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Bundle Formation of Supramolecular Fibers of Amphiphilic Diarylethene by Depletion Force

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Supramolecular nanofibers composed of the closed-ring isomer of a diarylethene formed bundles in methylcellulose aqueous solution by depletion force while the spheres composed of the open-ring isomer were not coagulated. Upon irradiation with UV light to the suspension of the open-ring isomer, the fibers were found to be generated and the formed submillimeter-sized bundles showed photoinduced shrinking over than 100 μm by the visible light irradiation.

Photoresponsive compounds such as azobenzene¹ and diarylethene² are widely known as photoswitching material. Supramolecular aggregates, which are formed by noncovalent bond such as hydrophobic interaction, hydrogen bond, and π - π interaction, are often used to amplify the photochemical molecular structural change into the macroscopic morphological change.³⁻¹² Although several supramolecular architectures exhibiting photoinduced reversible morphological change have been reported until now, the sizes of these supramolecular architectures are in general from a few tens of nanometers to a few micrometers, so that the motion is too small to utilize the mechanical force. In order to realize photoinduced macroscopic motion feasible for practical use, it is necessary to develop a larger and more highly ordered supramolecular architecture.

Depletion force, acting between colloidal particles in a polymer solution, can coagulates and aligns supramolecular architectures.¹³⁻¹⁵ The force tries to maximize the overlap volume between the colloidal particles, so that fibers tend to form parallel bundles.^{15,16} On the basis of this concept, many examples have been reported on the coagulation of microtubule,¹⁷⁻²¹ metal/semiconductor nanocrystal/rod,²²⁻²⁶ and other artificial/biological entities²⁷⁻³⁰ in the presence of depletant such as methylcellulose (MC) or polyethylene glycol

(PEG). Kakugo and co-workers reported the depletion force induced collective motion of microtubules driven by kinesin in the presence of MC.²¹

We previously reported that amphiphilic diarylethene **1** forms a micrometer-sized aggregate in water and exhibits a reversible morphological change between sphere and nanofiber phases upon irradiation with UV and visible lights (Fig. 1).¹² TEM measurement revealed that the open-ring isomer forms microspheres with a bicontinuous coacervate structure, whereas the closed-ring isomer forms fibers with uniform diameter. The sphere and nanofiber phases correspond to the dehydrated high-temperature and hydrated low-temperature phases, respectively, of lower critical solution temperature (LCST) transition. Length of the nanofiber was sometimes longer than 1 μm but diameter was ca. 10 nm,¹² therefore dispersed nanofibers could not be observed under optical microscope.

In this study, anisotropic coagulation of supramolecular nanofibers composed of the closed-ring isomer of diarylethene by depletion force was investigated in MC aqueous solution.

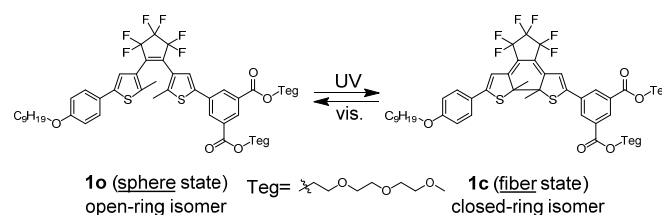


Fig. 1. Photoisomerization reaction of amphiphilic diarylethene **1** and changes in the supramolecular architectures.

An aqueous suspension of supramolecular architecture composed of diarylethene **1** containing MC was used for observation of morphological change by depletion force. The preparation was as follows: water was added to an acetonitrile solution of the open-ring isomer **1o** to give spherical supramolecular architecture whose mean diameter was estimated as 400 nm by DLS measurement (Fig. S2c in Supplementary Information(SI)), and then, subsequently MC (mean molecular weight, 4.0×10^4 ; mean degree of

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polymerization, 200) was added to the suspension. The spherical aggregates composed of **1o** did not show coagulation in this condition as shown in Fig. 2 (left column). The suspension was filled into glass cell and irradiated with UV (365 nm) and visible (546 nm) lights under an inverted microscope at room temperature.

The photoinduced morphological change with and without methylcellulose was investigated. For the microscope observation, microspheres of $> 10 \mu\text{m}$ in diameter were chosen, the sizes of which were much larger than the average (400 nm). Fig. 2a shows photoinduced morphological change when the suspension did not contain MC (0 wt%) (Movie S1). At the initial stage, the sphere had a pale blue color probably because the sample contained small amount of the closed-ring isomer owing to much larger cyclization quantum yield than the cycloreversion one as observed for similar derivatives.³¹ The nanofiber composed of the closed-ring isomer **1c** was generated from the sphere composed of **1o** upon irradiation with UV light and the nanofibers were observed as purple hazy region around the collapsed spheres as described in our previous report.¹² Fig. 2b shows growth of the fiber in the MC aqueous solution (1.3 wt%) (Movie S2). At the initial stage, coagulation of microspheres was not observed. Upon photoirradiation with UV light for 10 min, thick fibers with rod-like structure, whose size can be recognized by optical microscope, appeared around the sphere in the radial direction. The thick fibers coagulated with each other and got disordered at 20 min. The collapse of the sphere described in Fig. 2a was not observed. When the concentration of MC was high (4.1 wt%), thicker fibers were generated in the radial direction and subsequently bundled structure circumferentially surrounded the sphere (Fig. 2c, Movie S3). Due to the effect of the added MC, DLS measurement in MC aqueous solution could not provide accurate information on the size of the aggregates.

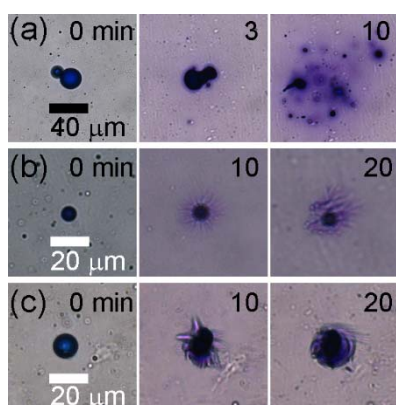


Fig. 2. The formation of bundled fibers from relatively large sphere ($> 10 \mu\text{m}$) composed of diarylethene **1** along with photocyclization reaction in (a) 0, (b) 1.3, and (c) 4.1 wt% MC aqueous solution.

When there was no MC, the aqueous suspension turned pale purple in the photostationary state (PSS) upon UV irradiation, but no structure was observed (Fig. 3a). In contrast, in the suspension with MC (4.1 wt%) in the PSS, in addition to the

generation of thick fibers around the spheres, the fibers of ca. $2 \mu\text{m}$ in diameter were found to be generated in the entire field of view (Fig. 3b, Movie S4).³² The closer look suggested that when the generated fibers came into contact, they got merged to the thicker fiber (Fig. 3c). TEM measurement suggested that the diameter of nanofiber composed of **1c** was ca. 10 nm, so that these structures were not observed by the optical microscope.¹² Meanwhile, the fibers composed of **1c** got bundled in the presence of MC, so the structure was supposed to be observed by the optical microscope.

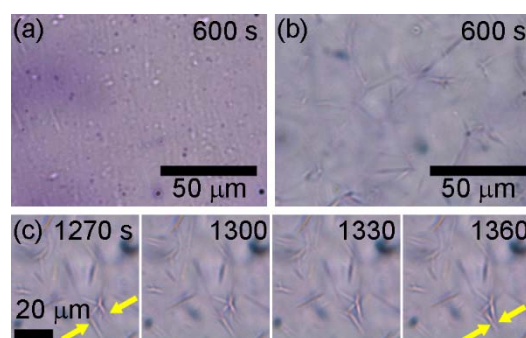


Fig. 3. The optical images at the photostationary state (365 nm) of diarylethene **1** containing (a) no MC and (b) MC (4.1 wt%). (c) The coagulation of the bundles upon continuous irradiation with UV light. Time required for the coagulation of bundles was $< 30 \text{ s}$.

When the linearly polarized light was used for UV irradiation, the bundles were oriented to parallel direction of polarized light as shown in Fig. S3 in SI. The orientation is considered to originate from the absorption anisotropy of **1c**, in a similar mechanism as the orientation of unbundled nanofibers reported in our previous work.³³

When the concentration of MC was low (1.3 wt%), the bundles were observed only around the large spheres (Fig. S4 in SI). The same result was observed when the high molecular weight (1.4×10^5) of MC aqueous solution was used.

To investigate the effect of depletion force on the molecular stacking and morphological change, the photoinduced change in color was measured. Figs. S2a and b show optical density (O.D.) spectral change upon UV irradiation in 0 and 3.4 wt% of MC solution, respectively. The behavior in pure water was reported previously, i.e., absorption band around 600 nm appeared at first and shifted to shorter wavelength (ca. 540 nm) by the formation of H-aggregate. The shift of absorption band was observed also in the case of 3.4 wt% of MC. Therefore, the H-aggregate was considered to be formed even in the presence of MC. The time required for the LCST phase transition, which was longer than the photochromism, was not affected by the presence of MC. The above result suggests that the nanofibers of ca. 10 nm in diameter composed of H-aggregate of the closed-ring isomer were formed regardless the presence of MC, and in the MC solution, the fibers got bundled by the depletion force.

By the way, the spherical aggregates composed of **1o** did not show coagulation. The difference in the assembling behavior

can be attributed to the difference in shape; the energy gain of the assembly of fibers is significantly larger than the energy gain of the assembly of spheres.¹⁴

The bundled nanofibers were observed by TEM. The samples were prepared in a similar manner to the optical observation, i.e., the suspension was placed on a TEM grid, irradiated with UV light, and dried. When the suspension did not contain MC, individual nanofibers¹² composed of **1c** were observed as shown in Fig. 4a. In contrast, thicker bundled fibers were observed when the suspension contained MC (Figs. 4b and c). The individual nanofiber of ca. 10 nm in diameter was found around the thicker fibers. The width of the individual nanofiber was the same regardless of the concentration of MC. The length of the bundles, e.g., > 3 μm in Fig. 4c, was longer than the individual nanofiber. Nanofibers with different lengths were supposed to be bundled into thicker and longer fibers.

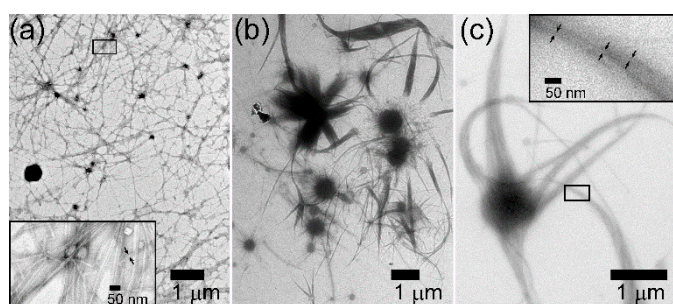


Fig. 4. TEM images of the bundles composed of diarylethene **1c** coagulated in the MC solution. (a) 0, (b) 1.3, and (c) 4.1 wt%. The samples were negatively stained. Insets show the expanded images and arrows indicate the diameter of nanofibers (ca. 10 nm). Brightness and contrast were controlled to aid visibility for the inset of (c).

The bundles got even longer by stirring the suspension. When the suspension of **1** in the PSS (365 nm) containing MC (3.4 wt%) was stirred with a pipette, the submillimeter- and millimeter-sized bundles were found as shown in Figs. 5a and b. Both length and diameter of the bundles was larger than the ones generated only by UV irradiation to the suspension containing sphere **1o** and MC (Fig. 3b). We believe that the growth of bundles was limited in the MC solution probably due to the restricted motion of the formed bundles and the restriction was removed by stirring.

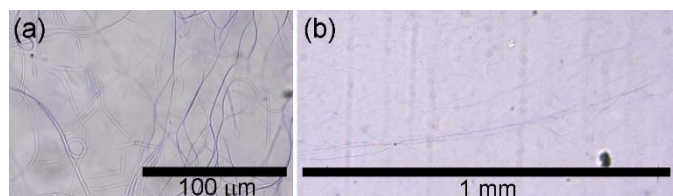


Fig. 5. The optical images of bundle prepared by stirring the suspension of diarylethene **1** in the photostationary state (365 nm) containing MC (3.4 wt%). Both images (a) and (b), which were obtained in the same sample, showed the presence of submillimeter- and millimeter-sized bundles.

The submillimeter-sized bundles got shrunk upon irradiation with visible light as shown in Fig. 6 (Movie S5). As an initial step, the initial network showed further coagulation with each other and formed a long bundle.³⁴ The formed long bundle got shrunk upon continuous irradiation with visible light. The shrinking motion was analysed as shown in Fig. S5 in SI. The length changed from >350 μm (70 s) to 170 μm (113 s). The speed of terminal point was obtained as 8.8 $\mu\text{m s}^{-1}$ under this irradiation condition (546 nm, 29 mW cm^{-2}). The shrinking continued even after stopping the irradiation probably due to relaxation of residual stress in the bundle. The shrunk bundle show deformation upon subsequent irradiation with UV light as shown in Fig. S6 in SI (Movie S6).

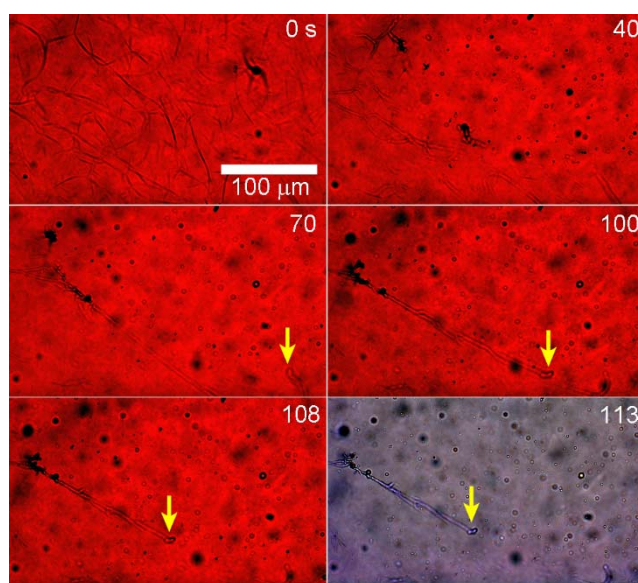


Fig. 6. Coagulation and shrinking of a long bundle upon irradiation with visible light for 108 s. The bundle had the mirror shape of alphabet "J" and its curved region was located outside of the image. Initial network was formed by the stirring shown in Fig. 5. Yellow arrow indicates the terminal point of the bundled fiber.

In conclusion, supramolecular nanofibers composed of the closed-ring isomer of amphiphilic diarylethene **1c** formed bundles of a few hundred micrometers in length by depletion force in methylcellulose aqueous solution. The spheres composed of the open-ring isomer **1o** were not coagulated with the depletant. Further growth was realized by stirring the suspension. This result showed guidelines for realizing submillimeter-sized morphological change of supramolecular architecture by depletion force.

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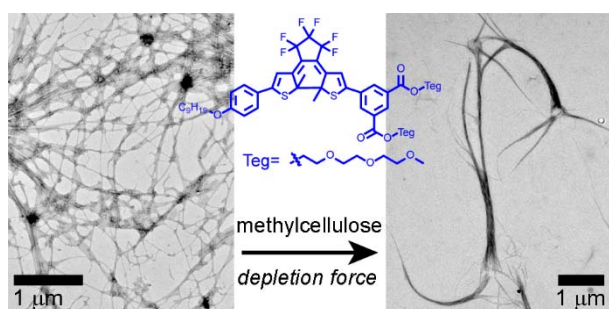
Conflicts of interest

There are no conflicts to declare.

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- 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.
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- At the initial step of visible light irradiation, the restricted motion of the formed bundles may be reduced, so that the further growth of the bundle becomes possible.

Table of contents entry



Supramolecular nanofibers composed of the closed-ring isomer of a diarylethene formed bundles in methylcellulose aqueous solution and showed photoinduced shrinking over than 100 μm by the visible light irradiation.