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

Yoshinori Takashima¹, Shogo Hatanaka¹, Miyuki Otsubo¹, Masaki Nakahata¹, Takahiro Kakuta¹, Akihito Hashidzume¹, Hiroyasu Yamaguchi¹ & Akira Harada¹

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.
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)\textsuperscript{1–3}. Many attempts have been made to realize organic, inorganic, electrostrictive and piezoelectric materials\textsuperscript{4–7}. Polymer-based actuators (polymer gels\textsuperscript{8–11}, liquid crystalline elastomers\textsuperscript{12–23}, conjugated polymers\textsuperscript{24} and carbon nanotubes\textsuperscript{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 azobenzene (Azo)\textsuperscript{29–32} or ferrocene\textsuperscript{33}. A novel host–guest gel is prepared by radical copolymerization of a mixture of guest and host molecules in dimethyl sulfoxide (DMSO). The mole percentage contents (x) of CD–AAm and Azo–AAm units are x = 1–3 mol%. The polymer chains in CD–Azo gels are crosslinked with MBAAm (the mole percentage content of MBAAm: y = 2 and 4 mol%). Figure 1a depicts the chemical structures of CD–Azo gels, which include the Azo and CD units. The Azo units cause 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 (xCD–Azo gel) with xCD and Azo (Supplementary Methods). xCD–Azo gel is synthesized by radical copolymerization of a mixture of xCD-modified acrylamide (xCD–AAm), azobenzene acrylamide (Azo–AAm), methylene bisacrylamide (MBAAm) and acrylamide (AAm) in dimethyl sulfoxide (DMSO). The mole percentage contents (x) of CD–AAm and Azo–AAm units are x = 1–3 mol%. The polymer chains in CD–Azo gels are crosslinked with MBAAm (the mole percentage content of MBAAm: y = 2 and 4 mol%). Figure 1a depicts the chemical structures of CD–Azo gel(x, y), xCD–Azo gel(1, 2) (without the Azo–AAm unit), Azo gel(1, 2) (without the CD–AAm unit) and AAm gel(0, 2) (without CD–AAm and Azo–AAm units).

\[^3\]H solid state NMR (\[^3\]H magic angle spinning NMR (\[^3\]H MAS-NMR)) and infrared spectroscopy characterized the chemical structure of xCD–Azo gels (Supplementary Figs S1 and S4), Azo gel(1, 2) (Supplementary Figs S2 and S4) and AAAm gel(0, 2) (Supplementary Figs S3 and S4).

**xCD–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 xCD–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 xCD–Azo gel(x, y) with an increase in the mole% of the xCD and Azo unit. As shown in Fig. 1c, substituting DMSO with water causes xCD–Azo gel(x, 4) to contract. In addition, the weights of xCD–Azo gel(2, 2) and (3, 2) decrease, reaching 10 ± 1.1 and 7.3 ± 4.7% of the initial weight, respectively. xCD–Azo gel(x, 2) with 2 mol% of MBAAm exhibits a greater contraction than xCD–Azo gel(x, 4) with 4 mol% of MBAAm. On the other hand, the weight ratio of xCD–Azo gel(1, 2), Azo gel(1, 2), and AAm gel(0, 2) increase upon solvent manipulation, reaching 197 ± 11, 179 ± 25 and 187 ± 18% of their original weights, respectively (Fig. 1b).

xCD–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 xCD–Azo gel(x, 2) with various amounts of host–guest units. The stress of xCD–Azo gel(x, 2) increases as xCD and the Azo units (x) increase. These results indicate that the formation of an inclusion complex between xCD and the Azo units causes xCD–Azo gels to shrink owing to the increase in crosslinks.

**Expansion of xCD–Azo gel with competitive molecules.** To demonstrate the complementary host–guest interaction between xCD and the Azo groups, xCD–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-butanediol (C\textsubscript{4} diol), 1,5-pentanediol (C\textsubscript{5} diol), 1,6-hexanediol (C\textsubscript{6} diol) and 1,7-heptanediol (C\textsubscript{7} diol))\textsuperscript{36}. Flat plates of xCD–Azo gels (size: 3 × 3 × 2 mm\textsuperscript{3}) were immersed in solutions with various concentrations of competitive guests or hosts. Figure 2a and b show the weight ratio of xCD–Azo gel(1, 2) or xCD–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 xCD–Azo gels. After immersion in an aqueous solution of competitive guests for 12 h, the weight ratio of the xCD–Azo gels depends on the association constant of xCD and the Azo units (Fig. 2c). The weight ratio of xCD–Azo gel(1, 2) is larger than that of xCD–Azo gel(1, 4), indicating that the smaller the crosslink ratio of xCD–Azo gels leads to the greater the change in volume. Immersing xCD–Azo gels(1, 2) in 10 and 100 mM of xCD aq leads to a 194 ± 4.2 and 256 ± 3.5% increase in the weight ratio, respectively (Fig. 2d). The weight ratio of xCD–Azo gel(1, 2) immersed in xCD aq is larger than those of βCD and γCD aq, owing to the low affinities of βCD and γCD for Azo derivatives\textsuperscript{36}. The expansion of xCD–Azo gels depends on the association constant of the competitive molecules with host or guest units on the polymer chains. These results indicate that xCD–Azo gels shrink in water owing to the formation of an inclusion complex between xCD and the Azo units, and then competitive molecules decompose the inclusion complexes, which function as crosslinkers, to swell xCD–Azo gels (Fig. 2e).
Photoresponsive volume change of αCD–Azo gels. We investigated the effects of photostimuli on the expansion–contraction behaviour of αCD–Azo gels by irradiating flat plates of αCD–Azo gels (size: 5–6 × 5–6 × 2–3 mm³) immersed in water for an hour. Photoirradiation with ultraviolet light (λ = 365 nm) isomerizes the trans-Azo group into the cis-Azo group, whereas the reverse occurs with visible (Vis) light (λ = 430 nm)37. Figure 3a shows the weight change of αCD–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 αCD–Azo gels increases the weight of the hydrogels, whereas continuous irradiation of Vis light to the αCD–Azo gels restores the initial weight and volume. These volume changes of αCD–Azo gels are correlated with the inclusion complex formation between αCD and Azo units (Fig. 3b). The association constant of αCD for trans-Azo is larger than that for cis-Azo30,31. The difference in the association constants of αCD for the Azo
Figure 2 | Expansion of αCD–Azo gels immersed in aqueous solutions of competitive molecules. (a) Weight ratio change of the αCD–Azo gel(1, 2) immersed in aqueous solutions of competitive molecules such as 1,4-butane diol (C₄ dio), 1,5-pentane diol (C₅ dio), 1,6-hexane diol (C₆ dio), 1,7-heptane diol (C₇ dio) and competitive hosts (CDs). Concentration of competitive molecules in water was changed from 0 to 1,000 mM. Data for 1,000 mM of αCD and γCD are not collected because they become saturated at 100 mM. Saturated concentration of βCD is 10 mM. Error bars, standard deviation for 5 measurements. (b) Weight ratio change of αCD–Azo gel(1, 4) immersed in competitive molecules. Error bars, standard deviation for 5 measurements. (c) Photographs of the volume change of αCD–Azo gel(1, 2) immersed in aqueous solutions of C₇ dio. Scale bar, 5mm. (d) Photographs of the volume change of αCD–Azo gel(1, 2) immersed in aqueous solutions of αCD. Scale bar, 5mm. (e) Schematic illustration of the expansion of αCD–Azo gels immersed in aqueous solutions of competitive molecules. Azo unit on the polymer chain is ejected from the αCD cavity by competitive guests. Added CDs competitively form inclusion complexes with the Azo units. Av., average.
isomers creates the expansion–contraction behaviour in αCD–Azo gels upon ultraviolet and Vis light irradiation.

The weight ratio of αCD–Azo gel(x, 2) with 2 mol% of MBAAm is larger than that of αCD–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 αCD–Azo gel(2, 2) is larger than that of αCD–Azo gel(3, 2). The inside of the Azo unit of αCD–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 αCD–Azo gel(3, 2). On the other hand, the weight ratio of βCD–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 αCD–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 λ = 365 nm increases, the intensity of π–π* transition band of the Azo group in αCD–Azo gel(1, 2) decreases and an n–π* transition band appears. Conversely, as the Vis irradiation time at λ = 430 nm increases, cis-Azo recovers the intensity of π–π* transition band around 350 nm and the n–π* transition band disappears. These results indicate that ultraviolet irradiation causes the trans-Azo group of the αCD–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 αCD–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 αCD–Azo gel is transcis = 70 ± 2.2:30 ± 2.2, whereas afterward, the ratio changes to transcis = 5 ± 1.2:95 ± 1.2. However, the isomer contents recovers to transcis = 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 αCD–Azo gel.

Figure 3c shows the proposed scheme for the expansion–contraction behaviour of αCD–Azo gels by photoirradiation. Before photoirradiation, αCD–Azo gels contract forcefully to form supramolecular noncovalent crosslinks between αCD and trans-Azo units through host–guest interactions. After ultraviolet irradiation (λ = 365 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 αCD–Azo gels to expand. However, after subsequent Vis irradiation (λ = 430 nm) the trans-form recovers, increasing the number of noncovalent crosslinks and forming inclusion complexes, which causes αCD–Azo gels to contract. Thus, the expansion–contraction process of these supramolecular hydrogels depends on the wavelength.

**Photoresponsive actuator of αCD–Azo gels.** We prepared photoresponsive actuators using the expansion–contraction ability of αCD–Azo gels. Figure 4a shows a component drawing of an αCD–Azo gel actuator where the plate gel is 20 × 10 × 1–2 mm³. We chose αCD–Azo gel(2, 2). Irradiating the plate gel with ultraviolet light (λ = 365 nm) from the left side bends the gel to the right, whereas irradiating the bent gel with Vis light (λ = 430 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 αCD–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...
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 CD–Azo gel(2, 2). Figure 4e shows the flexion angle of 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 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 CD–Azo gel(1, 2). The ribbon-shaped gel turns to a coil by the irradiation of ultraviolet light (λ = 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 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 CD–Azo gels.
We successfully prepared reversible expansion–contraction supramolecular hydrogels and a supramolecular actuator-like artificial molecular muscle system consisting of αCD–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 αCD 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. αCD–Azo gels may realize photoresponsive embolization application, where photoresponsive αCD–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 (αCD), βCD and γCD were obtained from Junsei Chemical Co., Ltd. Acetone, methanol, triethylamine, tetrahydrofuran (THF), dimethyl sulfoxide, azobisobutyronitrile (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 300 NMR spectrometer. Chemical shifts were referenced to the solvent values (δ = 2.49 ppm for DMSO and δ = 4.79 ppm, for HOCD). 1H MAS-NMR spectra were measured at 600 MHz on a VARIAN VNMR 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 (δ = 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 (Rheometer, 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 module and ultraviolet filter. The module was 20 cm from the lamp. αCD and γCD were dissolved in THF with a concentration of 5 mg/ml. The sample gels were irradiated with a UV light (λ = 355–470 nm) under a nitrogen atmosphere, which were immersed in a water bath. αCD gel was irradiated at a rate of 30 s. γCD gels were irradiated at 10 s. The intensity of transmitted ultraviolet light was measured through the gel.

References

1. Gandhi, M. V. & Thompson, B. S. Smart Materials and Structures (Chapman & Hall, London, 1992).
2. Marek, W. U. (ed.) Handbook of Stimuli-Responsive Materials (Wiley-VCH Verlag GmbH, 2011).
3. Minko, S. (ed.) Responsive Polymer Materials: Design and Applications (Blackwell Pub., 2006).
4. Tomatsu, I. et al. A large-area wireless power-transmission sheet using printed organic transistors and plastic MEMS switches. Nat. Mater. 6, 413–417 (2007).
5. Kobatake, S., Takami, S., Muto, H., Ishikawa, T. & Irie, M. Rapid and reversible shape changes of molecular crystals on photoradiation. Nature 446, 778–781 (2007).
6. Terasawa, F., Morimoto, M. & Irie, M. Light-driven molecular-crystal actuators: rapid and reversible bending of rodlike mixed crystals of diarylethene derivatives. Angew. Chem. Int. Ed 51, 901–904 (2012).
7. Coskun, A., Banaszak, M., Astumian, R. D., Stoddart, J. F. & Graybowski, B. A. Great expectations: can artificial molecular machines deliver on their promise? Chem. Soc. Rev. 41, 19–36 (2012).
8. Osada, Y., Okuzaki, H. & Harada, A. A polymer gel with electrically driven motility. Nature 355, 242–244 (1992).
9. Osada, Y. & Matsuda, A. Shape memory in hydrogels. Nature 376, 219 (1995).
10. Beebe, D. J. et al. Functional hydrogel structures for autonomous flow control inside microfluidic channels. Nature 404, 588–590 (2000).
11. Sidorenko, A., Krupenkin, T., Turoy, A., Fratil, P. & Aizenberg, J. Reversible switching of hydrogel-actuated nanostuctures into complex microstructures. Science 315, 487–490 (2007).
12. Ikeda, T., Mamiya, J.-I. & Yu, Y. Photomechanics of liquid-crystalline elastomers and other polymers. Angew. Chem. Int. Ed. 46, 506–528 (2007).
13. Ohm, C., Brehmer, M. & Zentel, R. Liquid crystalline elastomers as actuators and sensors. Adv. Mater. 20, 3366–3373 (2008).
14. Kumar, G. S. & Neckers, D. C. Photochemistry of azobenzene-containing polymers. Chem. Rev. 89, 1915–1925 (1989).
15. Ikeda, T. & Tsutsumi, O. Optical switching and image storage by means of azobenzene liquid-crystal films. Science 268, 1873–1875 (1995).
16. Hugel, T. et al. Single-molecule optomechanical cycle. Science 296, 1103–1106 (2002).
17. Yu, Y., Nakano, M. & Ikeda, T. Photomechanics: directed bending of a polymer film by light. Nature 425, 145 (2003).
18. Camacho-Lopez, M., Finkelman, H., Pallfy-Muhoray, P. & Shelley, M. Fast liquid-crystal elastomer swarms into the dark. Nat. Mater. 3, 307–310 (2004).
19. van Oosten, C. L., Bastiaansen, C. W. M. & Broer, D. J. Printed artificial cilia from liquid-crystal network actuators modularly driven by light. Nat. Mater. 8, 677–682 (2009).
20. Sekkat, Z., Wood, J. & Knoll, W. Reorientation mechanism of azobenzenes within the trans→cis photoisomerization. J. Phys. Chem. 99, 17226–17234 (1995).
21. White, T. J., Serak, S. V., Tabiryan, N. V., Vaiia, R. A. & Bunning, T. J. Polarization-controlled, photomechanical bending in monodomain liquid crystal elastomer cantilevers. J. Mater. Chem. 19, 1080–1085 (2009).
22. Hosono, N. et al. Large-area three-dimensional molecular ordering of a polymer brush by one-step processing. Science 330, 808–811 (2010).
23. Harris, K. D., Bastiaansen, C. W. M., Lub, J. & Broer, D. J. Self-assembled polymer films for controlled agent-driven motion. Nano Lett. 5, 1857–1860 (2005).
24. Lu, W. et al. Use of ionic liquids for π-conjugated polymer electrochemical devices. Science 297, 983–987 (2002).
25. Baughman, R. H. et al. Carbon nanotube actuators. Science 284, 1340–1344 (1999).
26. Kim, P. & Lieber, C. M. Nanotube nanowaveguides. Science 286, 2148–2150 (1999).
27. Zhang, Y. & Iijima, S. Elastic response of carbon nanotube bundles to visible light. Phys. Rev. Lett. 82, 3472–3475 (1999).
28. Spinks, G. M. et al. Pneumatic carbon nanotube actuators. Adv. Mater. 14, 1728–1732 (2002).
29. Takahshima, Y., Nakayama, T., Miyachi, M., Kawaguchi, Y., Yamaguchi, H. & Harada, A. A complex formation and gelation between copolymers containing pendant azobenzene groups and cyclodextrin polymers. Chem. Lett. 33, 890–891 (2004).
30. Tomatsu, I., Hashidzume, A. & Harada, A. Contrast visibility changes upon photoradiation for mixtures of poly(acrylic acid)-based α-cyclodextrin and azobenzene polymers. J. Am. Chem. Soc. 128, 2226–2227 (2006).
31. Tamasue, S., Takashima, Y., Yamaguchi, H., Shinkai, S. & Harada, A. Photoresponsive supramolecular hydrogels formed by cyclodextrins and azobenzene polymers. Angew. Chem. Int. Ed. 49, 7461–7464 (2010).
32. Yamaguchi, H., Kobayashi, Y., Kobayashi, R., Takashima, Y., Hashidzume, A. & Harada, A. Photoresponsive gel assembly based on molecular recognition. Nat. Commun. 3, 603 (2012).
33. Nakahata, M., Takashima, Y., Yamaguchi, H. & Harada, A. Redox-responsive self-healing materials formed from host-guest polymers. Nat. Commun. 2, 511 (2011).
Acknowledgements
We thank S. Adachi (Osaka University) for his support with the 2D-NMR experiments. This work was financially supported by the 'Core Research for Evolutional Science and Technology' programme of the Japan Science and Technology Agency, Japan.

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
Supplementary Information accompanies this paper on http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Takashima, Y. et al. Expansion–contraction of photoresponsive artificial muscle regulated by host–guest interactions. Nat. Commun. 3:1270 doi: 10.1038/ncomms2280 (2012).

This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-sa/3.0/