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ARTICLE TYPE

Macroscopic Motion of Supramolecular Assemblies Actuated by Photoisomerization of Azobenzene Derivatives

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Submillimetre size self-assemblies composed of oleate and azobenzene derivatives show forceful motions such as screw-type coiling-recoiling motion by photoirradiation.

¹⁰ In the past half century, many molecular-level machines which change their molecular structure upon exposure to stimuli have been reported.¹ Nowadays, studies on macroscopic thermal motion of soft matters received attentions from the viewpoint of biomimetics.^{2,3} Next key step for soft matters is to create a

¹⁵ material whose macroscopic motion is controlled by external stimuli.⁴ One of the strategies is to create soft materials consisting of subunits sensitive to external inputs, for instance, the photoinduced bending of polymer films consisted of azobenzene derivatives.^{5,6} Another strategy is to create soft materials in which macroscopic motions of molecular assemblies

²⁰ are actuated by small amount of molecular machines.⁷ To date, there are few reports describing macroscopic mechanical behaviour based on the latter strategy.⁸ Here, we report reversible and spatially controlled macroscopic motion of oleate

²⁵ assemblies which have submillimetre length.

Mixtures of oleic acid (**1H**) and oleate (**1**) (**Fig. 1**) are capable of self-assembly in aqueous solution. The morphology of the mixture depends on pH and ionic strength (*I*).^{9–11} In *I* = 0.1 pH 8–10 aqueous media, oleates form vesicles (**Fig. 2a**). Between pH 7

³⁰ and 8, they form several complex aggregates called “blocks” that exhibit an inverted hexagonal phase¹² (**Fig. 2b**). In the transition region, helical and straight multilayer assemblies are coexisted with vesicles and blocks.¹¹ It is considered that the shape of assembly depends on the ratio of **1H** and **1** in each assembly.

³⁵ According to the microscopic observations of shape and dynamics described in Ref. 11, the helical assemblies are sufficiently flexible to change their macroscopic helical pitch and curvature, but are also elastic because of the highly-ordered stacking structure of oleate molecules in the assembly. As

⁴⁰ demonstrated in **Fig. 3**, the helical assemblies exhibit a highly elastic response to mechanical stress. We assumed that this softness and elasticity of the self-assembly is suitable to the spatially moving material in which motion of molecular machine should be propagated.

⁴⁵ Azobenzene derivatives **2–5** (**Fig. 1**) display reversible photochromic behaviour under exposure to 366 nm UV light (*E-Z* isomerization) and 435 nm blue light (*Z-E* isomerization).¹³ Preparation of the assemblies generally involved hydration of a

mixture of 4.5 mg sodium oleate (**1Na**) and 0.45 mg (10wt%) of

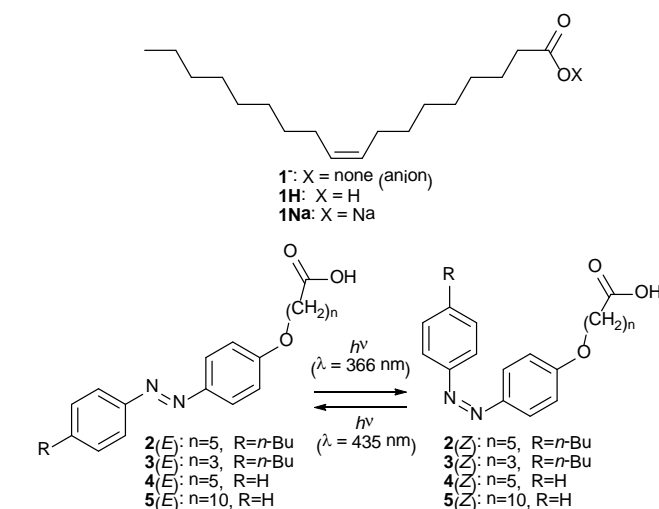


Fig. 1. Compounds and their photoisomerization.

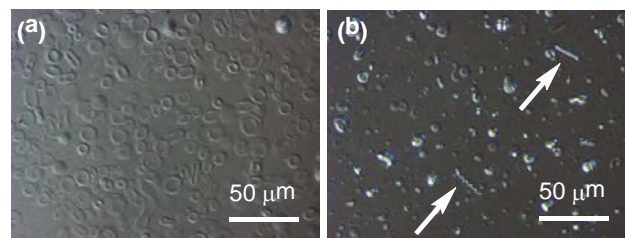


Fig. 2. Differential interference contrast (DIC) microscopic images of pH dependent oleate assemblies: (a) giant vesicles (pH 8), (b) blocks and helical structures (indicated by arrows) in pH 7.8 dispersion (0.1 M aq. NaCl).

2–5 by addition of 70 mM KH₂PO₄-K₂HPO₄ buffer solution (1.0 mL) and sonication for 20 min. A 125 μL aliquot of each suspension containing one of **2–5** was placed in a sealed microscope slide and incubated for 1 day at 25°C. All azobenzene derivatives dissolved into oleate assemblies. The pH range required for formation of helical assemblies was slightly lowered by the addition of **2–5**.¹⁴ Helical assemblies were formed when pH 7.3 buffer solution was used as the dispersing medium (the pH of the dispersion was approximately 7.5); pH values of buffer solution higher than 7.3 resulted in vesicle formation, and pH values lower than 7.3 led to the formation of

blocks.

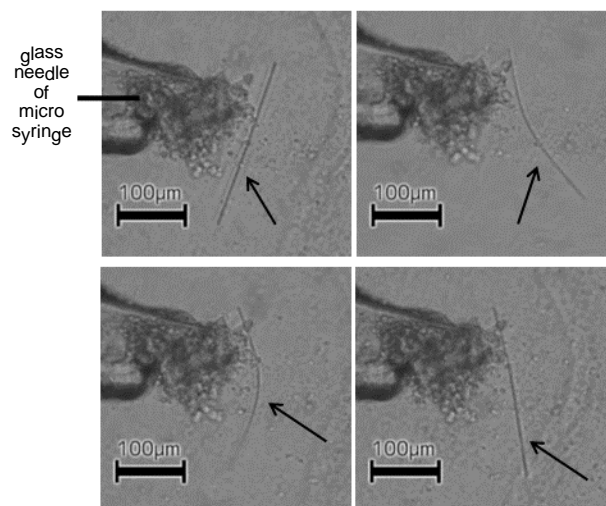


Fig. 3. Elasticity of helices responding to mechanical contact with a glass needle observed by a phase contrast microscope

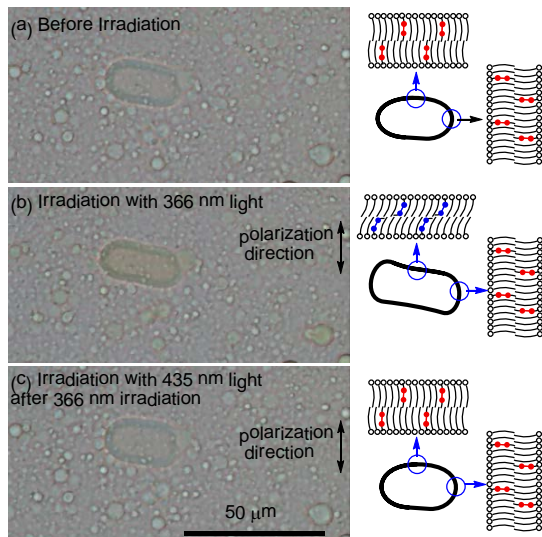


Fig. 4. Reversible deformation of giant vesicles induced by photoisomerization of azobenzene derivatives (pH 7.8) observed by DIC microscopy (**movie 1** in ESI): (left) micrographs showing ellipsoidal deformation of several vesicles; (right) schematic illustration of anisotropic deformation of vesicles induced by polarized light (red indicates *trans*-form of azobenzene, and blue indicates *cis*-form of azobenzene.). The photoisomerization of azobenzenes in the lateral sides of the vesicles is less efficient than that of azobenzenes located on the upper and lower sides of the vesicles.¹⁶

15 First we examined the effect of UV-light irradiation of the **2**-containing vesicular dispersion at pH 7.8. Irradiation with 366 nm light through an objective lens from an incident light component of a fluorescence microscope induced a slight increase in the size of vesicles. The vesicle restored to the original size by irradiation with 435 nm light. This reversible change in size is associated with the photochromic behaviour of the azobenzene derivatives. A unique change in vesicular shape was observed more distinctively when using polarized light. They deformed in an ellipsoidal manner by irradiation with light of 366 nm wavelength polarized longitudinally in **Fig. 4** and in

movie 1 contained in the Electronic Supplementary Information (ESI). Because the optical transition moment is parallel to the

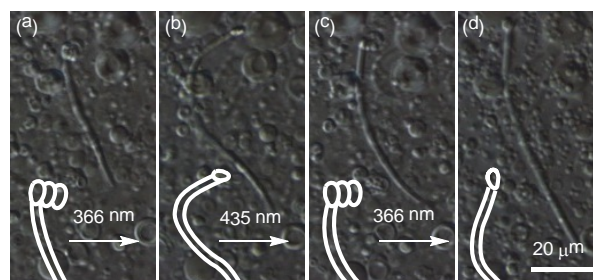


Fig. 5. DIC micrographs of reversible motion of multilayer assembly (pH 7.5) with illustrations (**movie 2** in ESI). The helical structure (top of a) was converted to a straight assembly following 366 nm irradiation (b), recoiled to a helical form following 435 nm irradiation (c), and straightened following 366 nm irradiation (d).

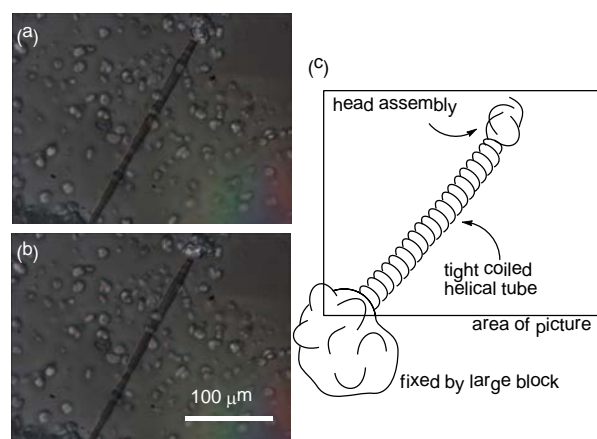


Fig. 6. Rotation motion of tightly coiled helical assembly composed of oleate and 10wt% of **3** by 366 nm irradiation (pH 7.4), observed by DIC microscopy (a) and (b), and illustration for description (c): (b) is the picture taken just after (a) under irradiation of 366 nm light. The change of the angle of the head assembly indicates the rotation of the helical assembly. The reverse rotation under irradiation of 435 nm was also observed, see **movie 3** in ESI.¹⁷

long axis of the azobenzene chromophore,¹⁵ this photoinduced deformation indicates that the azobenzene is oriented vertically against the membrane surface, and that azobenzene molecules on the upper and lower vesicular membrane surfaces absorbed light more efficiently than those on lateral surfaces (**Fig. 4**).¹⁶ Next, we examined the effect of light irradiation on the block-type aggregates containing **2**. In contrast to vesicles, the response of block-type aggregates was less intense, suggesting that the inverted hexagonal structure is difficult for propagating the structural change, compared with the lamellar structure of vesicles. Similar behaviours were observed in the assemblies containing **3–5**.

The highly ordered helical or straight multilayer assemblies containing the azobenzene derivative (**2–5**) exhibited forceful motion. Irradiation of a bold helical assemble with 366 nm light resulted in straightening of the helical assemble, and irradiation of the straightened assemble with 435 nm light re-coiled it to the helical structure (**Fig. 5** and **movie 2** in ESI). This uncoiling (straightening) and coiling motions were seen as rotation-rotation motion in tightly coiled helical assemblies (**Fig. 6** and

movie 3 in ESI).¹⁷ As far as we know, this type of macroscopic propelling motion has not been reported in artificial supramolecular chemistry.

We also observed the photoinduced macroscopic motion of oleate assemblies containing smaller amount of azobenzene derivatives (1 wt% of **2**). Unfortunately, rapidly and efficiently responded dynamics were not observed. However, interestingly, after continuous irradiation with 366 nm light for over 20 min, macroscopic motions suddenly occurred.¹⁸ Because the change was reversed by 435 nm light, it is considered that the change is not the result of thermal effect of long-term irradiation but the photoisomerization of **2**. The extended induction period after irradiation suggests that the morphological changes occur only after substantial amounts of **2** have been isomerized. In other words, some kinds of cooperation work among photoisomerized azobenzenes dispersed in oleate assembly and induce the macroscopic motion.¹⁹

The forceful motion exhibited by the helical assemblies and the presence of an induction period strongly suggest there are cooperatively propagating mechanisms such as domino effects occurring inside or at the surface of the supramolecular assemblies. We assume that the change of effective volume of azobenzene units by photoisomerization causes the propagation of expansion or contraction of inter-molecular geometry among oleate molecules. This change of effective molecular volume by light irradiation may occur and take an important role to orientation of molecules in the soft molecular assemblies, in which anisotropic molecular rotation and water diffusion takes place. We are trying to get an evidence to prove this hypothesis experimentally. The result presented here is noteworthy, since it is a demonstration that the microscopic motion of diluted small molecules can create macroscopically observable effects in supramolecular assemblies. Observed macroscopic motional mode depended on the morphology of molecular assemblies, such as vesicles, helical assemblies, and blocks. This result indicates the creation of highly organized motions is possible by designing the morphology of molecular assemblies. From these viewpoints, this work is of great importance in reference to the construction of supramolecular machinery.

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Notes and references

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† Electronic Supplementary Information (ESI) available: materials, Fig. S1 and S2, and movie1–3. See DOI: 10.1039/b000000x/

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- 12 By our preliminary microbeam small angle X-ray scattering utilized KEK PF-BL4A, hexagonal patterns and layer patterns were detected from block-type assemblies. The *d*-spacings values were depended on pH and were ranged 5.3 (pH 7.7) – 5.9 (pH 8.0) nm.
- 13 Synthesis of **2–5** and changes occurring in the UV-Vis spectra during photoisomerization of **2** are shown in ESI.
- 14 Generally, the morphology of self-assembly in aqueous media depends on the packing parameters of amphiphiles (J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1525–1568). We assumed that one of the significant reasons for the shift of pH regions for helical assemblies formation is a change of averaged packing parameter by addition of azobenzene derivatives
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- 16 The magnitude of the morphological changes was smaller when non-polarized light was irradiated, suggesting that the slower volume change of water in the interior restricts vesicular motion. The same rationale may be used to explain the inequality of response between the sides of the vesicles perpendicular and parallel to the incident light.
- 17 The experimental method was described in ESI.
- 18 We observed vesicular membrane formed from multilamellar assembly by 366 nm light (Figure S2). We could not define the induction time because it was dependent on the nature of the assemblies.
- 19 In a manner similar to the assemblies containing 1wt% azobenzene derivative, there were short induction times prior to observation of morphological transformations in assemblies containing 10wt% of **2** when exposed to weak light.

