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Expansion-contraction of photoresponsive artificial muscle regulated by host-guest interactions

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The development of stimulus-responsive polymeric materials is of great importance, especially for the development of remotely manipulated materials not in direct contact with an actuator. Here we design a photoresponsive supramolecular actuator by integrating host-guest interactions and photoswitching ability in a hydrogel. A photoresponsive supramolecular hydrogel with α -cyclodextrin as a host molecule and an azobenzene derivative as a photoresponsive guest molecule exhibits reversible macroscopic deformations in both size and shape when irradiated by ultraviolet light at 365 nm or visible light at 430 nm. The deformation of the supramolecular hydrogel depends on the incident direction. The selectivity of the incident direction allows plate-shaped hydrogels to bend in water. Irradiating with visible light immediately restores the deformed hydrogel. A light-driven supramolecular actuator with α -cyclodextrin and azobenzene stems from the formation and dissociation of an inclusion complex by ultraviolet or visible light irradiation.

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The construction of actuators, which are reminiscent of artificial muscles, is an important target in fields ranging from medicine to physics, materials science and materials engineering. One research topic to realize muscle-like movements in actuators is converting input energies (electric, thermal, charge, photo energies) into visualized movements (deformation, transformation, pressure, and so on)^{1–3}. Many attempts have been made to realize organic, inorganic, electrostrictive and piezoelectric materials^{4–7}. Polymer-based actuators (polymer gel^{8–11}, liquid crystalline elastomers^{12–23}, conjugated polymers²⁴ and carbon nanotubes^{25–28}) show reversible shape deformations in response to external stimuli. However, there are no examples of ‘artificial muscles’ in which polymeric materials are able to expand and contract owing to stimulus-responsive host–guest interactions. If such systems are realized, they can be used not only to confirm the mechanism for biological movement but also to realize ‘soft robotics’.

Previously, we have reported that stimulus-responsive supramolecular polymers are formed by mixing an aqueous solution of a host polymer containing cyclodextrin (CD) with that of a guest polymer containing azobenzene (Azo)^{29–32} or ferrocene³³. An external stimulus induces a sol–gel phase transition in these hydrogels. Formation of inclusion complexes acts as crosslink points for the polymers to yield supramolecular hydrogels, whereas decomposition of inclusion complexes yields the sol state. We hypothesized that if covalent bonds partly crosslink polymer chains, then external stimuli would induce an expansion–contraction behaviour, and not a sol–gel phase transition. However, to our knowledge, there are no reports on an external stimulus-responsive host–guest gel with expansion–contraction properties. Theoretically, the ionic strength and crosslink densities (effective network chain) have important roles in the expansion–contraction ability of hydrogels^{34,35}. Although previous papers have altered the expansion–contraction properties of hydrogels *via* ionic strengths, changing these properties using the crosslink density in a host–guest complex has yet to be reported.

We selected Azo compounds as guest molecules because the association constant of α -cyclodextrin (α CD) for *trans*-azobenzene (*trans*-Azo) is larger than that for *cis*-azobenzene (*cis*-Azo) (*trans*-Azo; $K_a = 12,000 \text{ M}^{-1}$, *cis*-Azo; $K_a = 4.1 \text{ M}^{-1}$)^{30,31}; Azo affects the photoinduced deformation and remote controllability. Herein, we report supramolecular materials with expansion and contraction abilities constructed by host–guest polymers. Using supramolecular hydrogels, which exhibit an expansion–contraction behaviour that depends on the photostimulus, we successfully prepared a photostimulus-responsive supramolecular actuator reminiscent of a natural muscle.

Results

Preparation of an expansion–contraction gel. Initially we prepared a host–guest gel (α CD–Azo gel) with α CD and Azo (Supplementary Methods). α CD–Azo gel is synthesized by radical copolymerization of a mixture of α CD-modified acrylamide (α CD–AAm), azobenzene acrylamide (Azo–AAm), methylene bisacrylamide (MBAAm) and acrylamide (AAm) in dimethyl sulphoxide (DMSO). The mole percentage contents (x) of α CD–AAm and Azo–AAm units are $x = 1–3 \text{ mol\%}$. The polymer chains in α CD–Azo gel are crosslinked with MBAAm (the mole percentage content of MBAAm: $y = 2$ and 4 mol\%). Figure 1a depicts the chemical structures of α CD–Azo gel(x, y), α CD gel(1, 2) (without the Azo–AAm unit), Azo gel(1, 2) (without the α CD–AAm unit) and AAm gel(0, 2) (without α CD–AAm and Azo–AAm units). ¹H solid state NMR (¹H magic angle spinning NMR (¹H MAS-NMR)) and infrared spectroscopy characterized the chemical

structure of α CD–Azo gels (Supplementary Figs S1 and S4), Azo gel(1, 2) (Supplementary Figs S2 and S4) and AAm gel(0, 2) (Supplementary Figs S3 and S4).

α CD–Azo gels feature three types of gels with host–guest units ($x = 1, 2$ and 3 mol\%) and crosslinking units ($y = 2$ and 4 mol\%). After gelation in DMSO, rinsing with water replaces the absorbed DMSO in the α CD–Azo gel(x, y). Figure 1b depicts the weight ratio of the gels upon substituting DMSO with water. The weight ratio of gel absorbed with DMSO is defined as 100%. Removing the absorbed DMSO significantly decreases the weight ratio of α CD–Azo gel(x, y) with an increase in the mol% of the α CD and Azo unit. As shown in Fig. 1c, substituting DMSO with water causes α CD–Azo gel($x, 4$) to contract. In addition, the weights of α CD–Azo gel(2, 2) and (3, 2) decrease, reaching 10 ± 1.1 and $7.3 \pm 4.7\%$ of the initial weight, respectively. α CD–Azo gel($x, 2$) with 2 mol% of MBAAm exhibits a greater contraction than α CD–Azo gel($x, 4$) with 4 mol% of MBAAm. On the other hand, the weight ratio of α CD gel(1, 2), Azo gel(1, 2) and AAm gel(0, 2) increase upon solvent manipulation, reaching 197 ± 11 , 179 ± 25 and $187 \pm 18\%$ of their original weights, respectively (Fig. 1b).

α CD–Azo gel(x, y) contracts upon substituting DMSO with water because host–guest complexation forms crosslinks, which was confirmed using creep rupture measurements. Supplementary Figure S5 shows the stress–strain curves of α CD–Azo gel($x, 2$) with various amounts of host–guest units. The stress of α CD–Azo gel($x, 2$) increases as α CD and the Azo units (x) increase. These results indicate that the formation of an inclusion complex between α CD and the Azo units causes α CD–Azo gels to shrink owing to the increase in crosslinks.

Expansion of α CD–Azo gel with competitive molecules. To demonstrate the complementary host–guest interaction between α CD and the Azo groups, α CD–Azo gels were immersed in aqueous solutions of competitive guest or host molecules for 12 h. We chose diol derivatives as competitive guest molecules (for example, 1,4-butane diol (C_4 diol), 1,5-pentane diol (C_5 diol), 1,6-hexane diol (C_6 diol) and 1,7-heptane diol (C_7 diol))³⁶. Flat plates of α CD–Azo gels (size: $3 \times 3 \times 2 \text{ mm}^3$) were immersed in solutions with various concentrations of competitive guests or hosts.

Figure 2a and b show the weight ratio of α CD–Azo gel(1, 2) or α CD–Azo gel(1, 4) with competitive guests or competitive hosts. In addition, we investigated the influence of the concentration of competitive molecules on the weight ratio of α CD–Azo gels. After immersion in an aqueous solution of competitive guests for 12 h, the weight ratio of the α CD–Azo gels depends on the association constant with α CD³⁶ as well as the concentration of competitive guests. When α CD–Azo gels(1, 2) are immersed in 100 and 1,000 mM of C_7 diol aq., the weight ratio of α CD–Azo gel(1, 2) after 12 h are 168 ± 6.0 and $217 \pm 9.5\%$ of the original weight ratio, respectively (Fig. 2c). The weight ratio of α CD–Azo gel(1, 2) is larger than that of α CD–Azo gel(1, 4), indicating that the smaller the crosslink ratio of α CD–Azo gels leads to the greater the change in volume. Immersing α CD–Azo gels(1, 2) in 10 and 100 mM of α CD aq. leads to a 194 ± 4.2 and $256 \pm 3.5\%$ increase in the weight ratio, respectively (Fig. 2d). The weight ratio of α CD–Azo gel(1, 2) immersed in α CD aq. is larger than those of β CD and γ CD aq. owing to the low affinities of β CD and γ CD for Azo derivatives³⁶. The expansion of α CD–Azo gels depends on the association constant of the competitive molecules with host or guest units on the polymer chains. These results indicate that α CD–Azo gels shrink in water owing to the formation of an inclusion complex between α CD and the Azo units, and then competitive molecules decompose the inclusion complexes, which function as crosslinkers, to swell α CD–Azo gels (Fig. 2e).

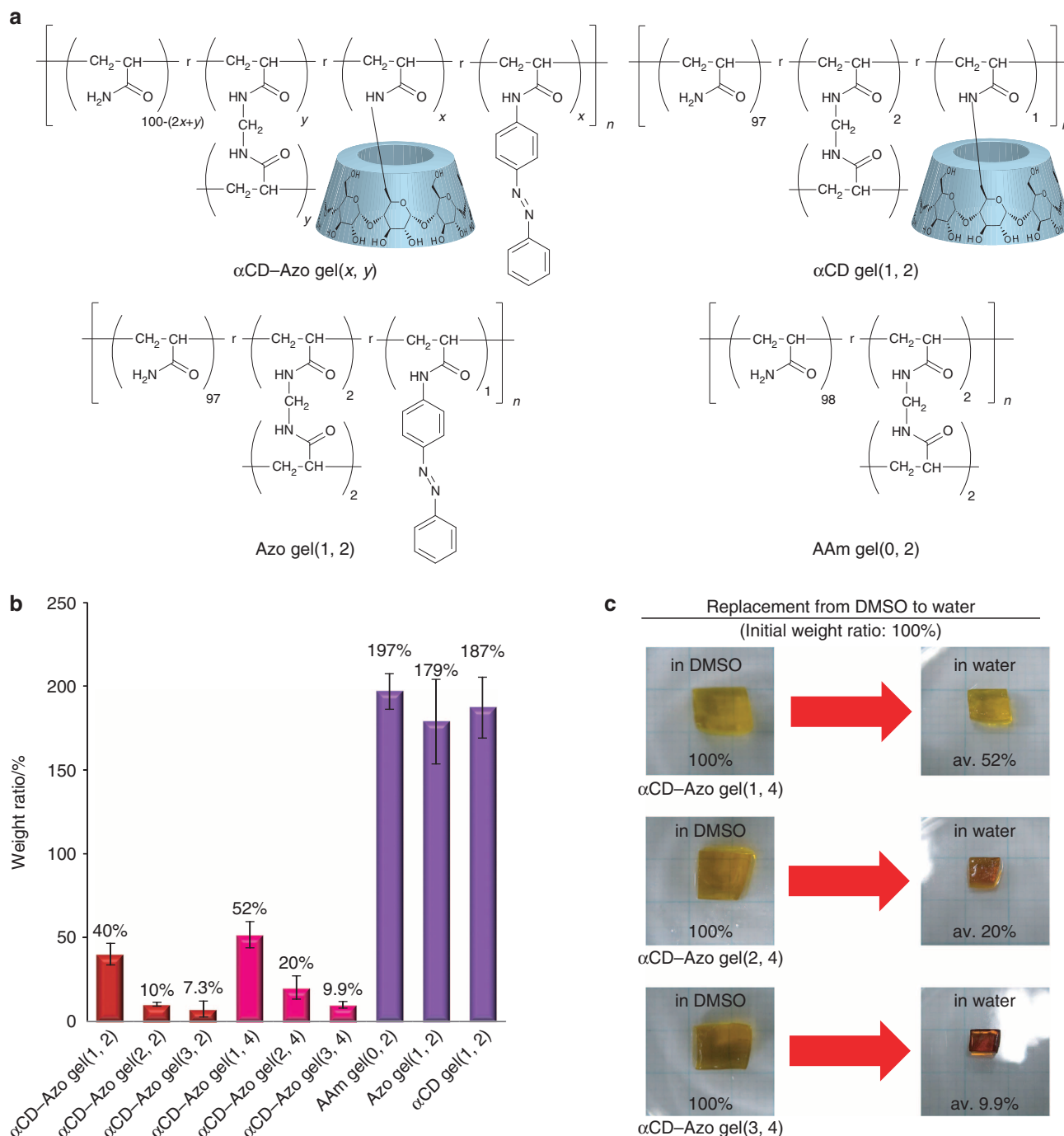


Figure 1 | Polymer gels used to prepare photoresponsive supramolecular actuators and their expansion-contraction behaviour. (a) Chemical structures of α CD-Azo gel, α CD gel (without the Azo-AAm unit), Azo gel (without the α CD-AAm unit) and AAm gel (without α CD-AAm and Azo-AAm units). x is the mole percentage of the host and guest units. y is the mole percentage of the crosslinking unit (MBAAm). **(b)** Weight ratio change in the gels upon replacing DMSO with water. Gels initially absorb DMSO. The weight ratio of gel absorbed with DMSO is defined as 100%. Error bars, standard deviation for 5 measurements. **(c)** Photographs of the volume change of α CD-Azo gel (x , 4) upon replacing DMSO with water. Av., average.

Photoresponsive volume change of α CD-Azo gels. We investigated the effects of photostimuli on the expansion-contraction behaviour of α CD-Azo gels by irradiating flat plates of α CD-Azo gels (size: $5-6 \times 5-6 \times 2-3 \text{ mm}^3$) immersed in water for an hour. Photoirradiation with ultraviolet light ($\lambda = 365 \text{ nm}$) isomerizes the *trans*-Azo group into the *cis*-Azo group, whereas the reverse occurs with visible (Vis) light ($\lambda = 430 \text{ nm}$)³⁷. Figure 3a shows the weight change of α CD-Azo gels upon ultraviolet and Vis light irradiation. The light source located above the gels had a 300W

Xenon lamp with a mirror module and band-pass filters to irradiate at a suitable wavelength. Ultraviolet irradiation of α CD-Azo gels increases the weight of the hydrogels, whereas continuous irradiation of Vis light to the α CD-Azo gels restores the initial weight and volume. These volume changes of α CD-Azo gels are correlated with the inclusion complex formation between α CD and Azo units (Fig. 3b). The association constant of α CD for *trans*-Azo is larger than that for *cis*-Azo^{30,31}. The difference in the association constants of α CD for the Azo

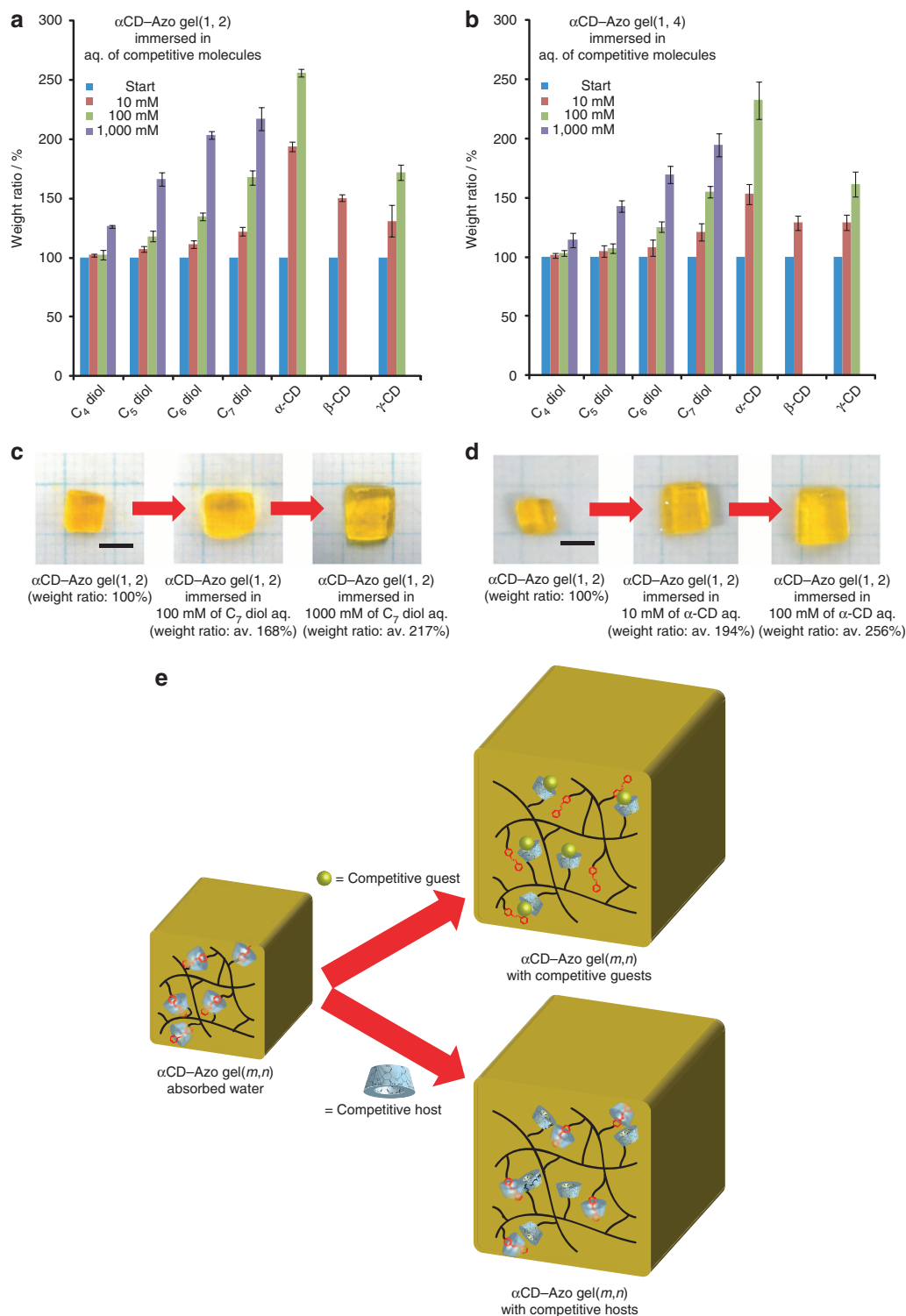


Figure 2 | Expansion of α CD-Azo gels immersed in aqueous solutions of competitive molecules. (a) Weight ratio change of the α CD-Azo gel(1, 2) immersed in aqueous solutions of competitive molecules such as 1,4-butane diol (C₄ diol), 1,5-pentane diol (C₅ diol), 1,6-hexane diol (C₆ diol), 1,7-heptane diol (C₇ diol) and competitive hosts (CDs). Concentration of competitive molecules in water was changed from 0 to 1,000 mM. Data for 1,000 mM of α CD and γ CD are not collected because they become saturated at 100 mM. Saturated concentration of β CD is 10 mM. Error bars, standard deviation for 5 measurements. (b) Weight ratio change of α CD-Azo gel(1, 4) immersed in competitive molecules. Error bars, standard deviation for 5 measurements. (c) Photographs of the volume change of α CD-Azo gel(1, 2) immersed in aqueous solutions of α -CD. Scale bar, 5mm. (d) Photographs of the volume change of α CD-Azo gel(1, 2) immersed in aqueous solutions of competitive molecules. (e) Schematic illustration of the expansion of α CD-Azo gels immersed in aqueous solutions of competitive molecules. Azo unit on the polymer chain is ejected from the α CD cavity by competitive guests. Added CDs competitively form inclusion complexes with the Azo units. Av., average.

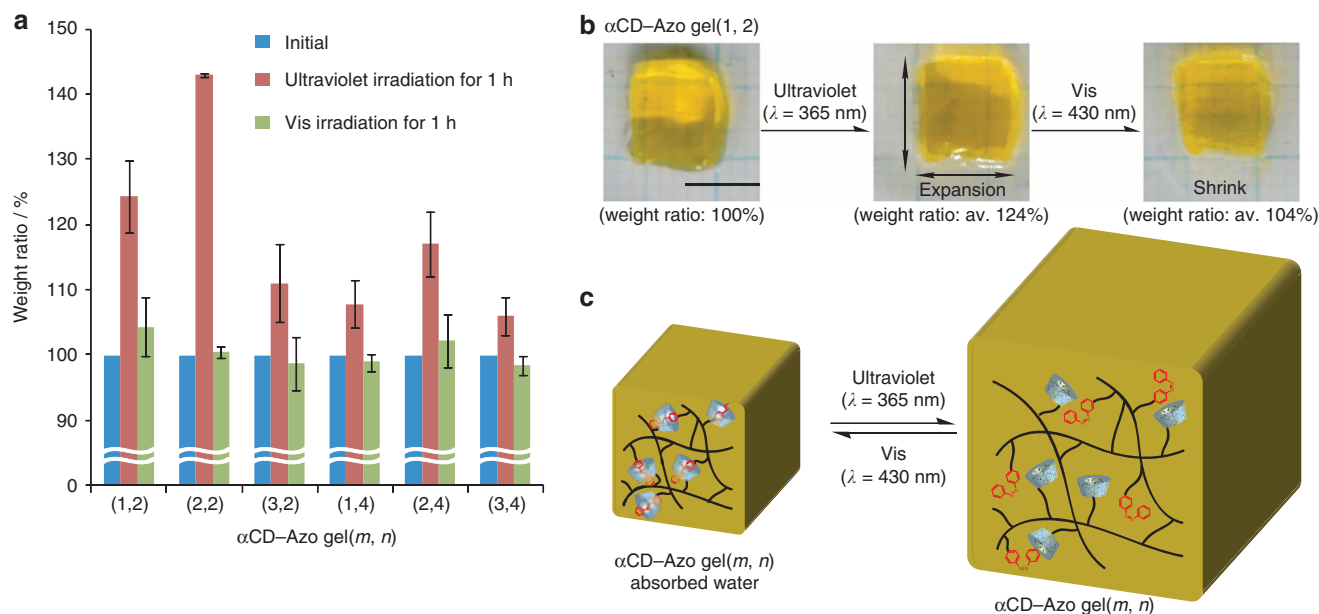


Figure 3 | Photoresponsive weight change of $\alpha\text{CD-Azo}$ gels in water. (a) Weight change of $\alpha\text{CD-Azo}$ gels before and after photoirradiation with ultraviolet light ($\lambda = 365 \text{ nm}$) and Vis light ($\lambda = 430 \text{ nm}$). Error bars, standard deviation for 5 measurements. (b) Photographs of the volume change of $\alpha\text{CD-Azo gel}(1, 2)$ irradiated by ultraviolet and Vis light. Scale bar, 5 mm. (c) Schematic illustration of the expansion-contraction of $\alpha\text{CD-Azo gel}$ irradiated by ultraviolet and Vis light. After ultraviolet irradiation, which induces isomerization from the *trans*- to *cis*-form, the complex between αCD and Azo units decomposes to expand $\alpha\text{CD-Azo}$ gels. Vis irradiation causes isomerization from the *cis*- to *trans*-form, and complexation between αCD and the Azo units regenerates, shrinking the $\alpha\text{CD-Azo gel}$. Av., average.

isomers creates the expansion-contraction behaviour in $\alpha\text{CD-Azo}$ gels upon ultraviolet and Vis light irradiation.

The weight ratio of $\alpha\text{CD-Azo gel}(x, 2)$ with 2 mol% of MBAAm is larger than that of $\alpha\text{CD-Azo gel}(x, 4)$ with 4 mol% of MBAAm, indicating that a smaller crosslinking ratio induces a larger volume change in the gel. Similarly, the weight ratio of $\alpha\text{CD-Azo gel}(2, 2)$ is larger than that of $\alpha\text{CD-Azo gel}(3, 2)$. The inside of the Azo unit of $\alpha\text{CD-Azo gel}(3, 2)$ does not isomerize from the *trans*- to *cis*-form because the concentration of the Azo group is too high to optically transmit through the opposite side, meaning ultraviolet light is absorbed on the surface of $\alpha\text{CD-Azo gel}(3, 2)$. On the other hand, the weight ratio of $\beta\text{CD-Azo gel}(1, 2)$ does not change with the irradiation because the association constants of βCD with *trans*-Azo and *cis*-Azo are comparable. These results indicate that the change in the photoresponsive volume of $\alpha\text{CD-Azo}$ gels is due to the extensive complementarity between the αCD and *trans*-Azo units.

We used ultraviolet-Vis spectroscopy (Supplementary Figs S6 and S7) to track the photoisomerization of the Azo group. As the irradiation time at $\lambda = 365 \text{ nm}$ increases, the intensity of $\pi-\pi^*$ transition band of the Azo group in $\alpha\text{CD-Azo gel}(1, 2)$ decreases and an $n-\pi^*$ transition band appears. Conversely, as the Vis irradiation time at $\lambda = 430 \text{ nm}$ increases, *cis*-Azo recovers the intensity of $\pi-\pi^*$ transition band around 350 nm and the $n-\pi^*$ transition band disappears. These results indicate that ultraviolet irradiation causes the *trans*-Azo group of the $\alpha\text{CD-Azo gel}$ to isomerize into the *cis*-form, whereas Vis irradiation causes the *cis*-Azo group to isomerize into the *trans*-form.

We characterized the *trans*- and *cis*-contents of the $\alpha\text{CD-Azo}$ gels by calculating the integral value of the Azo unit with ^1H MAS-NMR (Supplementary Fig. S8). Before ultraviolet irradiation, the isomer contents of $\alpha\text{CD-Azo gel}$ is *trans*:*cis* = 70 ± 2.2 : 30 ± 2.2 , whereas afterward, the ratio changes to *trans*:*cis* = 5 ± 1.2 : 95 ± 1.2 . However, the isomer contents recovers to *trans*:*cis* = 69 ± 0.57 : 31 ± 0.57 upon Vis light

irradiation (Supplementary Fig. S8). Consequently, the photoisomerization of the Azo unit is reversible even in the $\alpha\text{CD-Azo gel}$.

Figure 3c shows the proposed scheme for the expansion-contraction behaviour of $\alpha\text{CD-Azo}$ gels by photoirradiation. Before photoirradiation, $\alpha\text{CD-Azo}$ gels contract forcefully to form supramolecular noncovalent crosslinks between αCD and *trans*-Azo units through host-guest interactions. After ultraviolet irradiation ($\lambda = 365 \text{ nm}$), the *trans*-form isomerizes into the *cis*-form, decreasing the number of noncovalent crosslinks as the inclusion complexes between αCD and the Azo units decompose, causing the $\alpha\text{CD-Azo}$ gels to expand. However, after subsequent Vis irradiation ($\lambda = 430 \text{ nm}$) the *trans*-form recovers, increasing the number of noncovalent crosslinks and forming inclusion complexes, which causes $\alpha\text{CD-Azo}$ gels to contract. Thus, the expansion-contraction process of these supramolecular hydrogels depends on the wavelength.

Photoresponsive actuator of $\alpha\text{CD-Azo}$ gels. We prepared photoresponsive actuators using the expansion-contraction ability of $\alpha\text{CD-Azo}$ gels. Figure 4a shows a component drawing of an $\alpha\text{CD-Azo gel}$ actuator where the plate gel is $20 \times 10 \times 1-2 \text{ mm}^3$. We chose $\alpha\text{CD-Azo gel}(2, 2)$. Irradiating the plate gel with ultraviolet light ($\lambda = 365 \text{ nm}$) from the left side bends the gel to the right, whereas irradiating the bent gel with Vis light ($\lambda = 430 \text{ nm}$) from the same side for an hour restores the initial condition (Fig. 4b). Similarly, irradiating the plate gel from the right side causes the gel to bend to the left side, while irradiating with Vis light restores the initial state (Fig. 4c). This bending behaviour can be repeated for at least five cycles with varying strains. These results demonstrate that $\alpha\text{CD-Azo}$ gels bend in the opposite direction of the incident light.

In addition, we investigated the influence of irradiation time (1, 5, 10, 20, 30 and 60 min.) on the amount of the flexion angle in

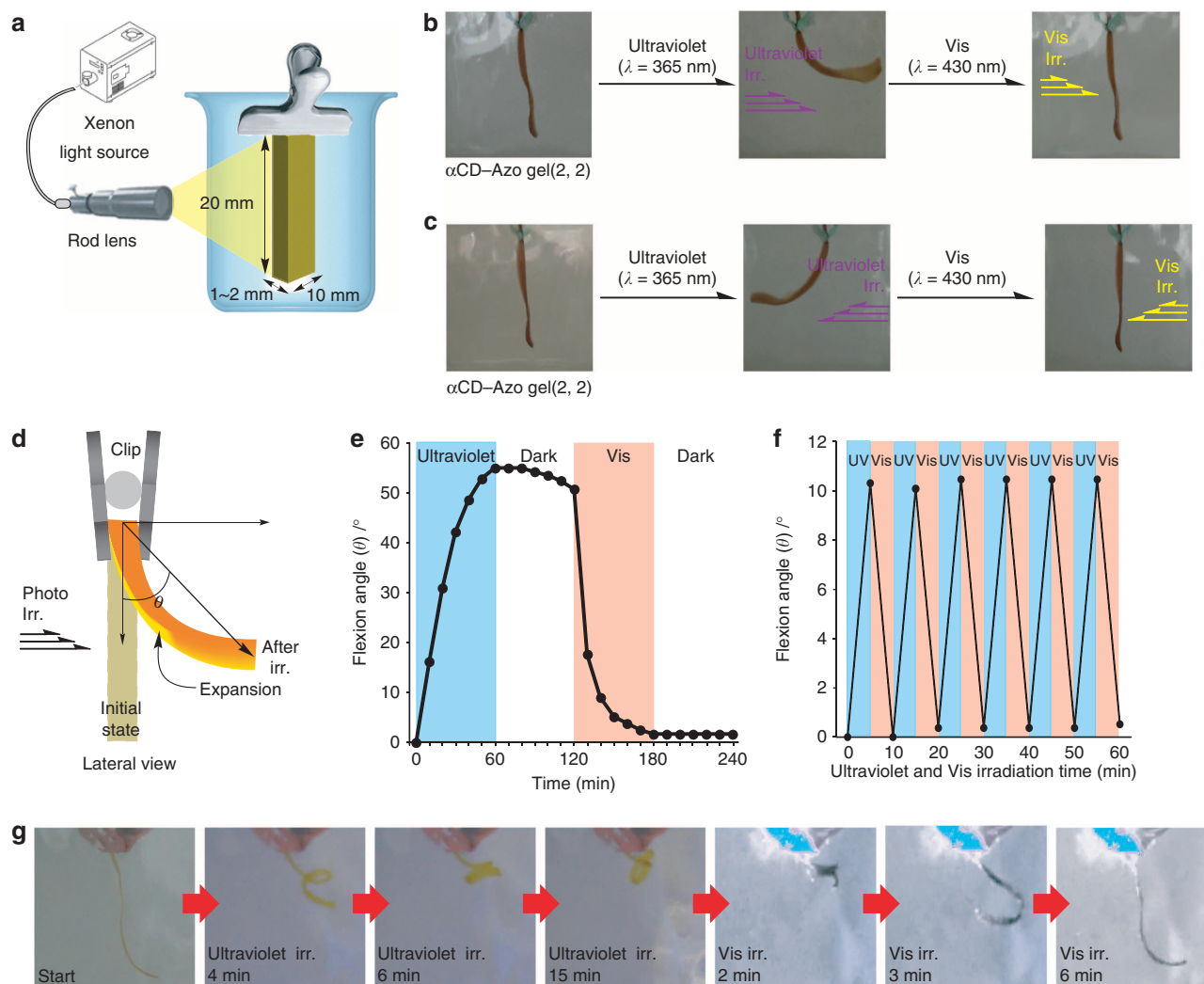


Figure 4 | Photoresponsive actuator of α CD-Azo gel in water. (a) Experimental devices and the size of α CD-Azo gel(2, 2) in water. (b) Light irradiation from the left side of α CD-Azo gel(2, 2) for an hour. After ultraviolet irradiation, α CD-Azo gel(2, 2) bends to the right side. Subsequent irradiation with Vis light restores the initial state. (c) Light irradiation from the right side of α CD-Azo gel(2, 2) for an hour. After ultraviolet irradiation, α CD-Azo gel(2, 2) bends to the left side. Subsequent irradiation with Vis light restores the initial state. (d) Lateral view of α CD-Azo gel(2, 2) hung with a clip. Flexion angle (θ) is defined here. (e) Plots of irradiation time versus the flexion angle (θ) in α CD-Azo gel(2, 2). Blue and red areas denote ultraviolet irradiation and Vis irradiation, respectively. Blank area indicates dark storage without light irradiation. Flexion angle (θ) is measured using snapshots. (f) The repeated experiment of α CD-Azo gel(2, 2) irradiated with ultraviolet and Vis lights for 5 min. Plots show the correlation between irradiation time and flexion angle (θ). (g) Light irradiation from the left side of the ribbon-shaped α CD-Azo gel(1, 2) for 15 min. After ultraviolet irradiation, α CD-Azo gel(1, 2) forms a coil. Subsequent irradiation with Vis light restores the initial state. The colour profile of pictures under Vis light irradiation is adjusted to create clear images. The actual movie is shown in Supplementary Movie 8.

α CD-Azo gel(2, 2) (Fig. 4e and Supplementary Figs S9 and S10). Figure 4d defines the flexion angle (θ), and Supplementary Movies 1–6 depict the flex behaviour of α CD-Azo gel(2, 2). Figure 4e shows the flexion angle of α CD-Azo gel(2, 2) irradiated with ultraviolet and Vis lights for an hour. The flexion angle (θ) becomes saturated after ultraviolet irradiation for about an hour, and does not significantly decrease upon standing under its own weight for an hour in the dark. Conversely, irradiation with Vis light for an hour restores the bent gel to the initial state and the flexion angle decreases. The Vis irradiation time required for the bent gel to return to a flat gel is similar to the ultraviolet irradiation time. Figure 4f and Supplementary Movie 7 show the repeated experiment of α CD-Azo gel(2, 2) irradiated with ultraviolet and Vis lights for 5 min. The gel plate clearly shows back-and-forth motion depending on the wavelength without

irradiation history. Moreover, to observe the deformation of the gel with irradiation, we prepare a ribbon-shaped α CD-Azo gel(1, 2). The ribbon-shaped gel turns to a coil by the irradiation of ultraviolet light ($\lambda = 365$ nm) from the left side (Fig. 4g and Supplementary Movie 8). The coil-shaped gel returns to the ribbon-shaped gel by Vis light irradiation. The ribbon-coil transition can be repeated at least five cycles. These results indicate that photoisomerization of the Azo group is correlated to the flex behaviour of the α CD-Azo gel plates. The plate or ribbon gels bend in the opposite direction of the incident light because the surface of the gel plate exposed to ultraviolet light expands in water, but the volume of the surface not exposed to ultraviolet light remains constant, suggesting that the strain deformation between the exposed and unexposed areas creates the flex behaviour of α CD-Azo gels.

Discussion

We successfully prepared reversible expansion–contraction supramolecular hydrogels and a supramolecular actuator-like artificial molecular muscle system consisting of α CD–Azo gel. Although microscale switching of supramolecular complexes by external stimuli is well known, achieving a macroscale mechanical change is difficult. Herein, we demonstrate that an intelligent supramolecular actuator could be formed using a main chain with a sufficient length and an adequate number of guest molecules to generate reversible crosslinks between α CD and the Azo units. Although various stimuli and functional groups can be used in responsive materials with host–guest complexes, we chose to employ external photostimuli. Photoisomerization of the Azo group alters the volume of the supramolecular hydrogel by controlling the formation of an inclusion complex. Especially, the plate- and ribbon-like gels showed the shape–memory properties controlled by photoirradiation.

Supramolecular hydrogels are important to realize ‘soft machines’ like biological systems. These stimulus-responsive expansion–contraction properties are similar to that of muscle fibrils, such as sarcomere, which consists of actin filaments. Moreover, photoresponsive materials have many general applications, including remotely controlled materials and medical devices. Currently, we aim to achieve a hydrogel system that moves faster and over a larger area. We believe that these stimulus-responsive stretching properties may eventually be used in stents and drug delivery carriers to selectively release drugs. α CD–Azo gels may realize photoresponsive embolization application, where photoresponsive α CD–Azo gels will be introduced into the vessels around a tumour using catheter techniques, and optical fibres will provide the photostimuli. It is hypothesized that the introduced gels will embolize the blood stream in arbitrary vessel positions controlled by photostimuli using optical fibres.

Methods

Materials. α -Cyclodextrin (α CD), β CD and γ CD were obtained from Junsei Chemical Co., Ltd. Acetone, methanol, triethylamine, tetrahydrofuran (THF), dimethyl sulphoxide, azobisisobutyronitrile (AIBN), N,N'-methylenebis(acrylamide) and acrylamide were obtained from Nacalai Tesque Inc. Acryloyl chloride was obtained from Wako Pure Chemical Industries, Ltd. A highly porous synthetic resin (DIAION HP-20) used for column chromatography was purchased from Mitsubishi Chemical Co., Ltd. Water used for the preparation of the aqueous solutions (except for NMR measurements) was purified with a Millipore Elix 5 system. Other reagents were used without further purification.

Measurements. ^1H NMR spectra were recorded at 500 MHz with a JEOL JNM-ECA 500 NMR spectrometer. Chemical shifts were referenced to the solvent values ($\delta = 2.49$ ppm for DMSO and $\delta = 4.79$ p.p.m. for HOD). ^1H MAS-NMR spectra were measured at 600 MHz on a VARIAN VNMRJ 600 NMR spectrometer with a sample spinning rate of 1.12–2 kHz and relaxation delay of 10 s at 30 °C. The solid-state ^1H FGMAS (Field Gradient Magic Angle Spinning) NMR spectra were recorded at 400 MHz with a JEOL JNM-ECA 400 NMR spectrometer. Sample spinning rate was 10 kHz. Chemical shifts were referenced to adamantane as an external standard ($\delta = 1.91$ ppm). The infrared spectra were measured using a JASCO FT/IR-410 spectrometer. The ultraviolet–Vis absorption spectra were recorded with a JASCO V-650 and a Hitachi U-4100 spectrometer in water with a 1-mm quartz cell at room temperature. Dynamic viscoelasticity and mechanical properties of the gel were measured using an Anton Paar MCR301 rheometer and mechanical tension testing system (Rheoner, RE-33005, Yamaden Ltd.), respectively.

Photoisomerization. Azo moieties were isomerized by photoirradiation using a 300 W Xenon lamp (Asahi spectra MAX-301) equipped with suitable mirror modules (ultraviolet mirror module, $\lambda = 250$ –385 nm; Vis mirror module, $\lambda = 385$ –740 nm) as a function of irradiation wavelength. Moreover, to extract specific wavelength, a band-pass filter (LX0365) for ultraviolet light and a band-pass filter (LX0430) for visible light were put on Xenon lamp. The intensities of transmitted ultraviolet light through the band-pass filters (LX0365) using a suitable mirror module is similar for that of Vis light ($\lambda = 430$ nm) using the band-pass filter (LX0430). The distance between the sample cell and the lamp was fixed at 10 cm.

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Author contributions

A. Harada and Y.T. conceived and directed the study, contributed to all experiments and wrote the paper. S.H., M.O., M.N. and T.K. performed syntheses, characterizations and

spectroscopic studies. A. Hashidzume and H.Y. contributed to the result discussion. A.Harada oversaw the project as well as contributed to the execution of the experiments and interpretation of the results.

Additional information

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