Azobenzene Based Photo-responsive Mechanical Actuator Fabricated by Intermolecular H-bond Interaction

Chun-Yan Yu, Jia-Hui Mu, Yun-Lei Fu, Yun-Chao Zhang, Ji-Shu Han, Rui-Yang Zhao, Jia Zhao, Zi-Hao Wang, Zhong-Cheng Zhao, Wei-Jun Li, and Fu-Sheng Liu

Abstract Photo-responsive mechanical actuator is a class of stimuli-responsive materials transferring light to mechanical energy through macroscopic transformation. To fabricate photo-responsive mechanical actuator, soft polymeric materials crosslinked with functional bridging structures are desired. Supramolecular interaction is a relatively common way to fabricate crosslinked materials due to its excellent self-assembly performance. And azobenzene and derivatives are ideal candidates of photo-responsive materials because of the unique photo-induced trans-cis isomerization. Here, a new kind of crosslinked materials based on supramolecular interaction between 4,4'-dihydroxyazobenzene and chitosan is reported. Under 355 nm irradiation, the macroscopic bending of polymeric materials occurs rapidly due to the photo-isomerization of 4,4'-dihydroxyazobenzene. Meanwhile, the photo-responsive mechanical actuator can also lift weight which is up to 200 times that of the actuator itself, and convert energy from light to mechanical work efficiently. This report suggests a new kind of photo-responsive actuator based on supramolecular interaction and may be helpful to contribute a theoretical basis to the design and synthesis of photo-responsive mechanical actuator suitable for large-scale manufacturing industrialization in future.

Keywords Photo-response; Supramolecular interaction; Mechanical actuator; Azobenzene; Energy conversion

INTRODUCTION

In recent years, biomimetic techniques have attracted intense interest with the development of materials science. In organisms, muscle as a mechanical actuator can convert ATP into energy to perform some mechanical work, such as pull, push or lift objects. Artificial mechanical actuator (AMA) is a kind of smart materials changing their own macroscopic shape by external stimulus to perform mechanical work. Compared to conventional metallic and ceramic actuators, polymeric AMA possesses some unique properties of light weight, flexibility, low cost, and quiet operation compliance. Polymeric AMA can be triggered by many kinds of stimuli, such as light, temperature, humidity, electric fields, pH and redox switching. Among these external stimuli, light is a widely used stimulus as the driving force of AMA macroscopic shape changing because of its especially attractive properties, such as easy operation, precise control, environment-friendliness, and abundance in nature. Therefore, photo-responsive AMA has been extensively investigated in recent years.

Azobenzene and its derivatives are one kind of the most widely used synthetic dyes in textile and garment dyeing. They are used in the dyeing and printing of a variety of natural and synthetic fibers, as well as the coloring of paints, plastics, rubber, etc. Meanwhile, due to the unique trans-cis photo-isomerization of azobenzene, it is also considered as one of the most classical photo-responsive candidates. As we all know, azobenzene possesses trans configuration and cis configuration because of the presence of N=N double bond, and it can be converted from trans configuration (stable state) to cis configuration (metastable state) under the irradiation of ultraviolet light with high photo-isomerization speed and photo-isomerization efficiency. It can be recovered from cis configuration to trans configuration under the stimulation of heat or visible light, and this kind of trans-cis photo-isomerization...
tion reveals great reversibility. It possesses some special properties in the process of reversible photo-isomerization between trans configuration and cis configuration, reflected in refractive index, solubility, shape, size, polarity, conductivity and so on.\[26\] Especially, the molecule size of azobenzene changes tremendously (from 0.90 nm to 0.55 nm) during trans-to-cis photo-isomerization.\[27\] So this kind of photo-responsive materials has potential applications in optical data storage,\[28−30\] molecular motors\[31−34\] and AMA.\[35−38\]

Azobenzene and its derivative as photo-responsive moieties to fabricate light-driven AMA have been investigated significantly in recent years.\[39−41\] Feng et al.\[42\] reported a cross-linked AAZO/PDAC actuator by electrostatic interaction which exhibited excellent cycling performance of photeomechanical deformation and recovery. Yu et al.\[43\] prepared a double-layer swimmer based on photoresponsive liquid crystal polymer and commercial polyimide, which exhibited rapid photoinduced bending towards the polyimide side under ultraviolet light and recovered immediately after removing the light. Yu et al.\[44\] prepared an actuator film of polymer-dispersed liquid crystal (PDLC)/graphene oxide (GO) nanocomposites, which showed great improvement of mechanic-al strength and light-responsive properties. To fabricate polymeric AMA, soft polymeric materials crosslinked with functional bridging structures are desired. The free radical polymerization is a common method for fabricating azo-AMAs, which can conduct azobenzene moiety on the side chain of crosslinked polymer.\[31,32\] Due to the mechanism of the free radical polymerization, the conventional way is unsuitable for large-scale manufacturing and even industrialization.\[45\]

EXPERIMENTAL

General Considerations

Chitosan ($M_w \sim 60 \, k$, based on viscosity, degree of deacetylation $\geq 90$%) and glacial acetic acid (99.5%) were purchased from Si-nopharm Chemical Reagent Co., Ltd. Hydrochloric acid (36.0%−38.0%), methanol (99.5%), ethanol (99.8%), dichloromethane (99.5%), petroleum ether (60−90 °C), potassium hydroxide (82.0%) and sodium hydroxide (96.0%) were purchased from Tianjin Damao Chemical Reagent Factory. All reagents were analytically grade and used without further purification.
The $^1$H-NMR spectrum was recorded on a BRUKER AVANCE spectrometer (400 MHz). UV-Vis spectra were obtained with a TU-1810 spectrometer at room temperature. FTIR spectra were recorded in the spectral range from 4000 cm$^{-1}$ to 400 cm$^{-1}$ with Thermo Nicolet 8700. SEM images were obtained on Zeiss merlin compact scanning electron microscope. The thickness of films was measured by a thickness gauge with SHOCK-PROOF. The mechanical properties were tested with a tensile speed of 10 mm·min$^{-1}$ on a Zwick Roell. The 355 nm UV light source was bought from Zhongshan Zigu Electric Appliance Factory with energy intensity of 5 mW·cm$^{-2}$. The visible light was normal domestic white LED light with energy intensity of 0.2 mW·cm$^{-2}$ without any light filter.

**Synthesis of 4,4′-Dihydroxyazobenzene**

The 4,4′-dihydroxyazobenzene was synthesized by the reduction of nitro group,[50] and its $^1$H-NMR spectrum is shown in Fig. S1 (in the electronic supplementary information, ESI).

**Preparation of 4,4′-Dihydroxyazobenzene/Chitosan Composite Films**

Chitosan (0.45 g) was added into 2% acetic acid and dissolved at 50 °C. 4,4′-Dihydroxyazobenzene (0.05 g) was dissolved in methanol to prepare the clarified solution. The two obtained solutions were mixed together, and then the mixture was placed at 5 °C to remove air bubbles for 24 h. Then the solution was poured into a round glass mold (diameter of 12 cm, height of 5 cm) and dried in 50 °C vacuum oven for 40 h. After evaporation of solution, the glass mold was immersed in NaOH solution (8 wt%) for 15 min to peel off the composite film. The obtained film was removed from the glass mold and washed with deionized water for 5 times, and then dried in a constant temperature and humidity incubator (26 °C, 25%). Then the composite film with 10 wt% of 4,4′-dihydroxyazobenzene was fabricated and marked as AzoCF-10, AzoCF-5, AzoCF-8, AzoCF-12, AzoCF-15 and PCF were prepared by the same method with different 4,4′-dihydroxyazobenzene mass fractions (5%, 8%, 12%, 15% and 0%). The AzoCF-10 was about 80 μm thick which was measured by a thickness gauge and the thickness could be controlled by the total weight of composite films as shown in Fig. S2 (in ESI).

**RESULTS AND DISCUSSION**

**Mechanical Properties of Films**

The composite films with different 4,4′-dihydroxyazobenzene mass fractions (5%, 8%, 10%, 12%, 15%) and pure chitosan film were prepared by the same method as described above and marked as AzoCF-5, AzoCF-8, AzoCF-10, AzoCF-12, AzoCF-15 and PCF, respectively. The mechanical properties of PCF and AzoCFs (80 mm × 5 mm × 0.08 mm) were tested by a tensile machine as shown in Fig. 1. It could be observed that the elongations of PCF and the five AzoCFs were 2.7%, 1.7%, 1.5%, 3.6%, 1.3% and 1.6%, corresponding to the breaking strength of 14.95, 12.30, 9.86, 21.68, 13.44, and 10.63 MPa, respectively. The AzoCF-10 performed the best tensile strength, even better than PCF. The outstanding tensile strength of AzoCF-10 could be attributed to the intermolecular hydrogen bonds between 4,4′-dihydroxyazobenzene and chitosan. AzoCF-12 and AzoCF-15 with higher concentration of 4,4′-dihydroxyazobenzene reveal-
To further prove the intermolecular hydrogen bonds between chitosan and 4,4'-dihydroxyazobenzene in AzoCF, the surface and cross section of AzoCF-10 and PCF were characterized by SEM in Fig. 3. The surface of PCF was not smooth with some obvious accumulation as shown in Fig. 3(a), and lots of small cracks in the inner structure of PCF were observed through the cross section SEM image as shown in Fig. 3(b). However, all the structural defects were improved in AzoCF-10, which can be observed through the surface and cross section SEM images of AzoCF-10 as shown in Figs. 3(c) and 3(d). The surface and inner structures were obviously improved due to the intermolecular hydrogen bonds between chitosan and 4,4'-dihydroxyazobenzene. Compared to the PCF, the composite film became more compact and smoother due to the hydrogen bonding interaction.

**UV-Vis Spectroscopic Characteristics**

The photo-isomerization property is the most important property to azobenzene derivatives for the application of AMA. Here, the UV-Vis spectroscopy was used to investigate the photo-isomerization property of 4,4'-dihydroxyazobenzene and AzoCF-10 as shown in Fig. 4. The strong peak at 360 nm in the UV-Vis spectroscopy of 4,4'-dihydroxyazobenzene THF solution was attributed to the $\pi \rightarrow \pi^*$ transition of trans configuration azobenzene in Fig. 4(a). When the solution was irradiated by 355 nm UV light, the characteristic peak of $\pi \rightarrow \pi^*$ transition reduced rapidly, which meant the trans configuration transferred to cis configuration under the UV light. When the photo-irradiation time reached to 3 s, the UV-Vis spectroscopy did not change any

![Fig. 3](image-url) SEM images of PCF and AzoCF-10: (a) surface and (b) cross section of PCF, (c) surface and (d) cross section of AzoCF-10.

![Fig. 4](image-url) UV-Vis spectra of 4,4'-dihydroxyazobenzene THF solution and AzoCF-10 film irradiated with 355 nm and visible light for different time periods: (a) 4,4'-dihydroxyazobenzene THF solution irradiated with 355 nm light, (b) 4,4'-dihydroxyazobenzene THF solution in PSS irradiated with visible light, (c) AzoCF-10 film irradiated with 355 nm light, (d) the photo-isomerization reversibility of AzoCF-10 shown by the peak value changes of AzoCF-10 at 368 nm irradiated with 355 nm light and visible light, respectively.
more, which meant that the irradiated 4,4′-dihydroxyazobenzene THF solution entered the photostationary state (PSS) and the photo-isomerization ratio was nearly 96%. Then the 4,4′-dihydroxyazobenzene THF solution was irradiated by visible light, and the peak at 360 nm in the UV-Vis spectroscopy began to enhance as shown in Fig. 4(b), and it recovered to initial state after 10 min of visible light irradiation. The $n \rightarrow n'$ transition of trans configuration azobenzene red-shifted from 360 nm to 368 nm due to the extended conjugation resulted from the H-bonds between 4,4′-dihydroxyazobenzene and chitosan as shown in Fig. 4(c). Meanwhile, the photochemistry process of AzoCF-10 was also investigated by UV-Vis spectroscopy. As the photo-irradiation time increased, the AzoCF-10 characteristic peak of $n \rightarrow n'$ transition at 368 nm reduced gradually. And after photo-irradiating for 60 s, the UV-Vis spectroscopy did not change any more, which meant the AzoCF-10 got to PSS. The photo-induced isomerization of AzoCF-10 possessed good reversibility as shown in Fig. 4(d). The significant attenuation of the absorption peak at 368 nm in UV-Vis spectroscopy was not observed in five cycles.

**Photo-induced Macroscopic Transformation of Films**

To investigate the photo-induced macroscopic transformation, AzoCFs were irradiated by 355 nm light at room temperature. All of the AzoCFs possessed good macroscopic transformation under photo-irradiation for a short time except AzoCF-5 as shown in Fig. S5 (in ESI) and Table S1 (in ESI). And AzoCF-10 possessed the best photo-induced transformation with the highest transformation speed and biggest shape variables, as shown in Fig. 5 and Video S1 (in ESI). In Fig. 5(a), the reversible time resolution transformations between initial straight state and photo-induced curving state of AzoCF-10 (45 mm × 5 mm × 0.08 mm) were recorded. The flexion angle $\theta$ of AzoCF-10 transformation was defined as the included angle between the two tangent lines $l_1$ and $l_2$ as shown in Fig. 5(b). In Fig. 5(c), the $\theta$ of AzoCF-10 was 21° under photo-irradiation for 5 s and the maximum of $\theta$ was 45° under photo-irradiation for 40 s.

![Fig. 5](https://doi.org/10.1007/s10118-021-2504-4)
conclusions could be drawn that the macroscopic transformation of AzoCF-10 performed a continuous bending ability with a certain photo-responsive speed and flexion angle. After removing the 355 nm light, the transformation of AzoCF-10 could return to its initial straight state after irradiating by visible light for 5 min or heating for 8 min at 50 °C. The reversible time resolution transformations between initial straight state and photo-induced curving state were recorded in Fig. 5(a). The AzoCF-10 film was also cut into a flower shape as shown in Scheme 1(a), and the flower-like film could possess controllable transformation between withering and blooming under 355 nm light irradiation and visible light irradiation or heating, respectively. The possible mechanism of the macroscopic transformation was that the azobenzene molecule on the top surface of AzoCF-10 transferred from trans configuration to cis configuration under the 355 nm light irradiation, meanwhile the azobenzene molecule on the bottom surface kept trans configuration instead of photo-induced isomerization due to the poor UV light penetration ability. And the different photo-induced isomerization efficiencies between the top and bottom surfaces of the composite film resulted in the different volume contractions of local space and reflected in macroscopic transformation (toward to the UV light source bending), as shown in Scheme 1(b). And the cis configuration azobenzene transferred to trans configuration under the visible light irradiation or heating, which resulted in volume expansion of local space and reflected in outside stretch of AzoCF-10 film to the initial state.

Fig. 6 shows the results of transformation testing and energy conversion of AzoCF-10 by 355 nm light stimulation. The AzoCF-10 with size of 45 mm × 5 mm × 0.08 mm was used to investigate the ability of lifting weights. A paper clip was hung at the bottom of the AzoCF-10 strip as shown in Fig. 6(a), then the strip was irradiated under 355 nm light. With the extension of irradiation time, the AzoCF-10 strip began to bend due to the trans-to-cis photo-isomerization. Finally, the flexion angle of the strip reached 15° under photo-irradiation for 60 s and the paper clip was lifted vertically upward by 2.8 mm as shown in Fig. 6(b). The weight of AzoCF-10 strip was 4.5 mg and the weight of the paper clip was 890 mg, which was nearly 200 times as heavy as the AzoCF-10 strip. Figs. 6(c) and 6(d) show the energy conversion from light to mechanical work. The mechanical work (W) produced by the AzoCF-10 strip was 24.44 μJ under UV light irradiation for 60 s, which was determined by W = mgx as shown in Fig. 6(c) (m: weight of the paper clip; g: acceleration of gravity; x: change of position). And energy-transfer efficiency from light irradiation to lifting weight was approximately 0.005%. Fig. 6(d) shows the change of weight position which the paper clip was lifted by AzoCF-10 strip versus illumination time. In comparison, AzoCF-10 possessed the optimal performance of weight-lifting and energy conversion among azobenzene based AMA materials in previous reports.[37–44]

**CONCLUSIONS**

In summary, we successfully prepared a photo-responsive actuator based on intermolecular hydrogen bonding between chitosan and 4,4′-dihydroxyazobenzene. Compared with the neat chitosan film, the tensile strength of AzoCF-10 composite film was enhanced due to the hydrogen bonding interaction. Furthermore, the obtained AzoCF-10 film possessed obvious macroscopic transformation with flexion angle of 45° under 355 nm light irradiation for 40 s. And the photo-induced transformation was highly reversible between 355 nm light and visible light irradiation. Moreover, a piece of AzoCF-10 of 4.5 mg weight was found to lift a paper clip of 890 mg which was nearly 200 times the weight of AzoCF-10. The ability to lift weight was very prominent among azobenzene based photo-responsive actuators. We believe that the simple fabrication method of photo-responsive actuator based on hydrogen bonding would contribute to the development of azobenzene based photo-responsive materials in AMA application field and even large-scale manufacturing industrialization.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2504-4.

https://doi.org/10.1007/s10118-021-2504-4
ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51703112 and 51673106), Natural Science Foundation of Shandong Province (Nos.ZR2017BEM040 and ZR2016BQ28), Open Fund of the State Key Laboratory of Luminescent Materials and Devices (No. 2017-skllmd-10, South China University of Technology), and China Postdoctoral Science Foundation (No. 2017M622152).

REFERENCES

1 Hirokawa, N. Kinesin and dynein superfamily proteins and the mechanism of organellar transport. Science 1998, 279, 519–526.
2 Vale, R.; Milligan, R. The way things move: looking under the hood of molecular motor proteins. Science 2000, 288, 88–95.
3 Majidi, C. Soft robotics: a perspective-current trends and prospects for the future. Soft Robot 2014, 1, 5–11.
4 Yamauchi, K.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H.; Harada, A. Switching between supramolecular dimer and nonthreaded supramolecular self-assembly of stilbene amide-α-cyclodextrin by photoirradiation. J. Am. Chem. Soc. 2008, 130, 5024–5035.
5 Tsuda, S.; Aso, Y.; Kaneda, T. Linear oligomers composed of a photochromically contractible and extendable Janus [2]rotaxane. Chem. Commun. 2006, 29, 3072–3074.
6 Liu, Y. Y.; Wu, W.; Wei, J.; Yu, Y. L. Visible light responsive liquid crystal polymers containing reactive moieties with good processability. ACS Appl. Mater. Interfaces 2017, 9, 782–789.
7 Stoychev, G.; Kirillova, G. Light-responsive shape-changing polymers. Adv. Opt. Mater. 2019, 7, 1–30.
8 Liu, J. Q.; Li, A. H.; Tang, J. G.; Wang, R.; Kong, N.; Davis, T. Thermoresponsive silver/polymer nanohybrids with switchable metal enhanced fluorescence. Chem. Commun. 2012, 48, 4680–4682.
9 Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai, Y.; Okano, T. Comb-type grafted hydrogels with rapid deswelling response to temperature changes. Nature 1995, 374, 240–242.
10 Hu, Z. B.; Lu, X. H.; Gao, J. Hydrogel opals. Adv. Mater. 2001, 13, 1708–1712.
11 Bowen, J.; Rose, M.; Konda, A.; Morin, S. Surface molding of microscale hydrogels with microactuation functionality. Angew. Chem. Int. Ed. 2018, 57, 1236–1240.
12 Ma, Y.; Zhang, Y. Y.; Wu, B. S.; Sun, W. P.; Li, Z. G.; Sun, J. Q. Polyelectrolyte multilayer films for building energetic walking devices. Angew. Chem. Int. Ed. 2011, 50, 6254–6257.
13 Chen, P. N.; Xu, Y. F.; He, S. S.; Sun, X. M.; Pan, S. W.; Deng, J.; Chen, D. Y.; Peng, H. S. Hierarchically arranged helical fibre actuators driven by solvents and vapours. Nat. Nanotechnol. 2015, 10, 1077–1083.
14 Palleau, E.; Morales, D.; Dickey, M.; Velev, O. Reversible patterning and actuation of hydrogels by electrically assisted iontoprinting. Nat. Commun. 2013, 4, 2257.
15 Must, I.; Kaask, F.; Poldsalu, I.; Mihkels, L.; Johanson, U.; Punning, A.; Aabloo, A. Ionic and capacitive artificial muscle for biomimetic soft robotics. Adv. Eng. Mater. 2015, 17, 84–94.
16 Wu, J.; Leung, K.; Benitez, D.; Han, J.; Cantrill, S.; Fang, L.; Stoddart, J. An acid-base-controllable [2]daisy chain. Angew. Chem. Int. Ed. 2008, 47, 7470–7474.
17 Coutrot, F.; Romuald, C.; Busseron, E. A new pH-switchable dimannosyl[2]daisy chain molecular machine. Org. Lett. 2008, 10, 3741–3744.
18 Bruns, C.; Frasconi, M.; Iehl, J.; Hartlieb, K.; Schneebeli, S.; Cheng, C.; Stupp, S.; Stoddart, J. Redox switchable daisy chain rotaxanes driven by radical-radical interactions. J. Am. Chem. Soc. 2014, 136, 4714–4723.
19 Bruns, C.; Li, J.; Frasconi, M. An electrochemically and thermally switchable donor-acceptor[2]daisy chain rotaxane. Angew. Chem. Int. Ed. 2014, 53, 1953–1958.
20 Stoychev, G.; Kirillova, A.; Ionov, L. Light-responsive shape-changing polymers. Adv. Optical. Mater. 2019, 7, 1–30.
21 Jiang, H.; Kelch, S.; Lendlein, A. Polymers move in response to light. Adv. Mater. 2006, 18, 1471–1475.
22 Habaui, D.; Zhang, H.; Zhao, Y. Light-triggered self-healing and shape-memory polymers. Chem. Sci. Rev. 2013, 42, 7244–7256.
23 Han, D.; Zhang, Y.; Ma; J.; Liu, Y.; Han, B.; Sun, H. Light-mediated manufacture and manipulation of actuators. Adv. Mater. 2016, 28, 8328–8343.
24 Bushuyev, O.; Aizawa, M.; Shishido, A.; Barrett, C. Shape-shifting azo dye polymers: towards sunlight-driven molecular devices. Macromol. Rapid Commun. 2018, 39, 1700253.
25 Jochum, F.; Theato, P. Temperature-and light-responsive smart polymer materials. Chem. Sci. Rev. 2013, 4, 7468–7483.
26 Natanson, A.; Rochon, P. Photoinduced motions in azo-containing polymers. Chem. Rev. 2002, 102, 4139–4176.
27 Wei, J.; Yu, Y. L. Photodeformable polymer gels and crosslinked liquid-crystalline polymers. Soft Matter 2012, 8, 8050–8059.
28 Liu, D.; Broer, D. Self-assembled dynamic 3D fingerprints in liquid-crystal coatings towards controllable friction and adhesion. Angew. Chem. Int. Ed. 2014, 53, 4542–4546.
29 Zhao, R. Y.; Zhan, X. P.; Yao, L.; Chen, Q. D.; Xie, Z. Q.; Ma, Y. G. Electrochemical deposition of azobenzene-containing network films with high-contrast and stable photosresponse. Macromol. Rapid Commun. 2016, 37, 610–615.
30 Zhao, R. Y.; Zhan, X. P.; Yao, L.; Sun, G. N.; Chen, Q. D.; Xie, Z. Q.; Ma, Y. G. Reversible photo-controlled mass transfer in a photo-responsive conjugated main-chain polymer film for high contrast surface patterning. Polym. Chem. 2013, 4, 5382–5386.
31 Yu, Y. L.; Nakano, M.; Ieda, T. Photomechanics: directed bending of a polymer film by light. Nature 2003, 425, 145–145.
32 Lopez, M.; Finkelmann, H.; Muhoray, P.; Shelley, M. Fast liquid-crystal elastomer swins into the dark. Nat. Mater. 2004, 3, 307–310.
33 Zeng, H.; Wasylyczk, P.; Parmeggiani, C.; Martella, D.; Burelli, M.; Wiersma, D. Light-fueled microscopic walkers. Adv. Mater. 2015, 27, 3883–3887.
34 Ichimura, K.; Oh, S.; Nakagawa, M. Light-driven motion of liquids on a photoresponsive surface. Science 2000, 288, 1624–1626.
35 Yu, H.; Ieda, T. Photocontrollable liquid-crystalline actuators. Adv. Mater. 2011, 23, 2149–2180.
36 Qin, C.; Feng, Y.; Luo, W.; Cao, B.; Hu, W.; Feng, W. A supramolecular assembly of cross-linked azobenzene/polymers for a high-performance light-driven actuator. J. Mater. Chem. A 2015, 3, 16453–16460.
37 Ikejiri, S.; Takashima, Y.; Osaki, M.; Yamaguchi, H.; Harada, A. Solvent-free photoresponsive artificial muscles rapidly driven by molecular machines. J. Am. Chem. Soc. 2018, 140, 17308–17315.
38 Takashima, Y.; Hayashi, Y.; Osaki, M.; Kaneko, F.; Yamaguchi, H.; Harada, A. A photoresponsive polymeric actuator topologically cross-linked by movable units based on a [2]rotaxane. Macromolecules 2018, 51, 4688–4693.
39 Mauro, M. Gel-based soft actuators driven by light. J. Mater. Chem. B 2019, 7, 4234–4242.
40 Iwase, K.; Takashima, Y.; Harada, A. Fast response dry-type
artificial molecular muscles with [c2]daisy chains. Nat. Chem. 2016, 8, 625–632.
41 Iamsaard, S.; Abhoff, S.; Matt, B.; Kudernac, T.; Cornelissen, J.; Fletcher, S.; Katsonis, N. Conversion of light into macroscopic helical motion. Nat. Chem. 2014, 6, 229–235.
42 Qin, C. Q.; Feng, Y. Y.; Luo, W.; Cao, C.; Hu, W. P.; Feng, W. A supramolecular assembly of cross-linked azobenzene/polymers for a high-performance light-driven actuator. J. Mater. Chem. A 2015, 3, 16453–16460.
43 Ma, S. D.; Li, X.; Huang, S.; Hu, J.; Yu, H. F. A Light-activated polymer composite enables on-demand photocontrol of biomimetic swimming towards transportation at liquid/air interface. Angew. Chem. Int. Ed. 2019, 58, 2655–2659.
44 Cheng, Z. X.; Wang, T. J.; Li, X.; Zhang, Y. H.; Yu, H. F. NIR-Vis-UV light-responsive actuator films of polymer-dispersed liquid crystal/graphene oxide nanocomposites. ACS Appl. Mater. Interfaces 2015, 7, 27494–27501.
45 Lv, J. A.; Wang, W.; Wu, W.; Yu, Y. L. A reactive azobenzene liquid-crystalline block copolymer as a promising material for practical application of light-driven soft actuators. J. Mater. Chem. C 2015, 3, 6621–6626.
46 Pang, X. L.; Xu, B.; Qing, X.; Wei, J.; Yu, Y. L. Photo-induced bending behavior of post-crosslinked liquid crystalline polymer/polyurethane blend films. Macromol. Rapid Commun. 2018, 39, 1700237.
47 Petr, M.; Katzman, B.; DiNatale, W.; Hammond, P. Synthesis of a new, low-Tg siloxane thermoplastic elastomer with a functionalizable backbone and its use as a rapid room temperature photoactuator. Macromolecules 2013, 46, 2823–2832.
48 Lahikainen, M.; Zeng, H.; Priimagi, A. Reconfigurable photoactuator through synergistic use of photochemical and photothermal effects. Nat. Commun. 2018, 9, 1.
49 Lu, X. L.; Zhang, H.; Fei, G. X.; Yu, B.; Tong, X.; Xia, H. S.; Zhao, Y. Liquid-crystalline dynamic networks doped with gold nanorods showing enhanced photocontrol of actuation. Adv. Mater. 2018, 30, 1706597.
50 Xiao, R. Q.; Zhou, L. P.; Dong, Z. Y.; Gao, Y. Z.; Liu, J. Q. A photo-responsive catalytic vesicle with GPx activity. Chinese J. Chem. 2014, 32, 37–43.
51 Babu, R. R.; Kumaresan, S.; Vijayan, N.; Gunasekaran, M.; Gopalakrishnan, R.; Kannan, P.; Ramasamy, P. Growth of 4,4’-dihydroxyazobenzene (DHAB) and its characterization. J. Cryst. Growth 2003, 256, 387–392.