered.

E. TEM microscopy

TEM microscopy was performed using a JEOL JEM-1400 instrument. Electron acceleration voltage was set at 80 kV. Samples on carbon-coated copper grids were prepared by air-drying an aqueous suspension of **1**. Sodium phosphotungstate was used for negative staining.

A suspension of the open-ring isomer **1o** (0.30 mg/mL, 3 μL) containing MC was dropped on the grid and allowed to stand for 20 min in a small vessel. The grid, onto which the aggregates were adsorbed, was set upside down under a slide glass (adhered with a small amount of pure water) and was irradiated for 5 min with focused UV (365 nm) light using the same setup as the observation by optical microscopy. Staining was carried out using an aqueous solution of sodium phosphotungstate and redundant supramolecular architecture was removed by washing with 2 wt% and then 0.25 wt% sodium phosphotungstate solution. The redundant solution was removed by filter paper, and then the grid was dried.

II. Additional Figures

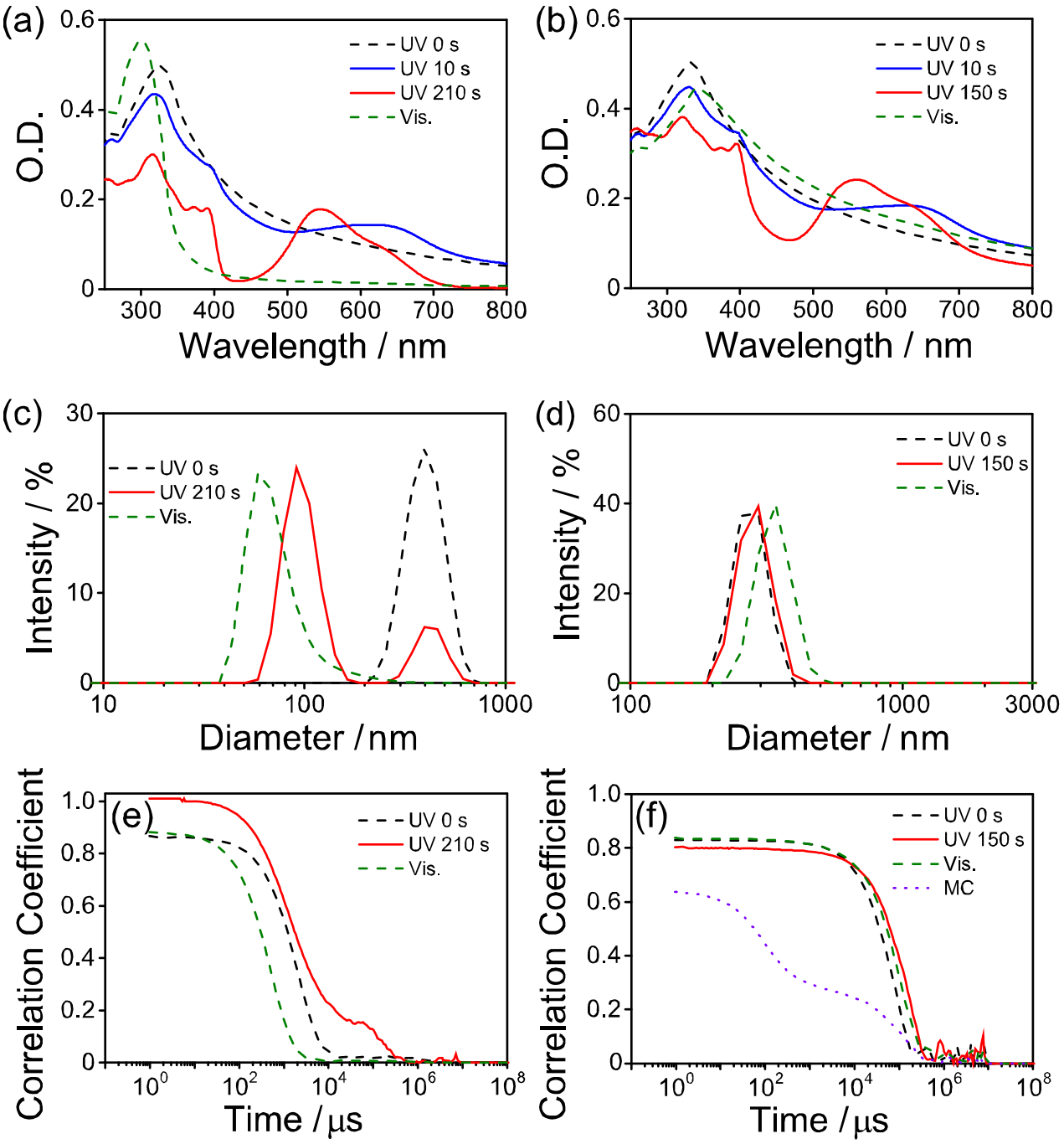

Fig. S2. (a, b) Photochromism, (c, d) change in volume size distribution, and (e, f) change in autocorrelation function of the aqueous suspension of diarylethene **1** containing no MC (0 wt%, left column) and containing MC (3.4 wt%, right column). The autocorrelation function of MC (purple dotted line) was different from the sphere and fiber. In (d), reliable data for the size change were not obtained because the viscosity of aqueous media containing MC was too high to determine the relatively small change in size shown in (c).

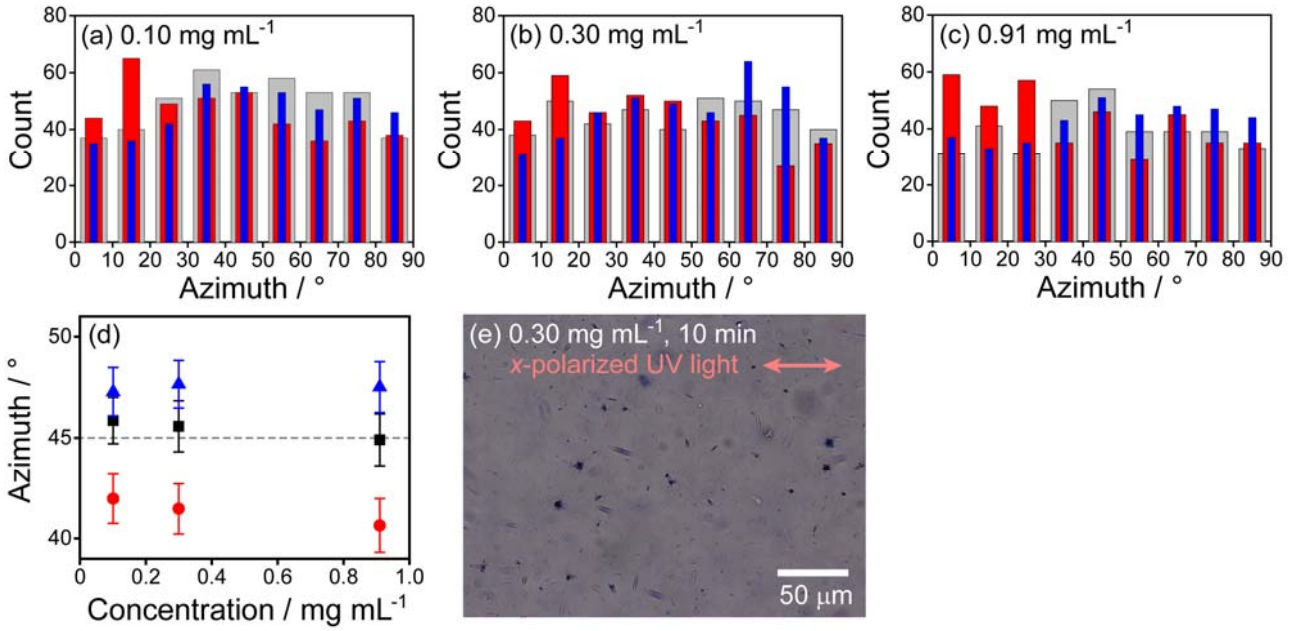

Fig. S3. Biased orientation of the bundles under various concentration of diarylethene **1** in MC aqueous solution (4.1 wt%) upon irradiation with linearly polarized UV light: (a-c) The histograms of azimuth angle: unpolarized (gray), *x*-(red), and *y*-(blue) polarized light. (d) Averaged azimuth angles: unpolarized (black), *x*-(red), and *y*-(blue) polarized light. When the bundles oriented randomly, the average azimuth becomes 45°. (e) The optical micrograph corresponding to red histogram shown in (b).

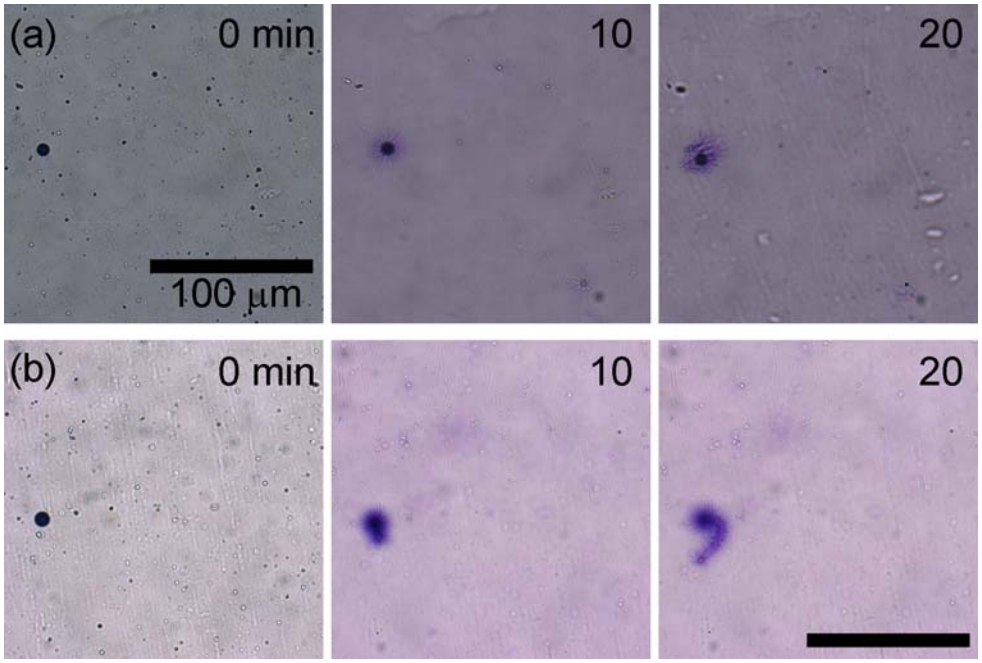

Fig. S4. The optical images of diarylethene **1** upon irradiation with UV light in 1.3 wt% aqueous suspension of MC having (a) low (4.0×10^4, corresponding to Fig. 2b) and (b) high (1.4×10^5) molecular weight. The bundles were observed only around the large spheres.

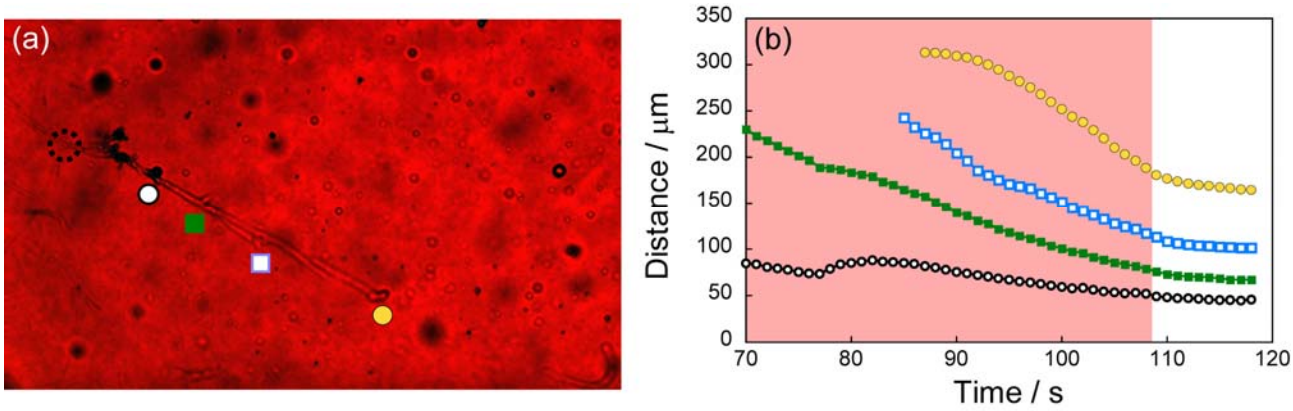

Fig. S5. Motion analysis of the shrinking of a long bundle corresponding to Fig. 6 in the main text. Specific positions having morphological feature indicated by colored circles and squares in panel (a) were used for tracking. The terminal point marked as yellow filled circle corresponds to yellow arrows in Fig. 6. Dotted circle indicates fixed point, where the bundle was crosslinked to other bundles. Panel (b) shows the change of distance between each point to the fixed point. Red region represents photoirradiation with visible (546 nm) light. Discontinuous change at 77 s was caused by partial breaking of the bundle. The shrinking speed of terminal point was calculated as 8.8 μm s^{-1} in the range from 102 to 106 s.

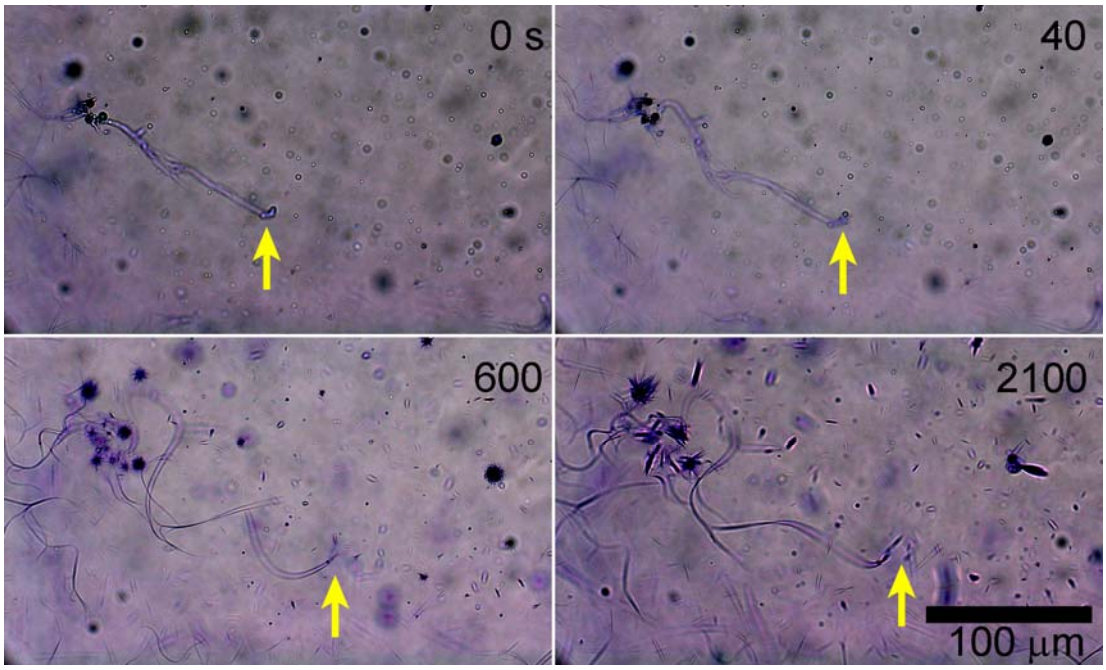

Fig. S6. Extension of the shrunk bundle corresponding to Fig. 6 in the main text upon subsequent irradiation with UV (365 nm) light for 2100 s. Yellow arrow indicates the terminal point.

III. Movie Captions

The field of view of all movies was 460 × 345 μm.

Movie S1. Formation of independent nanofibers from relatively large sphere composed of the open-ring isomer **1o** along with photocyclization reaction in aqueous suspension containing no MC (see Fig. 2a) by 100-fold speed of reproduction for 696 s.

Movie S2. Formation of bundles upon irradiation with UV light in aqueous solution of MC (1.3 wt%) (see Fig. 2b) by 100-fold speed of reproduction for 1632 s.

Movie S3. Formation of bundles upon irradiation with UV light in aqueous solution of MC (4.1 wt%) (see Fig. 2c) by 100-fold speed of reproduction for 1825 s.

Movie S4. Photogeneration of bundles from colorless small spheres and subsequent coagulation of the bundles in aqueous solution of MC (4.1 wt%) upon irradiation with UV light (see Figs. 3b and c) by 100-fold speed of reproduction for 1830 s. Yellow arrow shows the bundle formation and coagulation corresponding to Fig. 3c. The conditions for the measurement of Movies S3 and S4 are basically the same except the focus of the microscope. Movie S3 was taken to highlight the photoinduced change of the large sphere, so the focus was set at the bottom of the glass cell, but for Movie S4 the focus was set inside of the cell.

Movie S5. Coagulation and subsequent shrinking of a long bundle in aqueous solution of MC (3.4 wt%) upon irradiation with visible light (see Figs. 6 and S5) by 16-fold speed of reproduction for 118 s. The brightness was controlled for the visibility.

Movie S6. Extension of the shrunk bundle upon subsequent irradiation with UV light (see Fig. S6) by 33-fold speed of reproduction for the first 100 s (10 frames) and 330-fold speed to 2110 s.

References

S1. K. Higashiguchi, G. Taira, J.-i. Kitai, T. Hirose, K. Matsuda, *J. Am. Chem. Soc.* **2015**, *137*, 2722−2729.

S2. R. Metzler, J.-H. Jeon, A. G. Cherstvy, E. Barkai, *Phys. Chem. Chem. Phys.* **2014**, *16*, 24128–24164.

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