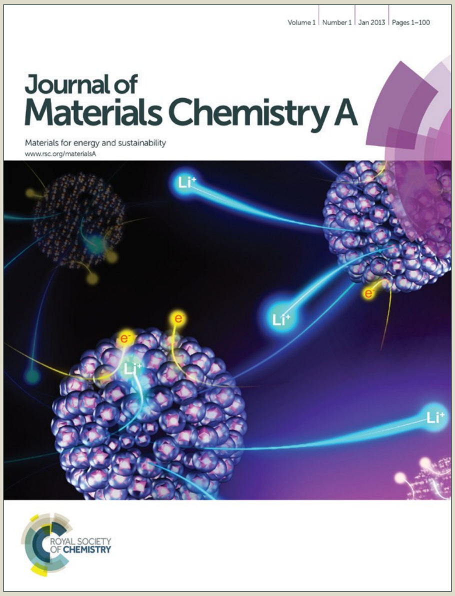
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

Journal of

Materials Chemistry A

RSCPublishing

ARTICLE

A Supramolecular Assembly of Cross-Linked Azobenzene/Polymers for a High-Performance Light-Driven Actuator

Cite this: DOI: 10.1039/x0xx00000x

Received 00th February 2015,
Accepted 00th xxxxxxxx 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Chengqun Qin,[a] Yiyu Feng,[a] Wen Luo,[a] Chen Cao,[a] Wenping Hu[b] and Wei Feng*[a]

A light-driven flexible actuator based on a photo-responsive polymer draws much interests due to its great ability for rapid and reversible light-to-work transduction based on a large deformation. An azobenzene chromophore with disulfonic groups (AAZO) was uncovalently grafted on the side-chain of a cationic polymer, poly(diallyldimethylammonium chloride) (PDAC), by electrostatic interaction with a specific weigh ratio. A supramolecular assembly of cross-linked AAZO/PDAC showed a reversible isomerization irradiated by UV light followed by the reversion with a good cycling stability for 50 cycles. Light-driven actuators based on AAZO/PDAC film exhibited a large deformation by rolling-up into a tube with double walls even when the light is off, along with a spontaneous shape recovery. This photomechanical deformation arose from different rates and degrees of the structure transformation of AAZO/PDAC between the front (facing UV light) and back side with the segment motion of polymers.

Introduction

Polymer-based actuators, capable of converting energies (electricity, heat, light) into mechanical stress output through the deformation based on the structural transformation, have drawn significant interests due to their reversibility, flexibility and stimuli-responsive properties.[1-5] Of particular is a light-driven polymer-based actuator, of which the output power can be controlled rapidly, remotely and wirelessly by regulating the intensity and wavelength of the incident light. Thus, various photo-responsive molecules have been employed to coupled with polymers for light-to-work transduction.[6-10] Azobenzene (AZO), a classic photochromic motif, has been widely used as a unique photo-responsive core for light-driven molecular actuators because of its tunable photo-sensitivity, reversible transformation and steric configuration.[11-15] Generally, upon the irradiation with UV light, AZO is able to change the shape from the rod-like *trans*-state to the bent *cis*-state, which is accompanied by the change in the molecular axis from 9 Å to 5.5 Å.[16] Thus, this light-induced transformation of AZO in the polymer matrix leads to a macroscopic deformation of the AZO/polymer by controlling the alignment of the polymer segment. Moreover, an AZO/polymer film shows a large deformation based on the transformation of steric configuration under the irradiation of a low-energy light, which is strong enough to induce the isomerization (2-3 kcal/mol) based on a large absorption coefficient of AZO.[6] Hence, the light-driven actuator using AZO/polymer shows a great potential for the application in artificial muscles, all-optical switches, optical micro-tweezers and solid photonic devices.[7,12,13]

The light-induced deformation of the AZO/polymers highly depends on their polymeric architectures at different levels. A variety of polymeric architectures including the main-chain, side-chain polymers, cross-linked networks and block copolymers has been designed and prepared for the light-to-work transduction with the covalent or uncovalent linkage between AZO and polymers.[17,18] In the past decades, crosslinked liquid crystal (LC)-polymers that possess both the order of LCs and the elasticity of polymer networks have been used for a basic polymer network or scaffold for AZO.[19-22] AZO-functionalized LC (AZO/LC) polymer films exhibit the light-induced three-dimensional (3D) deformation. Yu *et al.*[12] reported that the film of the AZO/LC network showed a substantial macroscopic volume contraction at the surface upon the exposure of light, resulting in striking bending properties due to the subtle reduction in microscopic size and ordering of the liquid-crystal components. This photomechanical effect is essentially important for the development of the high-speed light-driven actuator for microscale or nanoscale applications. Furthermore, this conversion from light to mechanical output has also been obtained in polymer networks covalently attached

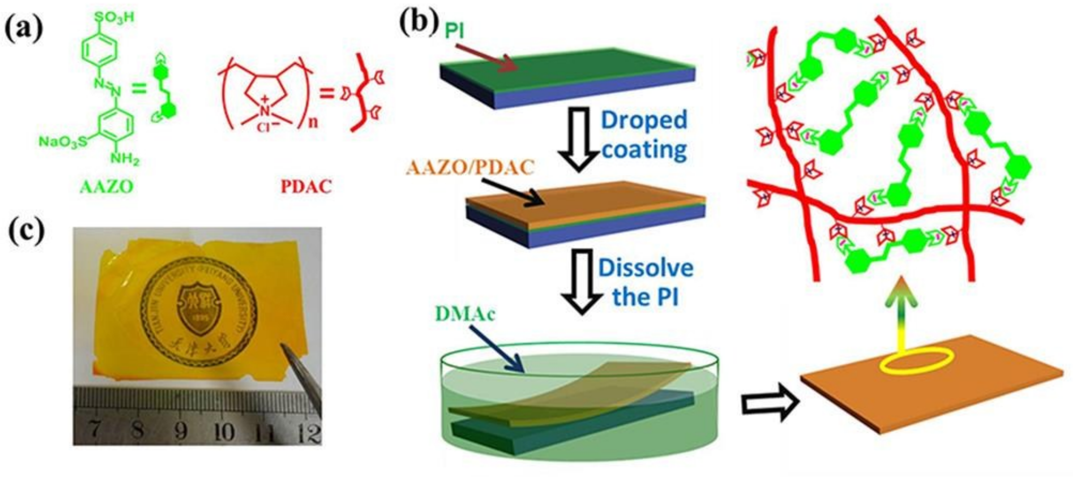


Fig. 1 (a) Chemical structures of AAZO and PDAC. (b) Schematic illustration of the preparation and structures of AAZO/PDAC film. (c) Optical image of a free-standing AAZO/PDAC film with an area of 5 cm ×3.2 cm.

by AZO as the side chain. Aide *et al.*[11] reported that a freestanding bimorph film of a polymer brush carrying AZO-containing mesogenic side chains was obtained by hot-pressing with two teflon sheets. The resultant polymer film with a wide-area bimorph configuration showed an excellent photomechanical motion (rapid and reversible bending) due to the unbalance between the tensile and contractile strains at different sides of the film, providing new possibilities in designing the advanced soft material.

Recently, a variety of supramolecular effects such as hydrogen bonds (H-bonds), electrostatic interaction, and coordination is utilized to assemble AZO (cross-linker) in polymer chains by the uncovalent cross-linking.[23-33] This cross-linking effect relying on supremolecular interaction is a facile and low-cost method and is different from the covalent cross-linking. Importantly, the photomechanical effect and the sensitivity of a supramolecular assembly using AZO/polymers can be tuned and optimized by changing the weight ratios of AZO (cross-linker) to polymers and the surrounding chemical environment such as the temperature, pH and humidity.[24,25] As a result, this AZO/polymer film shows a conspicuous affinity in the field of the macro- and micro-phase separation, holographic surface relief gratings (SRGs), and stable birefringence.[25-33] To date, few studies are focused on the light-driven deformation and the shape recovery of the free-standing AZO/polymer film by supramolecular assembly, which might be due to the difficulty in obtaining a uniform and free-standing film with the homogeneous microstructure based on the relatively weak cross-linking. The correlative research is motivated by Ikeda and his co-workers,[34] who reported that supramolecular cross-linking of polymers containing AZO moieties by H-bonds converted the microscopic motion of the AZO moieties into macroscopic bending of the films. The feature was due to the decrease in the alignment order of H-bonded LC structures during *trans*-to-*cis* photoisomerization of AZO cross-linkers. The result opens a pathway toward advanced light-driven actuators using supramolecular assemblies of AZO/polymers. However, the controllability and cycling stability were rarely reported.

Herein, a supramolecular cross-linked AZO/polymer was prepared by the electrostatic interaction between photochromic AZO with disulfonic groups and a cationic polyelectrolytes (Fig. 1b). Supramolecular effects and chemical structures of AZO/polymer were characterized by fourier-transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and UV-Vis absorption spectra. Light-driven actuators using a uniform AZO/polymer film exhibited a large deformation by rolling-up into a tube with double walls after UV irradiation induced by the low-density incident light. This film spontaneously recovered to original shape controlled by the transformation of AZO cross-linkers. Results indicate that a supramolecular assembly of AZO/polymer film can be developed to be a high-performance smart material for light-driven actuators by controlling the structural transformation.

Experimental

Materials

Poly(diallyldimethylammonium chloride) (PDAC, 20%, w/w, in water, Mw=200000-350000) were purchased from Sigma-Aldrich. Polyimide (PI) was obtained from Hangzhou Sumengte Co. Ltd.. 4-amino-1,1'-azobenzene-3,4'-disulfonic acid monosodium salt (AAZO, Sigma-Aldrich, 95%) was purified by recrystallization. N,N-dimethylformamide (DMF) and N,N-dimethyl acetamide (DMAc) were purified by distillation. Other reagents were used without further treatment.

Synthesis of AAZO/PDAC supramolecule.

AAZO (475 mg, 1.25 mmol) was dissolved in di-water (50 mL). PDAC solution (10 mL) was diluted to 50 mL by adding di-water (40 mL), and then the solution was added dropwise to AAZO solution under stirring. AAZO/PDAC supramolecules were acquired by electrostatic assembly in the solution with a weight ratio of AAZO to PDAC of 1:4.4. NaCl was removed by dialysis for several times. The solution (100 mL) was concentrated by the rotary evaporation at 80 ℃ , and the resulting concentrated solution (5 mL) was used to prepare the photo-responsive AAZO/PDAC film.

Preparation of AAZO/PDAC film.

AAZO/PDAC film was prepared by dip-coating on a quartz glass coated by PI (Fig. 1b). Typically, the quartz substrate was ultrasonically rinsed by di-water and alcohol successively, and it was dried under nitrogen gas at room temperature. PI solution (50 μL, 2.5%, w/w, in distilled DMF) was spin-coated on the quartz glass at the speed of 2500 rpm for 40 s. The residual

DMF on the PI film was removed in vacuum at 40℃ for 8 h. Afterwards, the AAZO/PDAC solution (3 mL, 2 mg/mL) was dip-coated on the surface of the PI film on the quartz glass. After dry in air, a free-standing AAZO/PDAC film was released from the substrate by soaking in DMAc to dissolve the PI layer (Fig. 1c).

Characterization.

Fourier-transform infrared (FT-IR) spectroscopy was carried out on a Bruker Tensor 27 spectrometer to analyze chemical structures. X-ray diffraction (XRD) patterns were taken by a Rigaku D/max 2500 v/pc X-ray diffractometer using Cu Kα radiation (k=0.15 nm) at a scanning rate of 8.0 °/min, using a voltage of 40 kV and a current of 200 mA. Morphologies of AAZO/PDAC films were observed by field-emission scanning electron microscopy (FESEM, Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) analyses were performed on a PHI 1600 model surface analysis system with a 450 W MgKa.

Time-evolved UV-Vis absorption spectra of AAZO/PDAC solution and films were recorded using a Hitachi 330 UV-Vis spectrophotometer. The *trans*-to-*cis* isomerization of AAZO moieties in AAZO/PDAC were induced by the irradiation of UV light at 350~380 nm at room temperature. The *cis*-to-*trans* reversion of AAZO moieties was also investigated using UV-Vis spectrophotometer after the storage in darkness. A free-standing film (10×15 mm) was used as a light-driven actuator. The whole shape deformation process of the AAZO/PDAC film was tested in the closed environment to keep an constant temperature (25 ℃) and humidity(20%~25%). The light-induced bending of the actuator was performed by a UV gun (ECL 410) at a distance of 1.5 cm, and the intensity of light to the film was 30 mW•cm^{-2} measured by the light density meter (Beijing Zhongjiaojinyuan Co., Ltd.). The shape recovery of the film was also observed in air without shielding from light.

Results and discussion

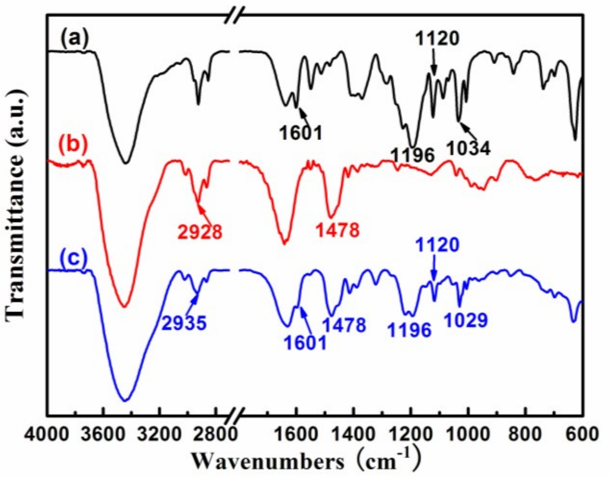


Fig. 2 FT-IR spectra of (a) AAZO, (b) PDAC and (c) AAZO/PDAC

The supramolecular interaction between AAZO and PDAC was analyzed using FT-IR spectroscopy. Compared with AAZO (Fig. 2a), AAZO/PDAC (Fig. 2c) exhibits a distinct shape change of the band at ~1196 cm^{-1} (*vas*(SO_3^-)) and a band shift of *vs*(SO_3^-) from 1034 to 1029 cm^{-1}, indicating a changed chemical environment of SO_3^- groups.[23,35] Simultaneously, PDAC (Fig. 2b) shows a sharp band at 2928 cm^{-1} assigned to the asymmetric -CH_3 stretching vibration. And this band in AAZO/PDAC shifts to 2935 cm^{-1}, attributed to the polarity change of the nitrogen atom in the dimethyl diallylammonium group of PDAC.[35] The change in the environment of the -SO_3^- groups of AAZO and the polarity of the nitrogen atom of dimethyl diallylammonium group of PDAC indicate that the AAZO/PDAC assembly forms by electrostatic interaction. This analysis is confirmed by three characteristic peaks of ν(ring C-C) at 1601 cm^{-1}, δ(CH_2) at 1478 cm^{-1} and ν(C-N) at 1120 cm^{-1}.[35] Moreover, the supramolecular assembly of AAZO/PDAC is also confirmed by different solubility of films in organic solvents (Fig. S1† and Table S1†). Different from AAZO soluble in all solvents including water, methanol, ethanol, DMF, acetone and $CHCl_3$, AAZO/PDAC films are insoluble in DMF, acetone and $CHCl_3$. This feature suggests that PDAC does not diffuse freely in those sovlvents because AAZO is uncovalently anchored on the PDAC.

The AAZO/PDAC assembly with a weight ratio of AAZO to PDAC of 1:4.4 without dialysis was observed by field-emission scanning electron microscopy (FESEM) (Fig. S2†). A large amount of NaCl crystals was deposited on the surface of AAZO/PDAC film according to energy dispersive X-ray spectrometry (EDS) data (Fig. S3†). This is due to the electrostatic interaction between SO_3^- and the dimethyl diallylammonium groups. NaCl crystals are also confirmed by X-ray diffraction (XRD) pattern (Fig. S4†). Compared with pure AAZO and PDAC, the complex shows three sharp peaks at 31.69°, 45.45°, 66.23°, respectively, corresponding to the (200), (220), (400) crystalline planes of NaCl (PDF#05-0628). This result indicates that AZO units are uncovalently attached on the polymer chains to form the AAZO/PDAC supramolecules by electrostatic interaction.

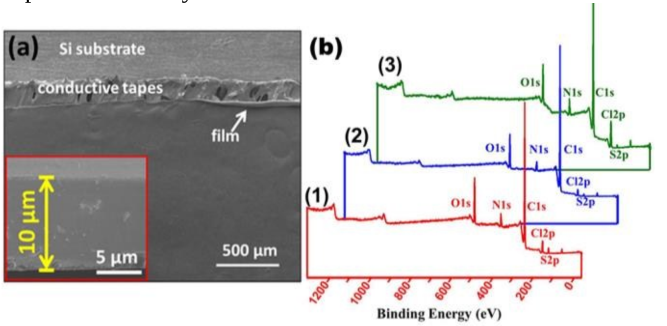


Fig. 3 (a) SEM image of a free-standing AAZO/PDAC film with a weight ratio of AAZO to PDAC of about 1:4.4 on Si substrate. Left bottom inset: SEM image of cross section of the film. (b) XPS spectra of AAZO/PDAC films prepared with different weight ratios of AAZO to PDAC of (1) 1:3.5, (2) 1:4.4 and (3) 1:6.

Table 1. Element composition of AAZO/PDAC films according to XPS spectra

Samples	C (At %)	O (At %)	Cl (At %)	N (At %)	S (At %)
(1)	81.84	6.89	3.31	5.87	2.09
(2)	87.77	3.69	2.21	5.28	1.05
(3)	79.63	3.48	7.49	8.37	1.03

Morphology of the free-standing AAZO/PDAC film on the Si substrate was observed by SEM. As shown in Fig. 3a, AAZO/PDAC film exhibits the smooth surface without aggregates. The cross section of the film (the left bottom inset of Fig. 3a) indicates that the thickness of the film is 10 μm. XPS (Fig. 3b) was carried out to estimate the elemental composition of AAZO/PDAC with different weight ratios. The quantitative calculation based on XPS data (Table 1) and EDS (Fig. S5†) suggests that one AAZO molecule is approximately

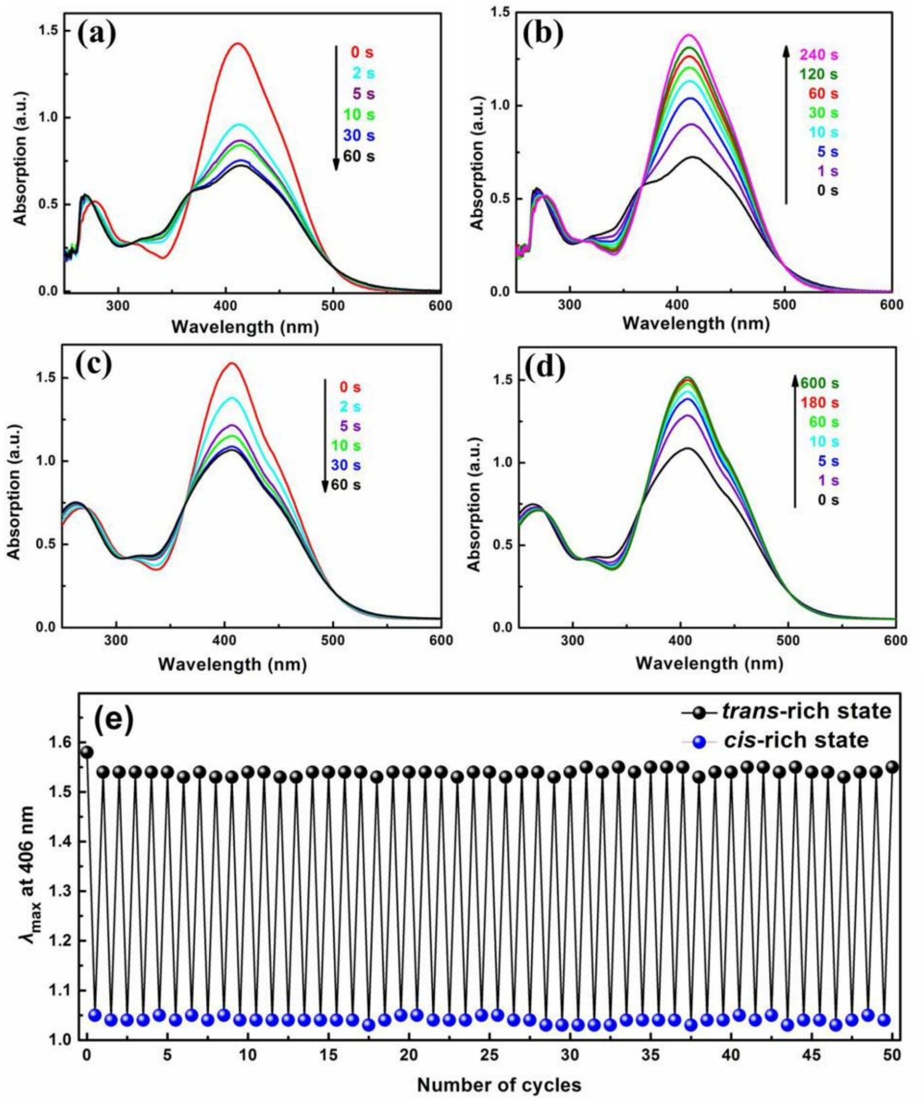


Fig. 4 Time-evolved absorption spectra of (a, b) AAZO/PDAC in DMF/H_2O mixture (50:1 in volume) and (c, d) free-standing film under the irradiation of UV light at 365 nm and in darkness after the irradiation. (e) Multiple *trans*-to-*cis* isomerization of AAZO/PDAC film as monitored by recording 50 cycles of the absorbance at 406 nm after UV irradiation for 60 s and kept in darkness for 600 s.

uncovalently supported by every 3~4 structural units in the polymer (PDAC) chains by electrostatic interaction. Previous studies showed that the content of AZO units in the AZO/polymer complex greatly affected photo-responsive properties of the complex based on different supramolecular interactions.[20,25,36] Thus, the weight ratio of AAZO to PDAC is critically important for the light-driven deformation or recovery of AAZO/PADC films. The AAZO/PDAC film with a low weight ratio of AAZO to PDAC of about 1:6 indicates that one AAZO molecule corresponds to 6~7 structural units in the PDAC chains according to XPS data (Table 1). Importantly, this film shows no light-driven deformation, indicating that the driven force produced by the photoisomerization of AAZO is too weak for light-to-work transduction. On the other hand, excessive AAZO inevitably forms several aggregates in the polymer, resulting in a decrease in light-absorption efficiency, and thus it affects the photoisomerization located inside the film.[25] This analysis is confirmed by another AAZO/PDAC film with a high weight ratio of AAZO to PDAC of about 1:3.5. Some aggregates are observed in the inhomogeneous surface of the film (Fig. S6†), thus apparently affecting the light-driven deformation.

Time-evolved absorption spectra of AAZO/PDAC in DMF/H_2O mixture (50:1 in volume) (a, b) and film (c, d) under the irradiation of UV light at 365 nm and after the irradiation in darkness were shown in Fig. 4. AAZO/PDAC solution shows a broad band at 411 nm due to π-π* electron transition of *trans*-AAZO. This band in AAZO/PDAC film shows a slight blue-shift by 5 nm (Fig. S7†) due to the formation of H-aggregates in the film.[37] Because of no photosensitivity of PDAC (Fig. S8†), the photoisomerization degree of AAZO/PDAC supramolecules is identified by the intensity of the band originated from π-π* electron transition of *trans*-AAZO (Fig. S9†). As shown in Fig. 4a, the AAZO/PDAC solution exhibits a continuous decrease in absorption at 411 nm due to *trans*-to-*cis* photoisomerization under UV irradiation. This feature is consistent with the photo-response of AZO/polymers as the side groups.[2,11,26] After the irradiation for 1 min, the band intensity of AAZO/PDAC solution at 411 nm (A_t) decreases to 50.3% of initial intensity (A_0). Time-evolved recovery of AAZO/PDAC

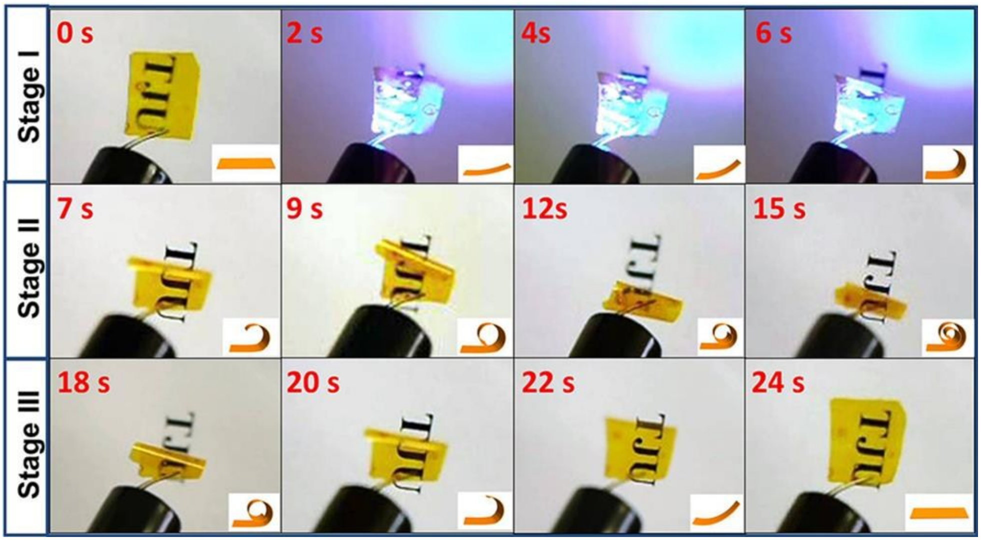


Fig. 5 Photographic frames of the light-driven deformation and shape recovery of AAZO/PDAC film. The film (10 mm ×15 mm) was held vertically with one side clamped. The UV light (30 mW•cm^{-2}) is switched on in **stage I** and switched off in **stage II** and **stage III**. The inset of each photograph is a schematic illustration of the film.

solution in darkness is indicated by a continuous increase in absorption band at 411 nm in Fig. 4b. Compared with pure AAZO (Fig. S10†), AAZO/PDAC shows a much slower reversion because of limited *cis*-to-*trans* transformation of AAZO anchored to the PDAC chain by electrostatic adsorption.

The isomerization and reversion of AAZO were also observed in the AAZO/PDAC film (Fig. 4c and 4d). This film shows a lower degree of *trans*-to-*cis* isomerization (A_t/A_0=67.3%, after the irradiation of 1 min) than that in solution (A_t/A_0=50.3%). It's known that free volume is critical for the isomerization and reversion of AZO moieties because *trans* and *cis*-isomers have different steric configurations.[24,38-41] Compared with that in solution, the transformation of AZO in the AAZO/PDAC films is limited by a decrease in free volume. On the other hand, the movement of polymer chains in the film is more difficult than that in solution, leading to a low degree of *trans*-to-*cis* isomerization of AAZO attached on the polymer chains by electrostatic interaction. This analysis is also confirmed by a slow *cis*-to-*trans* reversion of AAZO in the AAZO/PDAC film (Fig. 4d). The first-order rate constant for reversion ($\boldsymbol{K}_{\mathbf{rev}}$) (Equation S1†) of AAZO/PDAC film is 0.0168 s^{-1}, which is lower than that in solution (0.0322 s^{-1}) (Fig. S11†). Results indicate that the isomerization and reversion of AAZO in the AAZO/PDAC supramolecules can be controlled by the microstructures (free volume) based on the interaction between AAZO and PDAC.

The transformation between *trans* and *cis* isomer is based on a dynamic equilibrium. *Trans*-AZO transforms to the *cis*-isomers under the irradiation, and meanwhile, some *cis*-isomers revert to *trans*-isomers due to thermodynamic instability until a photostationary equilibrium is generated. The reversibility and stability of structural transformation of the AAZO/PDAC film was tested by recording the absorbance at 406 nm after UV irradiation for 60 s and kept in darkness for 600 s (Fig. 4e). The AAZO/PDAC film shows an excellent cycling stability for 50 cycles based on the reversible *trans*-to-*cis* transformation, which is critical for high-performance light-driven polymeric actuators.[24]

The light-driven deformation and shape recovery of AAZO/PDAC film are shown in Fig. 5 and Movie S1†. The film (10 mm ×15 mm) held vertically with one side clamped is capable of undergoing the large-scale macroscopic deformation under the illumination followed by the recovery to its original shape. This process is divided into three stages. **Stage I** (0-6 s): When exposed to UV light, AAZO/PDAC film was quickly bent inward to form a concave shape due to different rates and degrees of *trans*-to-*cis* isomerization between the front (facing UV light) and back surface. **Stage II** (6-15 s): Interestingly, the AAZO/PDAC film continues to curl and is rolled up into a tube with double walls within the following 9 s even when the light is off. **Stage III** (15-24 s): This rolling-up film starts to stretch spontaneously towards an opposite direction to recover its original flat shape within the next 9 s.

Generally, the photomechanical behavior of AZO/polymers depends on the light-induced changes in microstructures, and thus the light-driven deformation and shape recovery of AAZO/PDAC film are determined by the transformation of AAZO cross-linkers through electrostatic interaction and the resultant segment motion of polymers.[7,34] Specifically, the interaction between AAZO (two anionic sulfonate groups) and PDAC results in the uncovalent cross-linking of polymers to form supramolecules (Fig. 1b), and no orientation is observed by polarized optical microscopy. This analysis is confirmed by the experiment that no free-standing film is obtained due to weak cross-linking effect using 4-amino-4'-sulfonic acid azobenzene (only one sulfonate group) and PDAC (the weight ratio of AZO to PDAC: 1:3~1:6) for the assembly. Hence, the cross-linking of PDAC using AAZO cross-linkers by electrostatic interaction convert the microscopic motion of the mesogens into the macroscopic change of the films.

Schematic illustration of light-driven deformation and recovery of AAZO/PDAC film is shown in Fig. 6. In our supramolecular assembly, when exposed to UV light, AAZO undergoes the isomerization from the rod-like *trans*-isomer to the bent *cis*-isomer with the largely reduced molecular length from 9 Å to 5.5 Å.[16] Thus, this change of AAZO cross-linker anchored to PDAC causes the rearrangement of polymer networks. When the film is irradiated, the incident light is mainly absorbed by the front surface of the film (facing UV light) due to the large absorption coefficient of the AZO. Thus,

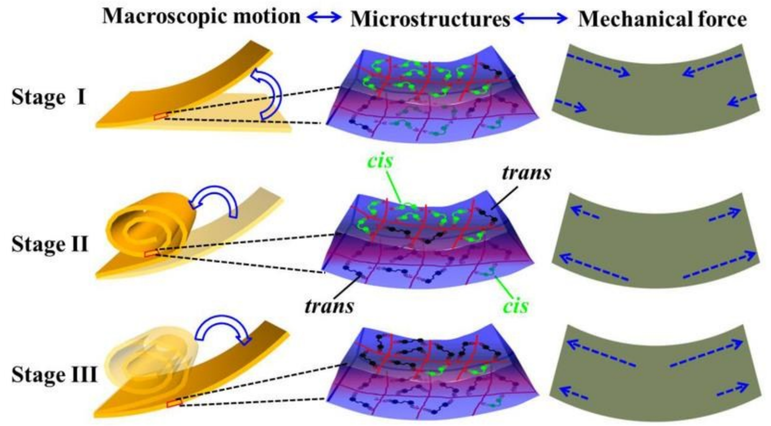


Fig. 6 Schematic illustration of light-driven deformation and shape recovery of AAZO/PDAC film controlled by different rates and degrees of transformation between the front surface (facing UV light) and back surface with a segment motion of polymers.

AAZO at the front surface of the film exhibits faster and higher degree of *trans*-to-*cis* isomerization than that at the back surface due to the intensity gradient of the incident light,[11,39,42] which can be proved by the obviously increased light absorption of film by increasing light density, especially below 30 mW cm^{-2} (Fig. S12†). Meanwhile, the *cis*-AAZO cross-linker with a short molecular length results in changes in microstructures of polymer network. Consequently, with the increasing amount of short *cis*-isomers, the AAZO/PDAC film shows a much larger contraction force at the front surface based on the relatively fast isomerizition than that on the backside. This asymmetric contraction force enables the film to bend towards the light, similar to the previous results in chemically-bonded and H-bonded polymer films.[14,15,19,21,34] The asymmetric contraction force is also measured. The supramolecular AAZO/polymer film shows an increase in stress and a decrease in strain under the UV irradiation according to uniaxial tension test (Fig. S13†).

The deformation controlled by different rates of the transformation of AAZO cross-linkers is confirmed by **Stage II** (6-15 s). AAZO/PDAC film shows the successive macroscopic deformation by rolling up into a tube with double walls within 9 s after the irradiation. This feature is attributed to the combined effect of the fast *cis*-to-*trans* reversion at the back surface and the hysteresis of the segment motion of polymers. When the light is off, *cis*-AAZO immediately start to reverse (Fig. 4d). And *cis*-AAZO at the back surface of the bended film shows the fast *cis*-to-*trans* reversion due to the lower steric hindrance (larger free volume) compared with that at the front surface.[24,39] The asymmetric reversion rate between the back surface and the front surface continuously generates a large gradient stretching force that is decreased from the back surface to front surface (Fig. 6). Besides, after the UV irradiation, the chain segments of PDAC do not immediately achieve a new balance through thermal motion due to the effect of internal friction. Therefore, the polymer network at the front surface also tends to contract due to the hysteresis of segment motion. As a result, AAZO/PDAC film is rolled up to a tube with double walls due to the combined effect of the gradient stretching force and the hysteresis of the segment motion controlled by the change in microstructures after the irradiation. However, the reversion of AAZO at the front surface can not completely restricted by steric hindrance. Thus, this rolling-up deformation stops when the stretching force controlled by the reversion of AAZO at the back surface is balanced by that at the front surface.

The shape recovery of AAZO/PDAC film is also observed in **Stage III** (15~24s) in Fig. 5. The rolling-up film flattens out spontaneously due to the internal stretching force dominated by *cis*-to-*trans* reversion of the AAZO cross-linker at the front surface. As indicated by **Stage I**, an increase in *cis*-isomers at the front surface is obtained due to a high degree of isomerization compared with that at the back surface. After **Stage II**, an increasing amount of *cis*-AAZO at the front surface starts to revert to *trans*-isomers. The increased molecular length of the AAZO cross-linker causes the expansion of the polymer networks, generating the asymmetric internal stress of the film.[19-22,34] Importantly, the expansion force at the front surface is remarkably higher than that at the back surface, resulting in the spontaneous shape recovery of the film (from rolling-up to a flat shape). Results indicate that the light-driven deformation and shape recovery of AAZO/PDAC are controlled by different rates and degrees of the transformation of AAZO between the front surface and back surface with changed microstructures.

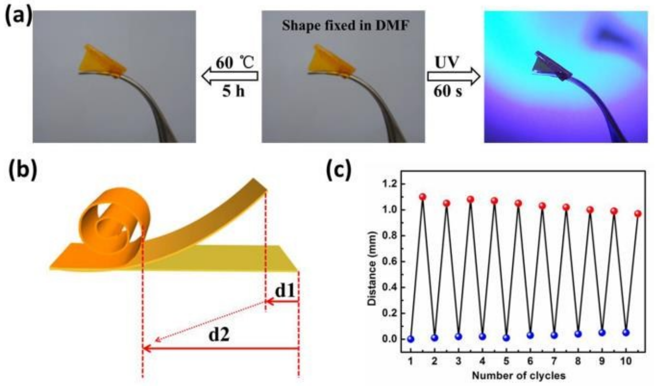


Fig. 7 (a) Optical image of AAZO/PDAC film with a fixed shape by soaking the rolling-up film in DMF solution, even after (left) heating or (right) UV irradiation (30 mW•cm-2). (b) Schematic illustration of rolling-up levels of the film by measuring the distance of the free edge of the film from the initial position. Larger distance (d2>d1) corresponds to a large deformation. (c) Cycling performance of AAZO/PDAC film by measuring the changes in distance of the film.

The shape recovery of the film can be restricted by soaking the rolling-up film in DMF solution (Fig. 7a). The diffusion of DMF molecules into the film partly disturbs the cross-linking and electrostatic interaction. As a result, the *cis*-to-*trans* transformation of AZO fails to drive the movement of polymers. The film keeps the fixed shape permanently even though it is heated or under the UV irradiation. By this method, the film with rolling-up shape is fixed during **Stage III**. The cycling performance of the photomechanical effect of the AAZO/PDAC film was also investigated. As shown in Fig. 7c and Movie S1†, the AAZO/PDAC film shows the reversible light-driven deformation and shape recovery for 10 cycles without an obvious decrease in response. The good cycling stability is attributed to the reversible *trans*-to-*cis* transformation of the AAZO/PDAC supramolecule consistent with the results of absorption spectra (Fig. 4e). The AAZO/PDAC film with the light-induced large-scale deformation and fast shape recovery is utilized for a photomechanical output power sources for advanced intelligent actuators.

Conclusions

A supramolecular cross-linked assembly of AAZO/PDAC with the specific weight ratio was prepared by uncovalently grafting AAZO on the side-chain of PDAC by electrostatic interaction. This supermolecular effect was demonstrated by FT-IR spectra, the solubility in different organic solvents and XRD patterns. The resultant free-standing AAZO/PDAC film showed the large deformation by rolling-up into a tube with double walls even when the light is off. This photomechanical deformation arose from different rates and degrees of the structure transformation of AAZO between the front (facing UV light) and back surface with the segment motion of polymers. It indicates that the cross-linking by electrostatic interactionc is able to convert the microscopic motion of the mesogens into a macroscopic change of the film. Moreover, the AAZO/PDAC film exhibits an excellent cycling performance of photomechanical deformation and recovery, and the rolling-up shape (large deformation) is easily fixed by soaking in DMF by disturbing electrostatic interaction. This supramolecular assembly of AAZO/PDAC with the reversible and controllable photomechanical output can be developed for high-performance light-driven smart actuators.

Acknowledgements

This work was financially supported by National Natural Science Funds for Distinguished Young Scholars (51425306), National Natural Science Foundation of China (Grant no. 51173127, 51273144, 51373116 and 513111129), and Natural Science Foundation of Tianjin City (No. 14JCZDJC37900) and Program for New Century Excellent Talents in University (NCET-13-0403).

Notes and references

[a] School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, China

[b] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

† Email: weifeng@tju.edu.cn Tel: +86-22-2740205 Fax: +86-22-27404724

Electronic Supplementary Information (ESI) available: [Photographs of AAZO/PDAC films in different solvents. SEM images and detailed EDS data. XRD patterns and UV-Vis absorption spectra of AAZO, PDAC, AAZO/PDAC. Stress-strain responses of AAZO/polymer films.]. See DOI: 10.1039/b000000x/

1 A. Lendlein, H. Jiang and O. Junger, *Nature*, **2005**, 434, 879.

2 Y. Wu, J. Hu, C. Zhang, J. Han, Y. Wang and B. Kumar, J. Mater. Chem. A, 2015, 3, 97.

3 Y. Feng, M. Qin, H. Guo, K. Yoshino and W. Feng, *Acs Appl. Mater. Interfaces*, 2013, **5**, 10882.

4 H. Meng and G Li, *Polymer*, 2013, **54**, 2199.

5 Q. Li, Intelligent Stimuli Responsive Materials: From Well-defined Nanostructures to Applications, John Wiley & Sons Inc, New Jersey, 2013

6 F. Liu and M. W. Urban, *Prog. Polym. Sci.*, 2010, **35**, 3.

7 J. Hu, Y. Zhu, H. Huang and J. Lu, *Prog. Polym. Sci.*, 2012, **37**, 1720.

8 Y. Wang and Q. Li, *Adv. Mater.*, 2012, **24**, 1926.

9 L. Wang, H. Dong, Y. N. Li, C. M. Xue, L. D. Sun, C. H. Yan and Q. Li, *J. Am. Chem. Soc.*, 2014, **136**, 4480.

10 R. Y. Sun, C. Xue, X. Ma, M. Gao, H. Tian and Q. Li, *J. Am. Chem. Soc.*, 2013, **135**, 5990.

11 N. Hosono, T. Kajitani, T. Fukushima, K. Ito, S. Sasaki, M. Takata, and T. Aida, *Science*, 2010, **330**, 808.

12 Y. Yu, M. Nakano and T. Ikeda, *Nature*, 2003, **425**, 145.

13 S. Iamsaard, S. J. Asshoff, B. Matt, T. Kudernac, J. J. Cornelissen, S. P. Fletcher and N. Katsonis, *Nat. Chem.*, 2014, **6**, 229.

14 M. Kondo, Y. Yu and T. Ikeda, *Angew. Chem. Int. Ed.*, 2006, **45**, 1378.

15 K. M. Lee, M. L. Smith, H. Koerner, N. Tabiryan, R. A. Vaia, T. J. Bunning and T. J. White, *Adv. Funct. Mater.*, 2011, **21**, 2913.

16 Y. Yu and T. Ikeda, *Macromol. Chem. Phys.*, 2005, **206**, 1705.

17 D. Wang and X. Wang, *Prog. Polym. Sci.*, 2013, **38**, 271.

18 Y. Zhao and J. He, *Soft Matter*, 2009, **5**, 2686.

19 K. M. Lee and T. J. White, *Macromolecules*, 2012, 45, 7163.

20 K. M. Lee, N. V. Tabiryan, T. J. Bunning and T. J. White, *J. Mater. Chem.*, 2012, **22**, 691.

21 Y. Yu, T. Maeda, J. Mamiya and T. Ikeda, *Angew. Chem. Int. Ed.*, 2007, **46**, 881.

22 Z. Jiang, M. Xu, F. Li and Y. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 16446.

23 O. Kulikovska, L. M. Goldenberg and J. Stumpe, *Chem. Mater.*, 2007, **19**, 3343

24 Y. Zhang, Y. Ma and J. Sun, *Langmuir*, 2013, **29**, 14919.

25 S. Wu and C. Bubeck, *Macromolecules*, 2013, **46**, 3512.

26 H. Yu, *Prog. Polym. Sci.*, 2014, **39**, 781.

27 J. E. Koskela, J. Vapaavuori, J. Hautala, A. Priimagi, C. F. J. Faul, M. Kaivola and R. H. A. Ras, *J. Phys. Chem. C*, 2012, **116**, 2363.

28 J. Gao, Y. He, F. Liu, X. Zhang, Z. Wang and X. Wang, *Chem. Mater.*, 2007, **19**, 387

29 T. Bian, L. Shang, H. Yu, M. T. Perez, L. Z. Wu, C. H. Tung, Z. H. Nie, Z. Y. Tang and T. Zhang, *Adv. Mater.*, 2014, **26**, 5613.

30 Q. F. Cheng, L. Jiang and Z. Y. Tang, *Acc. Chem. Res.*, 2014, **47**, 1256.

31 Y. Chen, H. J. Cui, L. S. Li, Z. Y. Tian and Z. Y. Tang, *Polym. Chem.*, 2014, **5**, 4441.

32 W. J. Liu, Z. N. Zhu, K. Deng, Z. T. Li, Y. L. Zhou, H. B. Qiu, Y. Gao, S. N. Che and Z. Y. Tang, *J. Am. Chem. Soc.*, 2013, **135**, 9659.
33 J. Lee, S. Oh, J. Pyo, J. M. Kim and J. H. Je, *Nanoscale*, 2015, **7**, 6457
34 J.-i. Mamiya, A. Yoshitake, M. Kondo, Y. Yu and T. Ikeda, *J. Mater. Chem.*, 2008, **18**, 63.
35 J. A. He, S. P. Bian, L. Li, J. Kumar, S. K. Tripathy and L. A. Samuelson, *J. Phys. Chem. B*, 2000, **104**, 10513.
36 K. M. Lee, D. H. Wang, H. Koerner, R. A. Vaia, L. S. Tan and T. J. White, *Angew. Chem. Int. Ed.*, 2012, **51**, 4117.
37 N. M. Ahmad, S. J. Ali and M. J. Saqib, *Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 1881.
38 S. Dante, R. Advincula, C. W. Frank and P. Stroeve, *Langmuir*, 1998, **15**, 193.
39 J. Han, D. Yan, W. Shi, J. Ma, H. Yan, M. Wei, D. G. Evans and X. Duan, *J. Phys. Chem. B*, 2010, **114**, 5678.
40 K. K. Lee, H. Koerner, D. H. Wang, L. -S. Tan, T. J. White and R. A. Vaia, *Macromolecules*, 2012, **45**, 7527.
41 J. J. Wie, D. H. Wang, K. M. Lee, L. -S. Tan and T. J. White, *Chem. Mater.*, 2014, **26**, 5223.
42 V. Toshchevikov, M. Saphiannikova and G. Heinrich, *J. Phys. Chem. B*, 2012, **116**, 913.