

Multiple Shape Manipulation of Azobenzene-Containing Polyimide by Combining Shape Memory Effect, Photofixity, and Photodeformation

Xuejie Sun, Menghan Zhang, Jia Wei,* and Yanlei Yu*



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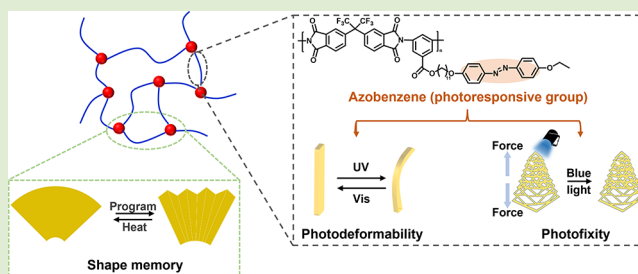
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ABSTRACT: The integration of different shape manipulation could greatly expand the versatility and functionality of smart materials, for which the achievement of synergism of different shape control is crucial. Here, we seek to create one kind of polyimide with integrated multiple shape manipulations by constructing the chemical network bearing azobenzene as a side chain. Trifunctional cross-linkers serving as net points of the chemical network render polyimide thermal-induced shape memory effects, which enables shape transformation. Azobenzene as a photoresponsive group is employed to achieve the photofixity and reversible photodeformability. Such photosensitive behaviors are independent of molecular prealignment and remain available after thermally shaping and fixing. As a result, these noninterfering performances induced by heat and light allow us to arbitrarily combine them to meet different needs. By integrating different shape manipulations, various shape changes and functional execution are conveniently achieved. The combination of the shape memory effect with photofixity enables the setting of diverse shapes, while the merging of it with reversible deformation facilitates the construction of actuators capable of executing functions. This study provides a new approach for the preparation of multifunctional actuators and has potential applications in the field of intelligent drivers.



Smart materials that present shape manipulation, including shape transformation, reprogramming, and reversible deformation, in response to external stimuli, such as heat,^{1–3} light,^{4–9} or magnetic field,¹⁰ are highly desirable in the fields of intelligent devices, soft actuators, and robotics. A wide range of shape manipulatable materials have been developed on the basis of diverse mechanisms, such as the shape transformation based on shape memory effect^{11–17} and the photodirected shape changes by photofixity or photoisomerization.^{18–26} Despite these efforts, most shape manipulatable materials only display a single shape-control ability, which restricts their applications in the execution of advanced tasks.

Driven by the goal of multiple shape manipulation, recent studies have demonstrated that the combination of photodeformability with shape memory effect provides a unique strategy.^{27–33} Yu et al. reported the multiple shape manipulation of a novel liquid crystal polymer containing azobenzene moieties, thereby realizing the reversible photodeformation and light-induced shape memory effect caused by UV light.²⁷ To avoid mutual interference of different shape manipulations under the same stimuli, they utilized the Diels–Alder (DA) network to construct ordered and disordered states in the polymer. Under UV light, the polymer in the ordered state exhibited photodeformation because of the *trans*–*cis* isomerization of azobenzene and otherwise exhibited

light-induced shape memory ability in the disordered state because of the light-switchable glass transition temperature (T_g). However, on account of the fact that both properties have not been achieved simultaneously in the same state, it is difficult to combine them to perform a complex function.

The integration of different stimuli-induced shape change behaviors is expected to realize multifaceted shape manipulation. To date, a few researches have successfully utilized light and heat stimuli to activate the deformation and shape memory effect in azobenzene-containing polyurethane (PU).^{29–31} Shape memory behavior typically involves shape programming and recovery processes at temperatures above the T_g . The photodeformation of PU relies on molecular alignment, which is easily disrupted by the heating and external force in the shape programming process, thereby ultimately resulting in the failure of photodeformation. Therefore, researchers incorporated an alignment process into the shape programming through hot-stretching to simultaneously achieve the shaping

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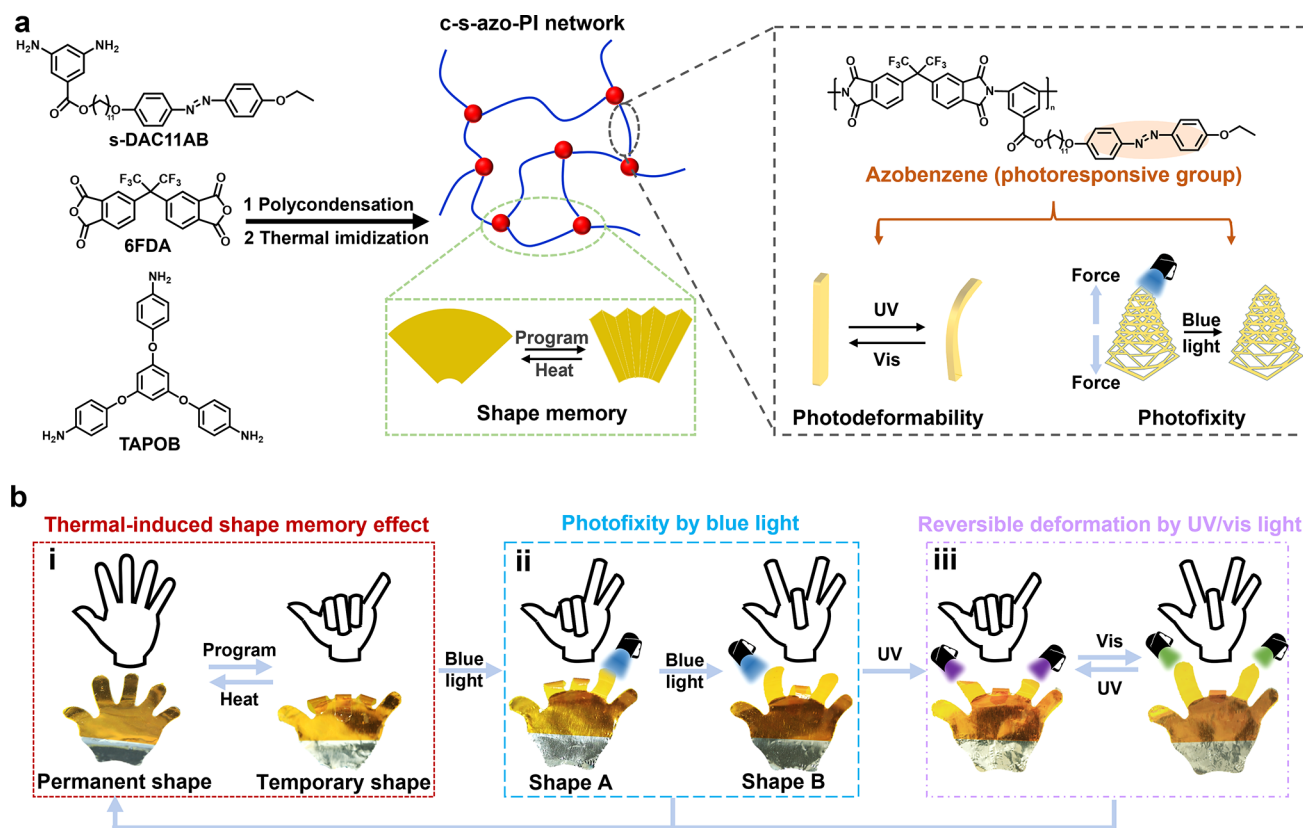


Figure 1. (a) The chemical structures of reactive monomers and cross-linkers, as well as the schematic network of the resulting polyimide with integrated multiple shape manipulation (c-s-azo-PI). (b) Photographs showing the shape programming (i), photofixity (ii), and photodeformation (iii) of the c-s-azo-PI film.

and molecular alignment. The obtained stretched shape with ordered structure showed photoinduced bending under UV light, which then returned to initial shape when heated again. Regardless of these efforts, the interference between heat and molecular alignment restricts the shape programming processing to hot-stretching and constrains the complexity and variety of shaping and deforming.

To address this issue, the design of a new material to avoid the interference of heating to the capability of photodeformation is crucial. Recently, smart polyimides exhibiting shape memory effect or photodeformation have attracted attention because of their good mechanical properties and thermal stability.^{14,34–42} In our previous work, we found that one kind of an azobenzene-containing polyimide is a promising material for developing multiple shape manipulation because it shows reversible bending behaviors upon UV/visible light irradiation without extra molecular alignment process, such as prestretching.⁴³ The combination of such photodeformable behavior with a shape memory effect would permit the material to be programmed into various shapes on demand without sacrificing photodeformability, thereby providing the possibility to integrate multiple properties and broaden their application in diverse actuators.

Herein, we explore a cross-linked azobenzene-containing polyimide (Figure 1a), which exhibits different shape manipulation, including thermal-induced shape memory effect and light-induced reversible deformation without prealignment. The shape memory effect remembers an original shape, a so-called permanent shape that can be recovered from a temporarily fixed shape by heating the polyimide above the T_g

(Figure 1b-i), and the programming of temporary shapes is primarily accomplished by heating and external force. The isomerization of azobenzene upon UV light irradiation results in a reversible photodeformation that requires no external force (Figure 1b-iii). Furthermore, this polyimide exhibits a special property of photofixity, which results from the light-directed rearrangement of the polymer chains in the glassy matrix. The mechanically deformed shape can be fixed through irradiation with blue light while applying an external force, thereby providing another way of shape manipulation (Figure 1b-ii). Overall, shape memory effect is used to realize the shape transformation, photofixity implements the local shape setting, and the reversible photodeformability is employed to perform specific functions. These photoresponsive capabilities remain available after an arbitrary thermal programming process. Therefore, we can combine them with thermal-induced shape memory effect to meet different shape change needs as required. Such unconstrained shape manipulation has the potential to enrich the complexity and diversity of shaping and deformation.

The reactive monomers 6FDA and s-DAC11AB were polymerized with cross-linker TAPOB to synthesize a cross-linked polyimide containing azobenzene in a side chain (c-s-azo-PI), wherein the cross-linker content was controlled at 2%, 5%, and 7% (Table S1). The detailed characterization is illustrated in the Supporting Information (Figures S1–S5, Table S2). The trifunctional fixed units were utilized to lock the permanent shapes, while the reversible units composed of chain segments were employed to switch off/on the molecular mobility to freeze/release the temporary shapes. Azobenzene

in a side chain acts as a photoresponsive group and exhibits repeated *trans*–*cis*–*trans* isomerization upon blue light irradiation and *trans*–*cis* isomerization under UV light.³⁶ The former enables the polyimide to bear photofixity, while the latter makes the polyimide present reversible photodeformability.

Chemical cross-linking is an effective approach to obtain permanent cross-link points, which is necessary to shape memory behavior.⁴⁴ However, some studies have confirmed that the formation of cross-linking increases the rigidity of a polymer,⁴² which could potentially affect the material's ability to undergo photoinduced deformation. Consequently, to balance good photodeformation and thermal-induced shape memory, the cross-linker content in polyimide requires a judicious tuning. The formulation was optimized according to the value of the photoinduced bending angle. It was found that the bending angle increases first and then decreases with the increasing cross-linker content (Figure S6). The film showed the best photodeformability when the cross-linker content was 5%. When irradiated with UV light, the film reached a maximum bending angle of 88° in 16 s even without molecular prealignment. Such photodeformability is attributed to the high isomerization conversion of azobenzene that generates sufficient stress to deform the material.⁴³ The bent film reverted to the initial state under visible light irradiation, thereby showing excellent reversible photodeformability (Figure 2a). It indicates that appropriate chemical cross-

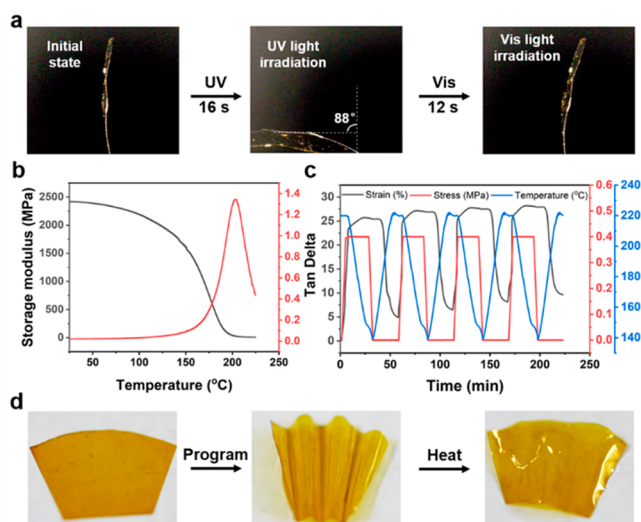


Figure 2. (a) Photographs showing the photoinduced bending behavior of the *c-s*-azo-PI film by alternative irradiation with UV (365 nm, 70 mW/cm²) and visible light (530 nm, 80 mW/cm²). The film size: 10 mm × 2 mm × 20 μm. (b,c) DMA curve and shape memory performance of the *c-s*-azo-PI film. (d) The thermal-induced shape memory process of the *c-s*-azo-PI film.

linking is conducive to improving the deformation performance. Therefore, the formulation with 5% cross-linker content was chosen for subsequent experimental studies.

The shape memory effect was preliminarily evaluated by DMA. The *c-s*-azo-PI presented a high glass transition temperature (T_g) of 204 °C, which was obtained from the peak of the loss factor. As the temperature increased, the storage modulus showed a gradual decrease until it experienced a sharp drop above T_g . The storage modulus at room temperature and $T_g + 20$ °C are ~2.4 GPa and 7.1 MPa,

respectively, which differs by 2–3 orders of magnitude (Figure 2b, Table S3). Such a large difference of the storage modulus is necessary for the polyimide to exhibit shape memory effect. To evaluate the heat-activated shape memory effect of the *c-s*-azo-PI film, we performed the stress-controlled consecutive tensile shape memory process of the strip by DMA. The detailed experimental information is illustrated in the Supporting Information. As shown in Figure 2c, the shape fixing ratio of the four cycles are 98.58%, 99.04%, 99.09%, and 99.01%, respectively. The shape recovery ratio is 80.65%, 90.12%, 92.34%, and 94.11%, respectively. The visualized thermal-induced shape memory process of the *c-s*-azo-PI film was displayed on a hot plate (Figure 2d). First, with the aid of folding fan-shaped molds, we programmed the film into a folding fan temporary shape at 220 °C; then, we took away the film from the hot plate and cooled it in air to obtain the above temporary shape. Subsequently, the film recovered to its original shape upon heating again (Movie S1). Moreover, we used a manual test method to verify the shape memory performance of the *c-s*-azo-PI film. As shown in Figure S7 and Movie S2, the *c-s*-azo-PI film showed good shape recovery behaviors, even after five shape memory cycles. The folding experiment was conducted to further demonstrate the shape memory of the *c-s*-azo-PI film, thereby confirming that the *c-s*-azo-PI film possesses a thermal-induced shape memory property (Figure S8, Movie S3).

Different from the response to UV light, the mechanically deformed shape of the polyimide could be fixed under blue light, and the deformed shape was still retained after the force and light sources were removed (Figure S9). This shape retention phenomenon referred to as photofixity has also been observed in some amorphous glassy azobenzene-containing liquid crystal polymers and polyimides.^{19,35,45} Differing from the photodeformation under irradiation of 365 nm, the distinctive photofixity is proposed to be a result of repeated *trans*–*cis* and *cis*–*trans* photoisomerization. The above repeated *trans*–*cis*–*trans* isomerization processes provide a chance to adjust the polymer chain morphology (entanglement, configuration) in the glassy matrix, which is similar to the thermal-fixing of glassy shape memory polymers.¹⁹ The repeated *trans*–*cis*–*trans* of azobenzene results in a highly stable, optically fixed shape in polymeric glasses without a substantial concentration of the thermally sensitive *cis* isomer.³⁵ White et al. utilized photofixity to reconfigure the thermal-fixed temporary shapes into a variety of secondary temporary shapes and confirmed that photofixity is possible with no discernible impact on the thermal-fixed temporary shape.¹⁹ The noninterference between photofixity and thermal-induced shape memory effect also supplies another design idea for shape manipulation.

We further studied the relationship between angle and irradiation time via photomechanical experiments (Figure 3a). With increasing irradiation time, the fixed angle ϵ_f of the *c-s*-azo-PI film changes from 0° to a maximum value of 160° in 3 to ~4 min (Figure 3b). Moreover, the temperature only increased by 7 °C under the illumination of blue light for 3 min; the temperature change induced by the photothermal effect was much lower than the T_g of the *c-s*-azo-PI film and not enough to trigger the shape change (Figure S10). It indicates that the *c-s*-azo-PI film possesses an excellent photofixity property.

Some shapes are challenging to construct directly by shape memory effect but can be achieved through photofixity. As

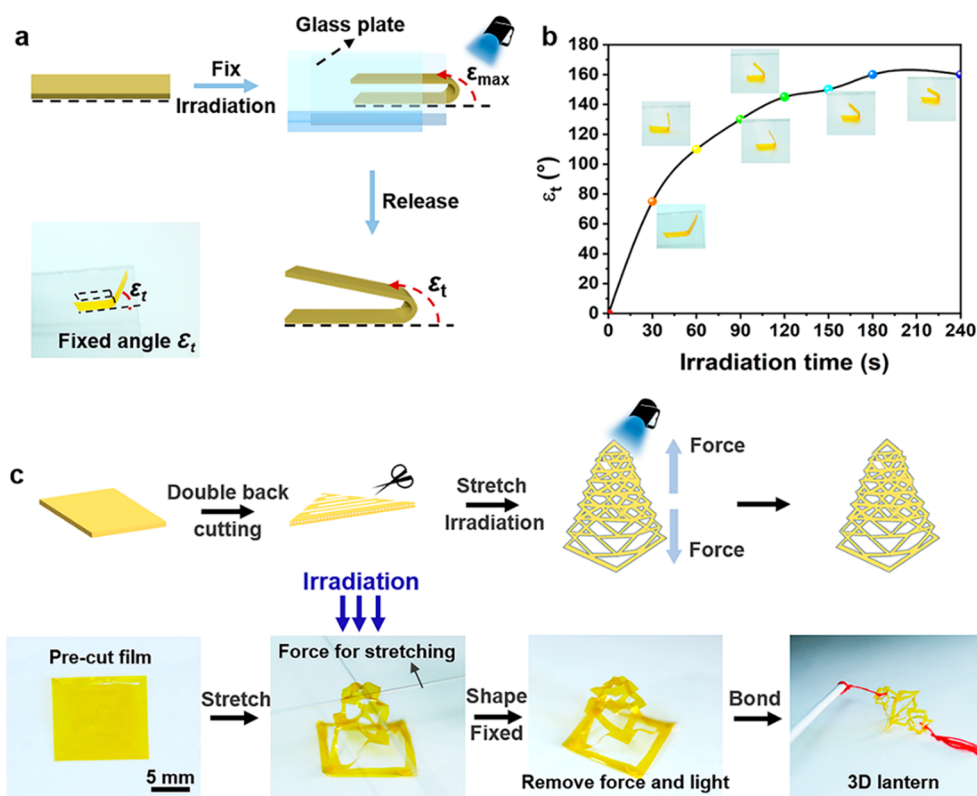


Figure 3. (a) Schematic diagram to show the photofixing process of *c-s-azo-PI* film under blue light irradiation. (b) The relationship between the photofixing angle and irradiation time of *c-s-azo-PI* film. (c) The fabrication of the lantern by photofixity.

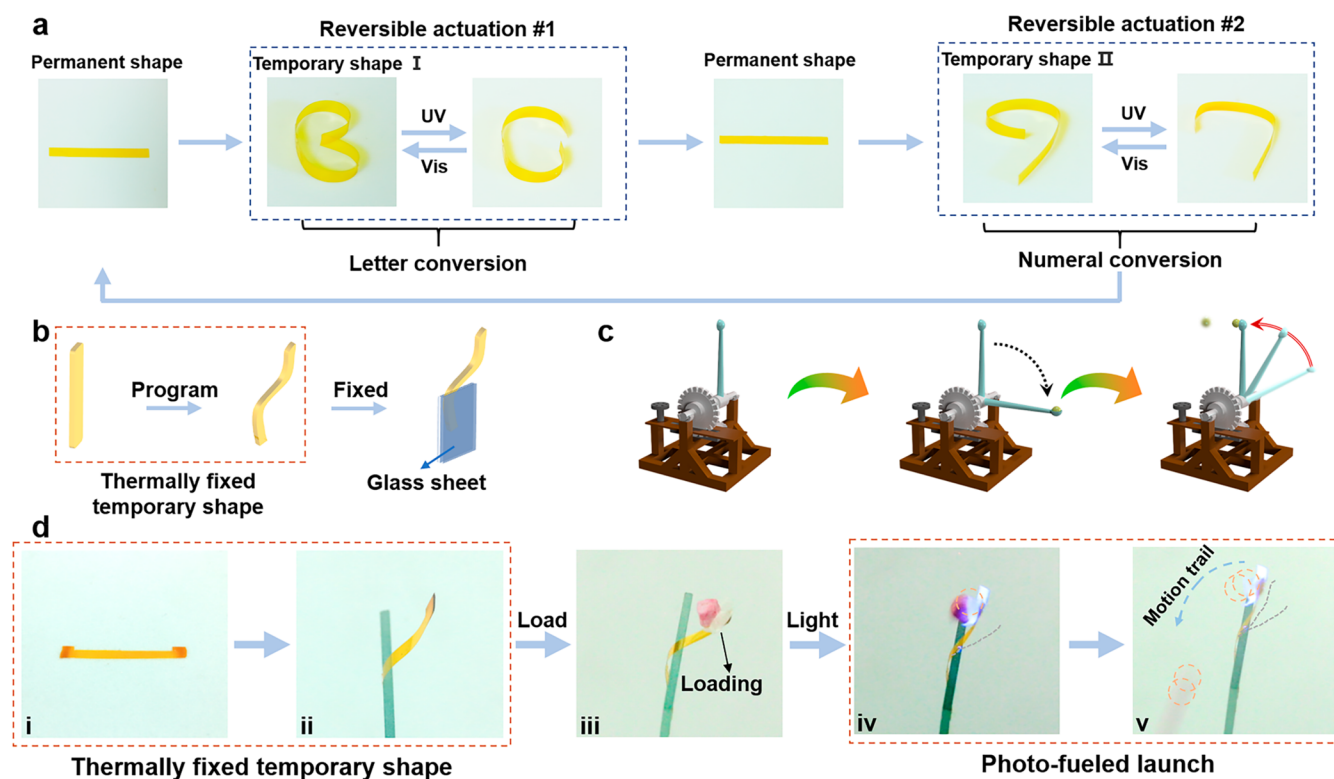


Figure 4. (a) Photographs showing the combination of shape memory effect and photodeformation to achieve reversible actuation and shape reprogramming. The *c-s-azo-PI* film size: 15 mm \times 2 mm \times 20 μ m. (b) Schematic illustration to show the fabrication of an "S"-like trebuchet through a shape memory mechanism. (c) Schematic illustration of a trebuchet throwing an object. (d) Photographs showing the photo-fueled launching of the trebuchet made by *c-s-azo-PI* film (15 mm \times 2 mm \times 20 μ m).

shown in Figure 3c, we combined photofixity with the paper-cutting process to demonstrate the ability to fabricate a relatively complex structure. The precut film was stretched first and fixed by external force, followed by irradiation of blue light at room temperature for 3 to ~4 min. After removal of the light and external force, the three-dimensional structure was fixed. Subsequently, we obtained a three-dimensional lantern by bonding the two same structures.

Thanks to the fact that both the photodeformability and photofixity still work after thermal shape programming, the aforementioned three shape manipulations do not interfere with each other, thereby providing more freedom to manipulate the shape. Figure 1b illustrates that, indeed, the three shape manipulations are independent. The *c-s-azo-PI* film in a permanent shape (palm) was programmed into a temporary shape (gesture “6”) via a shape memory mechanism (Figure 1b-i). In the presence of external force and blue light irradiation, the temporarily fixed gesture “6” gradually spread out to form new gestures (shape A and shape B) because of the photofixity property (Figure 1b-ii). Without the photofixity, the gesture “6” cannot be reformed into new different gestures through gradual shape changing using heat and it will recover to the original shape because of the shape memory effect. It can be seen that combining the shape memory effect with photofixity is an important step toward the realization of various shape control for more advanced applications. Moreover, these shape program pathways have no impact on the reversible deformation of the film. When irradiated by UV/visible light, the index and ring fingers in shape B present the bending and unbending behaviors, which still show good reversible photodeformability (Figure 1b-iii).

The noninterfering characteristics, especially, allow us to arbitrarily combine them to fulfill different demands. As shown in Figure 4a, a flat *c-s-azo-PI* film in a permanent strip shape was programmed to a temporary “B” shape. Under irradiation with UV light, the letter “B” opens to yield a new letter “C,” which recovers to “B” when irradiated with visible light because of the reversible deformation (Movie S4). The letter returns to its permanent shape because of shape memory effect when heated again and is subsequently reprogrammed to a number “9” by an identical programming process, thereby showing reversible actuation between the number “9” and “7” when exposed to UV/visible light.

Besides, inspired by the launching behavior of a trebuchet (Figure 4c), we utilized *c-s-azo-PI* to design a self-supporting launcher to hurl a projectile in response to stimuli. Taking advantage of the shape memory effect, the initial stripe was programmed and quenched to fix the “S”-like temporary shape (Figure 4b). By vertically placing the “S”-shaped cantilever and fixing its one end to a glass plate, a self-supporting launcher is obtained (i → ii). A small ball is then put in the pallet at the other end, followed by light irradiation. The launcher deforms slowly, and it suddenly launches the ball once it reaches the critical point (iii → v, Movie S5), which is challenging for the material with only one of the above manipulation abilities.

In addition, by integrating these three shape manipulations into polyimide, gradual shape changes and functional execution are easily achieved to show the multifunctional shape manipulation. As shown in Figure 5, the cantilever is thermally fixed to a temporary spiral shape and it will recover to its original shape when heated above T_g (Movie S6). After electrostatic bonding with polyethylene, the bilayer actuator exhibits repeatable photoelastic deformation, i.e., the spiral

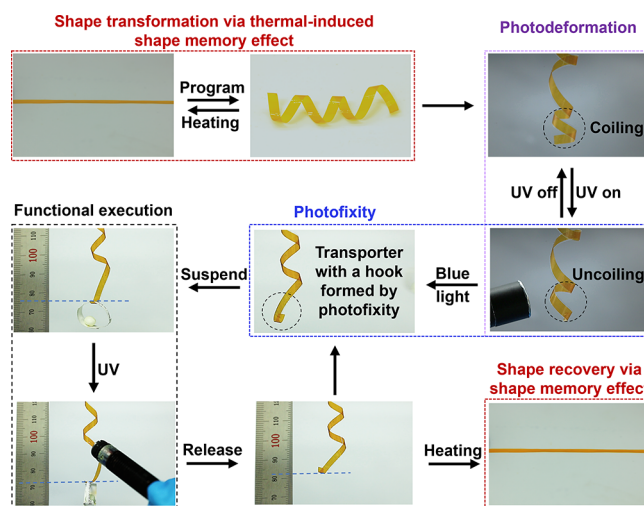


Figure 5. Photographs show the actuators capable of different functional execution through arbitrarily combining shape memory effect, photofixity, and photodeformability.

cantilever undergoes uncoiling upon UV light irradiation and then automatically returns to its initial state when the UV light is turned off. Subsequently, a hook is constructed at one end of the spiral temporary shape via photofixity, thereby realizing the gradual shape change. Eventually, the spiral actuator is converted to a transporter, which acts as an unloading machine. The hook served as a “hand” to hold objects, while the spiral structure acted as an “arm” to lower objects. Upon UV light irradiation, the deformation of the “arm” led to a reduction in the degree of spiraling, thereby transporting the object from a higher position to a lower position (Movie S7). Upon releasing the objects, the transporter resumed its original spiral shape to facilitate retransportation, thereby imitating the process in which the unloading machine rises to a high position for loading objects and then slowly descends to transport them to a lower position. Additionally, the spiral transporter still had the ability to recover to a permanent shape for reprogramming.

In conclusion, we have reported a distinctive polyimide material with the integration of thermal-induced shape memory, photodeformation, and photofixity for the first time. First, unlike those materials that rely on ordered molecular alignment for deformation, the photodeformability of the polyimide in this work is independent of molecular prealignment, which still remains available after thermal programming. This property is significant to avoid the interference of heating with the capability of photodeformation. Second, the T_g (204 °C) of the polyimide is much higher than room temperature, which is favorable to photofixity and the shape retention. Such advantages are the key point toward realization of the integration of different properties for more advanced applications, which allows us to arbitrarily combine them to meet different needs as required. In this scenario, actuators, including a trebuchet and spiral actuator, are demonstrated to show the potential of this idea to realize multiple shape manipulations in one material. This work provides a new idea for the design of multifunctional materials and demonstrates a bright application prospect in the fields of shape manipulation and functional execution.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00195>.

Experimental procedures, characterization, and additional results (Figures S1–S10); Tables S1–S3; and supporting movie captions (Movies S1–S7) (PDF)

Thermal-induced shape recovery of the fan temporary shape of the c-sazo-PI film (MP4)

Thermal-induced shape memory cycle performance of the bent c-s-azo-PI film (MP4)

Thermal-induced shape recovery of the folded c-s-azo-PI film (MP4)

Reversible deformation of the temporary shape programmed by shape memory effect under UV and visible light irradiation (MP4)

Light-driven launching behavior of the trebuchet prepared by c-s-azo-PI film (MP4)

Thermal-induced shape recovery of the spiral temporary shape of the cs-azo-PI film (MP4)

Light-controlled transport of the screw transporter (MP4)

■ AUTHOR INFORMATION

Corresponding Authors

Jia Wei – Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China; orcid.org/0000-0001-6749-8593; Email: weijia@fudan.edu.cn

Yanlei Yu – Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China; orcid.org/0000-0002-4623-3331; Email: ylyu@fudan.edu.cn

Authors

Xuejie Sun – Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

Menghan Zhang – Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

Complete contact information is available at:

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Author Contributions

CRediT: **Xuejie Sun** conceptualization (equal), formal analysis (lead), investigation (lead), writing-original draft (lead), writing-review & editing (lead); **Menghan Zhang** formal analysis (supporting), writing-review & editing (supporting); **Jia Wei** conceptualization (equal), funding acquisition (lead), resources (equal), supervision (equal), writing-review & editing (lead); **Yanlei Yu** resources (equal), supervision (equal).

Notes

The authors declare no competing financial interest.

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