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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This paper by Zhang et al presents a fluorescent robust photoactuator via photo-crosslinking induced single-layered Janus polyimide film, and demonstrates several interesting applications. The key point of this work is the development of a mild and rapid thiol-ene click method to obtain photosensitive double bonds in the main chain for spatial manipulation. The functionality is further enriched by introducing TPE into PI. This work shows high novelty, however, there are some problems that need to be addressed.

1. The actuation mechanism of this actuator should be discussed in depth, by comparing with other reported bimorph actuators. The actuation performance including response time, bending angle, response speed, etc. should be compared with other polymer-based actuators, such as *Adv. Funct. Mater.* 2019, 29, 1808995, *Small* 2023, 2303228, *Adv. Fiber Mater.* 2023, 5, 868, and *eScience*, 2024, 100250, etc.
2. The influence of thickness and light intensity on actuating performance should be studied in detail.
3. For the investigation of actuation performance, the PI film should first irradiate by UV light for 30 minutes to produce a cross-linking gradient. The author demonstrates the gradient crosslinking actuation mechanism by using SEM images. The characterization of related structures should be conducted.
4. Figure 3c exhibits the bending angle-time curve, please recheck and confirm the initial bending angle. The infrared thermal image of the actuator without UV light is not clear (Figure 3h), please provide a clear image.
5. The reported thiol-ene click polymerization is efficient compared to the previously reported click-polymerization based on activated alkynes, please investigate the mechanism or give a discussion.
6. The microstructures of the thiol-based PIs should be investigated by WAXD measurements. The double bonds are photosensitive, please confirm if the double bond can be thermally cross-linked at high temperatures.
7. The TPE-based polymer has a significant secondary transition at around 180°C compared to the other two polymers, further explanation is needed. The authors mixed TPE monomer into PMMA to study the fluorescence properties. The authors should provide the preparation process of the monomer and composite film in the Methods part.
8. The expression of some statements need to be checked and corrected, for instance, P4, lines 132-134, P4, lines 140-141, and P8, lines 283-287.

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors reported a fluorescent robust photoactuator via photo-crosslinking induced single-layered Janus polyimide. The authors developed a novel method to prepare single-layered Janus polyimide for photoactuator, however, the performance of the photoactuator is not attractive. To some extent, the free space UV light source may encounter many problems in practical applications. Also, the capabilities for encrypting, reading, and erasing fluorescent information seem to deviate from the theme of actuators. While I do not question the validity of this work, I am not persuaded that these

findings represent a sufficiently striking advance to justify publication in Nature Communications.

Reviewer #3 (Remarks to the Author):

The manuscript reports synthesis of three photoresponsive polyimides with catalyst-free thiol-yne click polymerization. Interestingly, the fluorescent photoinduced actuators with single-layered janus structure were successfully obtained with UV cause photo-crosslinking. Due to the photothermal effect, the photoresponsive polyimide film exhibited quickly bending deformation behaviours, causing diverse actuators. These contribute to the development of photo-driven actuating materials, which merits publication in NC after considering the following possible revisions.

- 1) What is the highest resolution of the present PI obtained upon photopatterning?
- 2) In Figure 3f, I cannot understand that why microtraces appeared after UV irradiation of the PI film? Generally, only the photo cross-linking cannot induce microscopic deformation of photoresists?
- 3) What is the thermal expansion efficiency of the PI film with and without UV irradiation? This is very important for explaining the photomechanical deformation behaviours.
- 4) The leaping polymer is interesting. What is the stored energy upon UV irradiation to escape from the adhesive?
- 5) In Line 67, "Achieving reversible actuation requires the operation of dual wavelength (UV and visible light) and typically exhibits slow response time." It is not true since the reversible actuation can be obtained by lamellar or composite ways using only one beam of UV light. Please refer to *Angew. Chem. Int. Ed.* 2019, 58, 2655-2659; *Nano Energy*, 2021, 87, 106207; *ACS Applied Materials & Interfaces* 2022, 14, 15632-15640
- 6) Since TPE is importance in the AIE performance, why not using TPE to replace the 6FD to prepare full TPE-containing PIs?

Point-by-point response to the reviewer's comment

Responses to Reviewer #1:

This paper by Zhang et al presents a fluorescent robust photoactuator via photo-crosslinking induced single-layered Janus polyimide film, and demonstrates several interesting applications. The key point of this work is the development of a mild and rapid thiol-yne click method to obtain photosensitive double bonds in the main chain for spatial manipulation. The functionality is further enriched by introducing TPE into PI. This work shows high novelty, however, there are some problems needs to be addressed.

Response: We are grateful for the reviewer's positive comments and valuable suggestions for our manuscript and thank the reviewer for allowing us to revise the manuscript. Given the referee's comments, we have significantly addressed these specific points as you suggested. Our point-by-point answers are listed below.

Specific Comments:

1. The actuation mechanism of this actuator should be discussed in depth, by comparing with other reported bimorph actuators. The actuation performance including response time, bending angle, response speed, etc. should be compared with other polymer-based actuators, such as *Adv. Funct. Mater.* 2019, 29, 1808995, *Small* 2023, 2303228, *Adv. Fiber Mater.* 2023, 5, 868, and *eScience*, 2024, 100250, etc.

Response: Thank you for the kind suggestion. Photoactuators exhibit reversible photomechanical deformation when stimulated by light. It is important to understand the actuation mechanisms to achieve controllable mechanical deformation. Among photoactuators, light energy is mainly converted into thermal or chemical energy in actuating materials. Photothermal actuators are widely developed owing to their simple preparation and design principles. Generally, they have a bi-layered or tri-layered structure and the actuation occurs due to a mismatch in the expansion between layers. For example, Liu et al. (*Adv. Funct. Mater.* 2019, 29, 1808995) designed trilayered photothermal actuators containing a cooling layer, which also enhances the actuation performance by water evaporation-induced volume shrinking. It can achieve fast responses of 0.36, 0.20, and 0.27 s under NIR, white, and blue light, respectively, at relatively small temperature changes (9.9, 4.9, and 12.8 °C). In addition to optical actuators, multi-layer structures can also be used to construct moisture-driven actuators. Zhou et al. (*Small* 2023, 2303228) reported a moisture-driven tri-layer Yin–Yang-interface actuator by combining a polyacrylamide (PAM) hydrogel layer and a polymer layer with an obvious property difference using a tough adhesion interface. The actuator exhibited a large bending curvature of 581×10^{-4} and a response speed of $215 \times 10^{-4} \text{ s}^{-1}$ when exposed to moisture, achieving fast jumping actuation.

The current work reported a fluorescent robust photoactuator via photo-crosslinking induced single-layered Janus polyimide (PI). Weak UV light at 50 mW/cm^2 could trigger the bending of a film, where the bending angle reached 90° in approximately 4 s (Supplementary Fig. 38). Further increasing the light intensity to 200 mW/cm^2 improved the response speed of the actuator, allowing it to bend 90° in 0.43 s. Compared to the azobenzene-containing PIs reported recently (*ACS Macro Lett.* 2023, 12, 921–927) that showed slow response time (maximum bending angle of 88° in 16 s,

70 mW/cm²) and needed the operation of dual wavelength (UV and visible light) for reversible actuation, the actuating performance is significantly improved. The driving mechanism is due to a mismatch of thermal expansion on two sides of the actuator, which is similar to reported bimorph photothermal actuators. The difference is that the actuator was efficiently prepared in one step by irradiating PI film containing photosensitive double bonds with ultraviolet light, which is simpler than a composite approach. The obtained actuators have a gradient cross-linked single-layer structure and there is no typical layer interface, which avoids the interface problems that may exist in multi-layer materials. Importantly, photo-activated deformation was achieved utilizing the photothermal effect of the PI film itself under lower power UV irradiation without the need for any photothermal reagents, facilitating wireless, directional, remote and spatial control when compared with other stimuli.

We have incorporated the following text in the revised manuscript and the actuation mechanism of this actuator has been discussed with bimorph actuators (Page 8, 1st paragraph);

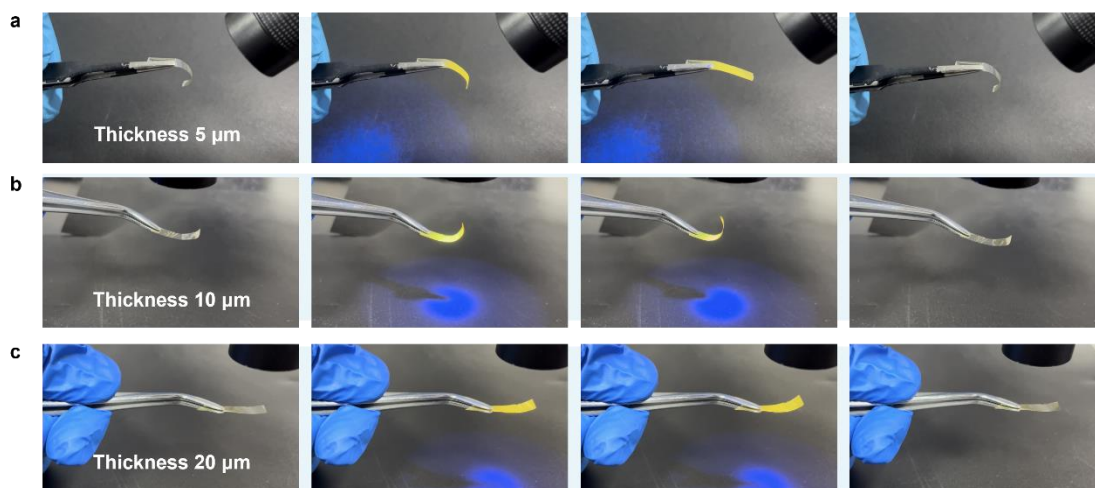
“Photoactuators exhibit reversible photomechanical deformation when stimulated by light. It is important to understand the actuation mechanisms to achieve controllable mechanical deformation. Among photoactuators, light energy is mainly converted into thermal or chemical energy in actuating materials. Photothermal actuators are widely developed owing to their simple preparation and design principles. Generally, they have a bi-layered or tri-layered structure and the actuation occurs due to a mismatch in the expansion between layers to achieve fast responses. The driving mechanism of our current work is due to a mismatch of thermal expansion on two sides of the actuator, which is similar to reported bimorph photothermal actuators. The difference is that the actuator was efficiently prepared in one step by irradiating PI film containing photosensitive double bonds with ultraviolet light to form heterogeneity, which is simpler than a composite approach. As the light attenuation with the penetration depth owing to absorption and scattering, the obtained actuators have a gradient cross-linked single-layer structure (Fig. 3a) and there is no typical layer interface, which avoids the interface problems that may exist in multi-layer materials.”

2. The influence of thickness and light intensity on actuating performance should be studied in detail.

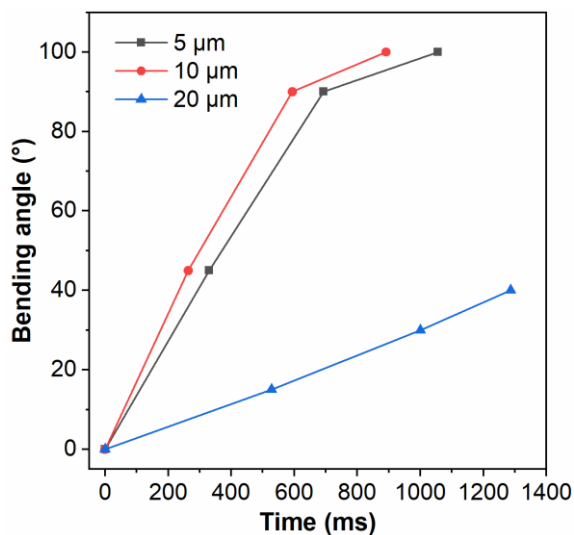
Response: Thank you for your kind suggestion. Following the valuable suggestion from the reviewer, the influence of thickness and light intensity on actuating performance has been studied in detail. Firstly, three 6FDA-PI films of different thicknesses were prepared, which were 5 μm, 10 μm, and 20 μm respectively. These films are illuminated by UV light (intensity: 100 mW/cm² for 30 min) to obtain photoactuators of different thicknesses. Then, the influence of thickness on actuating performance was studied under UV light of about 150 mW/cm² (Supplementary Fig. 35 and 36). The results show that the actuators (thickness 5 μm and 10 μm) can bend about 100° in approximately 800-1000 ms upon exposure to UV light. Continuously increasing the thickness to 20 μm, the actuating performance will be influenced. Therefore, the thickness of the actuators is better to smaller than 20 μm. The performance reduction may be assigned to that when a thicker film is irradiated to form heterogeneity, the thickness of the photo-crosslinked layer is basically the same as that of the thinner film, but the thickness of the uncrosslinked layer is significantly increased.

In addition, the driving properties of actuators (thickness 10 μm) under different light intensities were investigated. As shown in Supplementary Fig. 37 and 38, weak UV light at 50

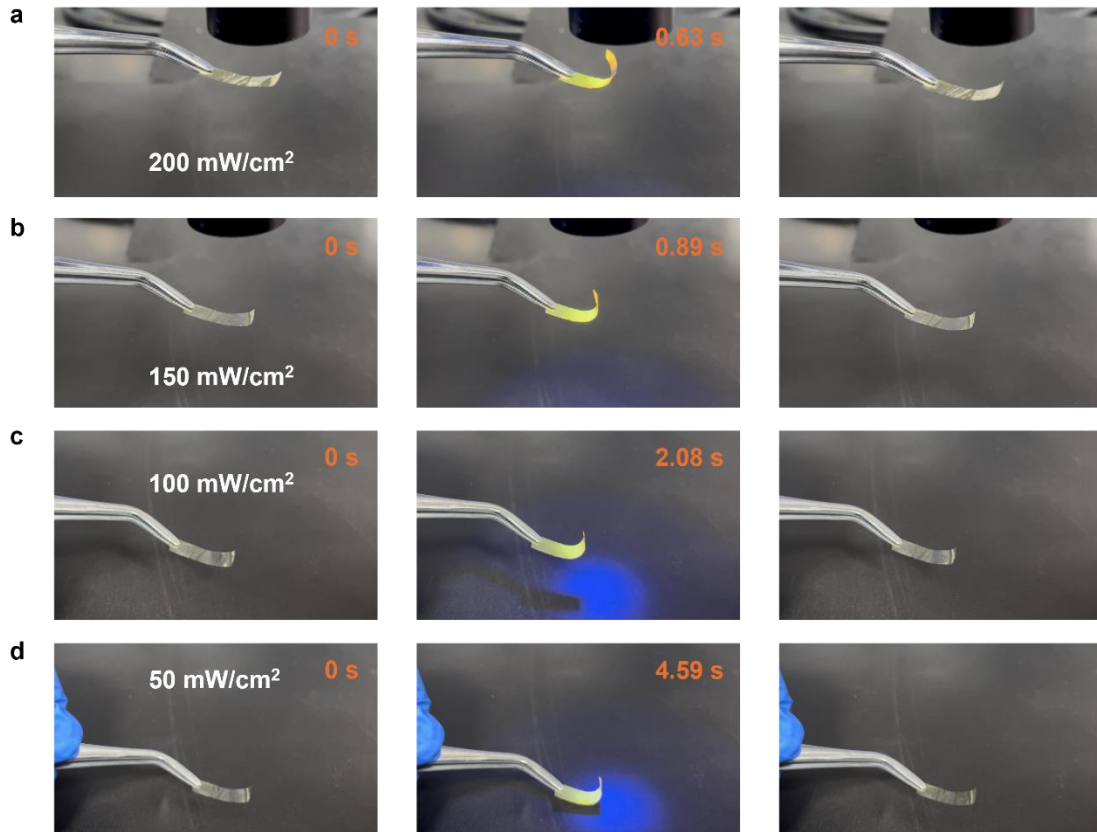
mW/cm² can also trigger the bending of a film, where the bending angle reaches 90° in approximately 4.02 s. Further increasing the light intensity to 100 mW/cm² improves the response speed of the actuator, allowing it to bend 90° in 1.45 s. By increasing the light intensity to 150 and 200 mW/cm², the actuator can bend 90° in 0.59 s and 0.43s, respectively. Compared to the reported azobenzene-containing PIs (*ACS Macro Lett.* 2023, 12, 921–927; *ACS Macro Lett.* 2021, 10, 469–475; *ACS Macro Lett.* 2017, 6, 1432–1437) that showed slow response time and needed the operation of dual wavelength (UV and visible light) for reversible actuation, the actuating performance of PIs in current work is significantly improved.



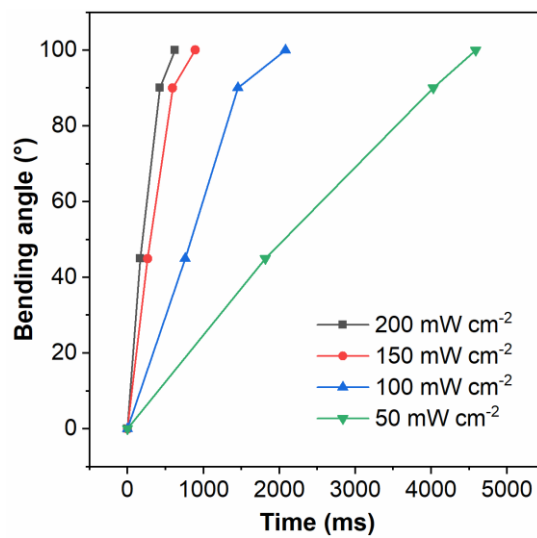
Supplementary Fig. 35 | Photographs to show actuation of the exposed 6FDA-PI films with different thicknesses.



Supplementary Fig. 36 | The bending angles of the exposed 6FDA-PI films with different thicknesses.



Supplementary Fig. 37 | Photographs to show actuation of the exposed 6FDA-PI films under the UV exposure of different intensity.



Supplementary Fig. 38 | The bending angles of the exposed 6FDA-PI films under the UV exposure of different intensity.

We have incorporated the following text in the revised manuscript (Page 9, 1st paragraph);

“Firstly, three 6FDA-PI films of different thicknesses were prepared, which were 5 μm , 10 μm , and 20 μm respectively. These films were illuminated by UV light (intensity: 100 mW/cm^2 for 30 min) to obtain photoactuators of different thicknesses. Then, the influence of thickness on actuating

performance was studied under UV light of about 150 mW/cm² (Supplementary Fig. 35 and 36). The results showed that the actuators (thickness 5 μm and 10 μm) can bend about 100° in approximately 800-1000 ms upon exposure to UV light. Continuously increasing the thickness to 20 μm, the actuating performance will be influenced. Therefore, the thickness of the actuators is better to smaller than 20 μm. The performance reduction may be assigned to that when a thicker film is irradiated to form heterogeneity, the thickness of the photo-crosslinked layer is basically the same as that of the thinner film, but the thickness of the uncrosslinked layer is significantly increased. In addition, the driving properties of actuators (thickness 10 μm) under different light intensities were investigated. As shown in Supplementary Fig. 37 and 38, weak UV light at 50 mW/cm² could also trigger the bending of a film, where the bending angle reached 90° in approximately 4.02 s. Further increasing the light intensity to 100 mW/cm² improved the response speed of the actuator, allowing it to bend 90° in 1.45 s. By increasing the light intensity to 150 and 200 mW/cm², the actuator could bend 90° in 0.59 s and 0.43s, respectively. Compared to the reported azobenzene-containing PIs that showed slow response time and needed the operation of dual wavelength (UV and visible light) for reversible actuation, the actuating performance of PIs is significantly improved.”

3. For the investigation of actuation performance, the PI film should first irradiate by UV light for 30 minutes to produce a cross-linking gradient. The author demonstrates by using SEM images. The characterization of related structures should be conducted.

Response: We thank reviewer 1 for giving this important and constructive suggestion. In the current study, we have prepared fluorescent robust photoactuators via photo-crosslinking induced single-layered Janus polyimide films, exhibiting reversible response driven by a pronounced mismatch in expansion between the front and back sides of the films. It is known to us that most photochemical reactions induced by the strong UV irradiation initiate at the surface, thus causing morphological and chemical differences in the materials' surface (*Macromolecules* 2024, 57, 1266–1276). Therefore, in the current work, SEM was used to examine both sides of the irradiated film to verify the janus structure caused by gradient crosslinking. It can be seen in Fig. 3e that the two sides of the untreated PI film have the same smooth surface morphology. However, after irradiation by UV lamp, microtraces appear on the front side, while the back side remains smooth morphology (Fig. 3f), indicating that a cross-linking gradient is produced due to the insufficient penetration depth of UV light.

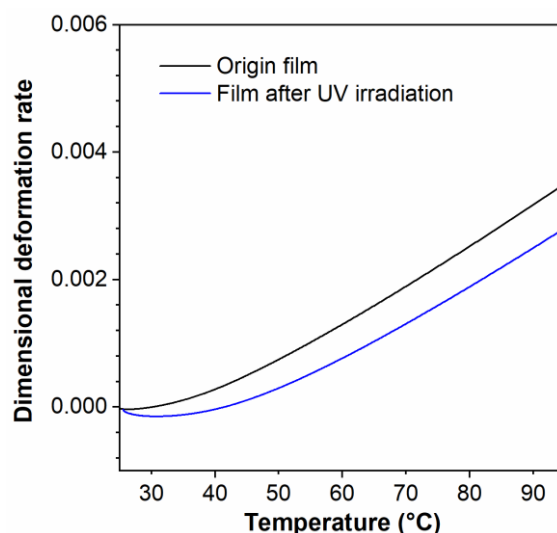
The characterization of related structures was further proved by tests of thermal expansion on the films before and after UV treatment. If the film undergoes cross-linking after irradiation, the dimensional expansion rate should be lower than that of the original film. Since the actuator obtained by irradiating only one side of the film also responds to heat, the irradiated film can be driven during the heating process, which affects the test results. Based on this consideration, both sides of the PI film were irradiated by the same condition (UV irradiation for 30min, 100 mW/cm²) to obtain the irradiated film. Then these films were heat treated, followed by a thermal mechanical analysis (TMA) test and the results were shown in Supplementary Fig. 39. It can be seen that the original film gradually begins to expand as the temperature increases from room temperature, while the irradiated film doesn't expand significantly from 25 °C to about 45 °C. At about 45 °C, the dimensional deformation rate of the untreated film is nearly 5 times that of the irradiated film. Therefore, the actuators obtained by irradiating only one side of the film have a cross-linking gradient, which leads

to reversible actuation.

We have incorporated the following text in the revised manuscript (Page 9, 1st paragraph);

The characterization of related structures was further proved by tests of thermal expansion on the films before and after UV treatment. If the film undergoes cross-linking after irradiation, the dimensional expansion rate should be lower than that of the original film. Since the actuator obtained by irradiating only one side of the film also responds to heat, the irradiated film can be driven during the heating process, which affects the test results. Based on this consideration, both sides of the PI film were irradiated by the same condition (UV irradiation for 30 min, 100 mW/cm²) to obtain the irradiated film. Then these films were heat treated, followed by a thermal mechanical analysis test and the results were shown in Supplementary Fig. 39. It could be seen that the original film gradually began to expand as the temperature increased from room temperature, while the irradiated film didn't expand significantly from 25 °C to about 45 °C. At about 45 °C, the dimensional deformation rate of the untreated film is nearly 5 times that of the irradiated film. Therefore, the actuators obtained by irradiating only one side of the film have a cross-linking gradient.

We have incorporated the following figure in the revised supplementary information (Page S30);



Supplementary Fig. 39 | The thermal expansion curves of the 6FDA-PI films before and after UV irradiation.

4. Figure 3c exhibits the bending angle-time curve, please recheck and confirm the initial bending angle. The infrared thermal image of the actuator without UV light is not clear (Figure 3h), please provide a clear image.

Response: Thank you for your kind suggestion. The initial bending angle has been corrected to 0°, and the maximum bending angle when exposed to UV light is 180° (Fig. 3c). Besides, a clear infrared thermal image of the actuator with and without UV light is provided as shown in Fig. 3h.

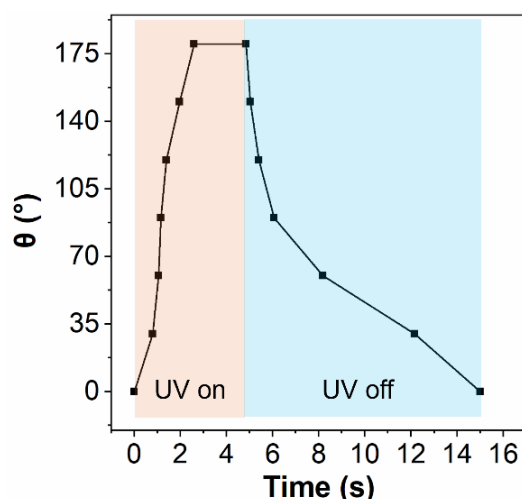


Fig. 3c. Dependence of the bending angle on the operation time for 6FDA-PI film.

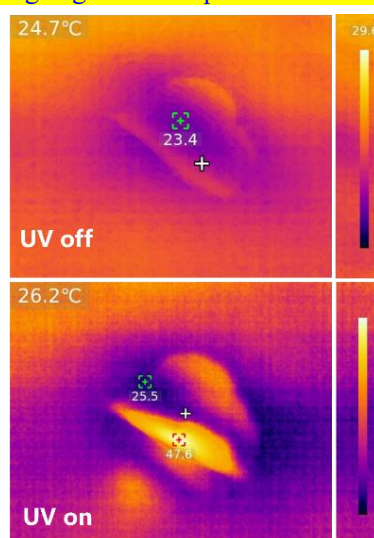


Fig. 3h. Infrared thermal images of a 6FDA-PI based actuator with and without UV light (100 mW cm^{-2}).

5. The reported thiolene click polymerization is efficient compared to the previously reported click-polymerization based on activated alkynes, please investigate the mechanism or give a discussion.

Response: Thank you for your kind suggestion. Alkynes with electron-withdrawing substituents in conjugation with the acetylenic moiety (i.e., activated alkynes) are extremely useful synthetic intermediates due to their high reactivity with nucleophiles in conjugate addition reactions. Ubiquitous nucleophiles such as thiols, amines, and alcohols are commonly employed and, consequently, among the most well-developed. With improvements in reaction design, including catalyst development and an expansion of the substrate scope to feature more electrophilic alkynes, many examples now present features that are congruent with click chemistry. In this context, reactions based on non-activated alkynes seem to have been forgotten due to their undesirable reactivity. However, it is not only activated alkynes that exhibit the features of click chemistry.

In 2014, Tang et al. (*Macromolecules* 2014, 47, 1325–1333) reported a facile and powerful click polymerization of aromatic diynes and dithiols to produce soluble and regioregular functional poly(vinylene sulfide)s, which could be completed under very mild conditions (in THF at 30 °C)

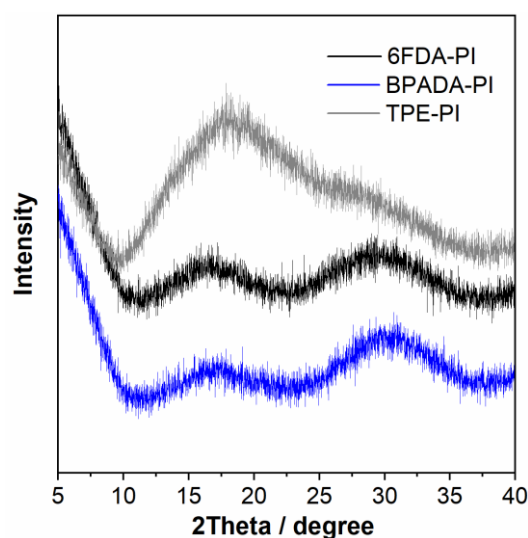
without using external catalyst after as short as 2 h. This demonstrated the strong potential of non-activated alkynes in polymerization reactions. In 2021, our group (*Macromolecules* 2021, 54, 11256–11268) reported a click polymerization of non-activated alkynes containing bisimide with aromatic dithiols, which could be accomplished without any catalyst within 2 h at 25 °C and produced PIs with fairly high weight-average molecular weight (M_w up to 156,000 g·mol⁻¹). The PI films showed good tensile strength as high as 114.9 MPa, desirable thermal resistance with a glass transition temperature of 214 °C, and thermal decomposition temperature above 360 °C, demonstrating its ability in the field of engineering plastic preparation. Further exploration of the mechanism revealed that the polymerization mechanism of non-activated alkynes with thiols was based on a radical-mediated mechanism, which was different from the nucleophile-based pathway of activated alkynes. Based on these exciting findings, we wondered if the polymerization rate of non-activated alkynes with thiols could be further improved by structural design. In 2021, Erdem et al. (*J. Phys. Chem. A* 2021, 125, 3556–3568) systematically investigated the mechanism of radical-mediated thiol-yne reactions, focusing on the structural influences of thiol and alkyne functionalities. The results showed that the effect of substitution at the para position of a thiophenol radical is highly significant. While the electron-withdrawing groups at this position increase the forward rate constant, electron-donating groups decrease the constant for the propagation step since the more electrophilic sulfur atoms react faster with alkynes.

In the current work, we designed the monomer structure of dithiol, that is, 6FDA was reacted with 4-aminothiophenol to prepare 6FSH, so that the electron-withdrawing group was introduced at the para position of a thiophenol radical. Through the screening of polymerization conditions, we found that the polymerization rate of 6FSH and non-activated diynes was further improved. Simply mixing the two polymeric monomers in THF without any catalyst for 15 min could produce PIs with high molecular weights up to 126 kDa for robust self-standing films, demonstrating the important potential of polymerization based on non-activated alkynes in polymer synthesis.

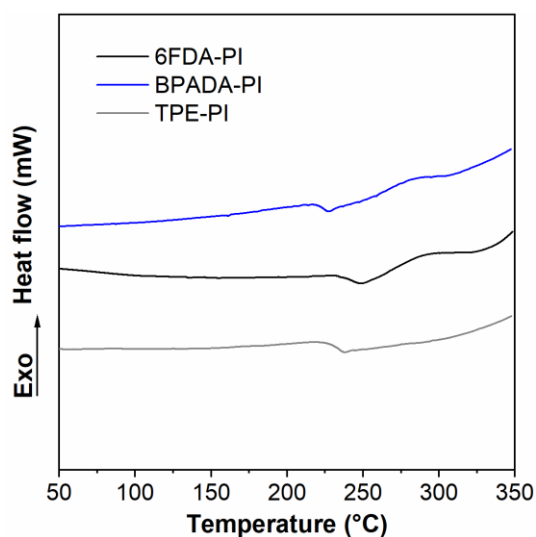
6. The microstructures of the thiol-based PIs should be investigated by WAXD measurements. The double bonds are photosensitive, please confirm if the double bond can be thermally cross-linked at high temperatures.

Response: Thank you for your kind suggestion. With the suggestions of reviewers, we conducted WAXD tests on several polymers, as shown in Supplementary Fig. 40. All PI films exhibited an amorphous-like morphology with a broad peak. To determine if the double bond can be thermally cross-linked at high temperatures, DSC tests were performed. The results (Supplementary Fig. 41) showed that during the process of heating up to 350 °C, the polymer only underwent a significant glass transition without thermal crosslinking. Therefore, the photosensitive double bond was thermally stable within 350 °C.

We have incorporated the following figures in the revised supplementary information (Page S30 – S31);



Supplementary Fig. 40 | WAXD curves of PIs.



Supplementary Fig. 41 | DSC curves of PIs.

7. The TPE-based polymer has a significant secondary transition at around 180°C compared to the other two polymers, further explanation is needed. The authors mixed TPE monomer into PMMA to study the fluorescence properties. The authors should provide the preparation process of the monomer and composite film in the Methods part.

Response: Thank you for your kind suggestion. The difference between TPE based polymer and the other two types of polymers lies in the dianhydride units. Compared to the BPADA and 6FDA based PIs, TPE-PI has two free benzene groups, allowing for secondary transformation below the glass transition temperature. We have provided the preparation process of the monomer and composite film and incorporated the following text in the Methods part of the revised manuscript (Page 21, 2nd paragraph);

“The TPE-APA thin films were prepared by spin-coating the dichloromethane solutions of TPE-APA (~20 mg/mL) on silicon wafers at 1000 rpm for 1 min. The PMMA was dissolved in dichloromethane solution and prepared into 18 wt% solution, followed by dissolving TPE-APA monomer in the solution (~20 mg/mL) and spin-coating on silicon wafers at 1000 rpm for 1 min to

obtain TPE-APA /PMMA films.”

8. The expression of some statements need to be checked and corrected, for instance, P4, lines 132-134, P4, lines 140-141, and P8, lines 283-287.

Response: Thank you for your kind suggestion. The expression of the statements has been checked and corrected. The revised statements are as follows:

P4, lines 132-134: “This powerful catalyst-free thiol-yne click polymerization provides a way for the preparation of linear mono-addition polymers.”

P4, lines 140-141: “We later demonstrate the effects of material thickness and UV irradiation time on driving performance.”

P8, lines 283-287. “Because this concept depends on light attenuation, the thickness of the PI film also plays a crucial role in affecting the reversible actuation. Firstly, three 6FDA-PI films of different thicknesses were prepared, which were 5 μm , 10 μm , and 20 μm respectively. These films are illuminated by UV light (intensity: 100 mW/cm^2 for 30 min) to obtain photoactuators of different thicknesses. Then, the influence of thickness on actuating performance was studied under UV light of about 150 mW/cm^2 (Supplementary Fig. 35 and 36). The results showed that the actuators (thickness 5 μm and 10 μm) can bend about 100° in approximately 800-1000 ms upon exposure to UV light. Continuously increasing the thickness to 20 μm , the actuating performance will be influenced. Therefore, the thickness of the actuators is better to smaller than 20 μm . The performance reduction may be assigned to that when a thicker film is irradiated to form heterogeneity, the thickness of the photo-crosslinked layer is basically the same as that of the thinner film, but the thickness of the uncrosslinked layer is significantly increased. In addition, the driving properties of actuators (thickness 10 μm) under different light intensities were investigated. As shown in Supplementary Fig. 37 and 38, weak UV light at 50 mW/cm^2 could also trigger the bending of a film, where the bending angle reached 90° in approximately 4.02 s. Further increasing the light intensity to 100 mW/cm^2 improved the response speed of the actuator, allowing it to bend 90° in 1.45 s. By increasing the light intensity to 150 and 200 mW/cm^2 , the actuator could bend 90° in 0.59 s and 0.43s, respectively. Compared to the reported azobenzene-containing PIs that showed slow response time and needed the operation of dual wavelength (UV and visible light) for reversible actuation, the actuating performance of PIs is significantly improved.”

Responses to Reviewer #2:

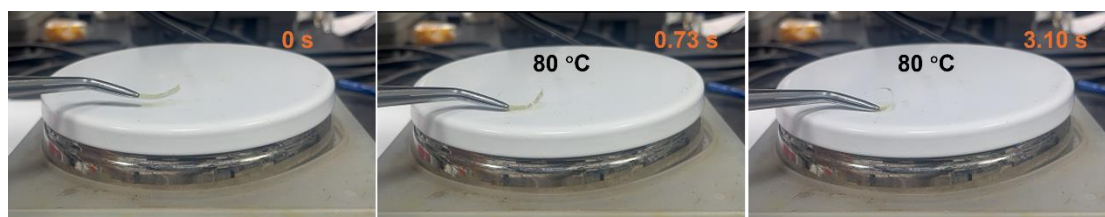
In this manuscript, the authors reported a fluorescent robust photoactuator via photo crosslinking induced single-layered Janus polyimide. The authors developed a novel method to prepare single-layered Janus polyimide for photoactuator, however, the performance of the photoactuator is not attractive. To some extent, the free space UV light source may encounter many problems in practical applications. Also, the capabilities for encrypting, reading, and erasing fluorescent information seems to deviate from the theme of actuators. While I do not question the validity of this work, I am not persuaded that these findings represent a sufficiently striking advance to justify publication in Nature Communications.

Response: We thank Reviewer #2 for the kind and valuable perspective as they correctly described the synthesis of a fluorescent robust photoactuator via photo crosslinking induced single-layered Janus polyimide. The purpose of this study was to demonstrate the ability of thiol-yne click reaction to create photosensitive polyimides and develop a flexible and convenient way to access functional photoactuators. Firstly, an efficient and mild thiol-alkyne click polymerization was developed. The two monomers could be polymerized without any catalyst at 30 °C for 15 min to obtain high molecular weight PIs. At the same time, the reaction of alkyne and thiol could take place through anti-Markovnikov addition pathway, thereby retaining the photosensitive double bond in the polymer backbone. Compared with the complicated preparation of azo-containing polymers or multi-layer composite structures to achieve optical actuation, only UV light treatment of PI films is needed to construct single-layered PI actuators with reversible deformation. Furthermore, the introduction of tetraphenylethylene (TPE), a prototype AIEgen into PI achieves a combination of actuation and other functionalities.

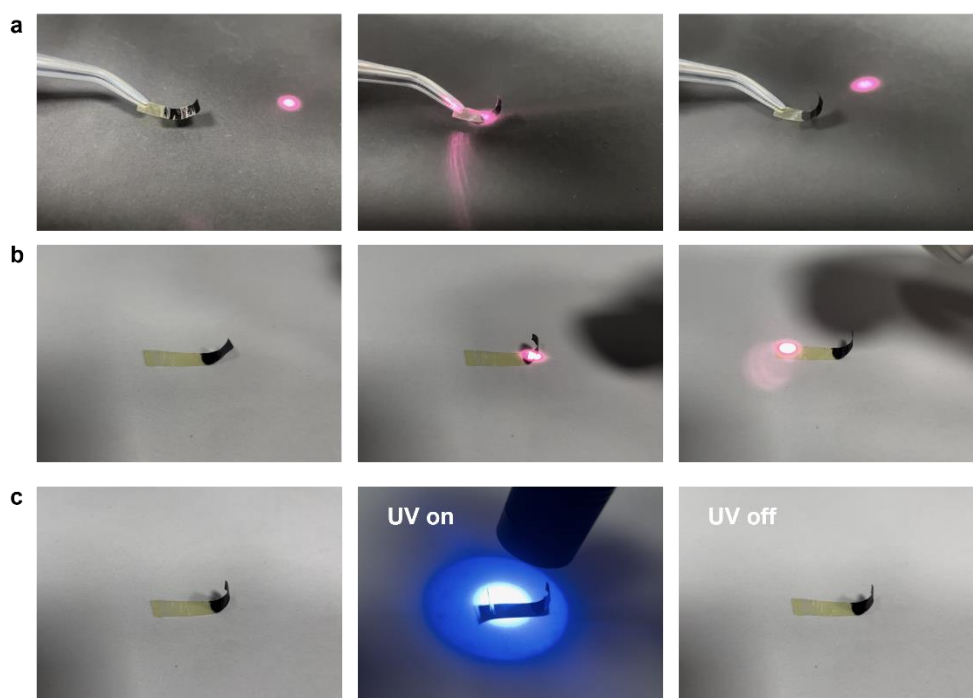
We are extremely sorry for the confusion that we have not compared the performance of the current PI actuators with the previously reported ones. Up to now, soft materials such as LCE and hydrogel have been widely studied due to their large deformation and excellent programmability. Single rigid materials, especially PIs, although they possess excellent mechanical and thermal properties, actuators based on PI often have limited photoresponse. How to endow high-performance PI materials with fast photoresponsive properties is a challenge. Although some works based on azobenzene-containing PI (azo-PI) for achieving reversible deformation demonstrate the application prospect of high-performance materials in the fields of shape manipulation and functional execution, there are still some important issues that need to be addressed. For example, the driving speed of these deformable PI materials is relatively slow. Meanwhile, as the driving mechanism is based on the trans-cis isomerization of azobenzene, visible light is required to quickly restore the initial state. In response to these challenges, a Janus strategy is proposed in the current work to endow rigid PI materials with fast reversible actuation using a single wavelength. As shown in Supplementary Fig. 37 and 38, weak UV light at 50 mW/cm² can also trigger the bending of a film, where the bending angle reaches 90° in approximately 4.02 s. Further increasing the light intensity to 100 mW/cm² improves the response speed of the actuator, allowing it to bend 90° in 1.45 s. By increasing the light intensity to 150 and 200 mW/cm², the actuator can bend 90° in 0.59 s and 0.43s, respectively. After the UV light is removed, the bent film quickly returns to its original state without using visible light.

We also thank the reviewer for raising the concern that to some extent the free space UV light source may encounter many problems in practical applications, which is indeed a challenge that

researchers working on actuator materials should address in the future. Among different stimuli, light has arisen as a particularly attractive alternative due to its wireless, directional, remote, and spatial control. Most of the photoresponsive materials are based on UV light stimulation because molecules or polymers can easily undergo reversible structural changes when illuminated by UV light, such as azobenzene (*Nature*, 2017, 546, 632; *Nat. Commun.* 2018, 9, 4148; *Adv. Funct. Mater.* 2022, 32, 2208312;) or diarylethene (DAE) (*Nat. Mater.* 2023, 22, 1152–1159), a typical two-state photomechanical switch that undergoes UV photoinduced ring opening and closing upon relaxation via a conical intersection. Given the potential problems of using UV light, photothermal actuators responsive to infrared or visible light are widely studied owing to their simple method of preparation and design principles, and safe operation environment. Although the current work did not use visible or infrared light to drive the films, the actuation is based on photothermal mechanism with a low driving temperature. Supplementary Fig. 34 demonstrates that the actuator can also perform slow response under thermal stimulation at a lower temperature of 40 °C. Further heating to 80 °C (Supplementary Fig. 42), its driving speed and amplitude are greatly improved. Following a valuable suggestion from the reviewer, we added some experiments to demonstrate that our proposed strategy could also easily prepare actuators responsive to infrared light. As shown in Supplementary Fig. 43 a, one side of the film was painted black with a marker pen, and it was found that under the light irradiation of 808 nm, the film could undergo reversible actuation. This simple strategy can further achieve the response of multi-wavelength lights in one material. As shown in Supplementary Fig. 43 b, the right side of a long strip of actuator was blackened with a marker while leaving the left side untreated. When 808 nm light was irradiated on the right side of the film, reversible actuation occurred due to the photothermal effect of the black film, while the left part of the film could not be driven by irradiation due to the non-absorption of infrared light. However, when the entire film was exposed to UV light (Supplementary Fig. 43 c), reversible driving occurred throughout the film. Overall, the preparation strategy of photoinduced single-layer Janus PI films proposed in this work is an extensible idea, which is not only limited to response to UV light, but also can achieve reversible actuation of high-performance PIs through thermal and near-infrared light irradiation. Thank you again for your kind suggestions, which provide research direction for our follow-up work focusing on actuators responsive to infrared or visible light.



Supplementary Fig. 42 | Actuation of the exposed 6FDA-PI film at 80 °C heating table.



Supplementary Fig. 43 | Actuation of the exposed 6FDA-PI film under 808 nm light and UV light.

We also thank Reviewer 2 for raising the query that the capabilities for encrypting, reading, and erasing fluorescent information seem to deviate from the theme of actuators. Yes, in this work, we have demonstrated the capabilities for encrypting, reading, and erasing fluorescent information of the photoactuators. In nature, many organisms are able to collaboratively change their shape and color to camouflage, communicate, or intimidate to survive in their environment. For example, cephalopods change their appearance to blend with their surrounding environment while hunting or avoiding predators. Therefore, intelligent responsive materials should not be limited to changing shape when stimulated, but be able to adjust their color and shape according to environmental changes. Aggregation-induced emission (AIE) luminogens are weakly emissive or non-emissive in the solution but present high emission in the aggregation state, which is believed to be caused by the limitation of intramolecular motion effects. Some materials containing AIEgen (*Angew. Chem. Int. Ed.* 2021, 60, 11247-11251; *Adv. Funct. Mater.* 2021, 31, 2010578; *Adv. Mater.* 2020, 32, 1906493) change fluorescence color or brightness and perform actuation at the same time, making these materials similar to living organisms. Inspired by these materials, the current work prepared a diyne containing TPE and introduced it into PI, which endows the polymer with UV-activated fluorescence properties. Based on this characteristic, the combination of patterning and driving performance of the actuator was achieved using a photomask (Fig. 5f). This is because photo crosslinking simultaneously achieves the construction of non-uniform structures and enhances fluorescence intensity. The advantage lies in 1. the combination of multifunctionality makes the functionality of smart materials more like advanced organisms in nature. For example, when stimulated by invaders, mimic octopuses simultaneously change their shape and exhibit patterns on their bodies to mimic poisonous anemones, thereby achieving the goal of transmitting threatening information. 2. Further irradiation with UV light can eliminate the PL pattern (Fig. 5c), allowing the material to recover its characteristics as a single actuation material without deviating from the theme of actuators. 3. The UV-activated fluorescence property enables the FL pattern to be encrypted on the material and can be erased after reading, establishing TPE-PI as a multifunctional smart

fluorescent material, which holds promise for applications in information encryption, anticounterfeiting, and other related fields.

Responses to Reviewer #3:

The manuscript reports synthesis of three photoresponsive polyimides with catalyst-free thiol-yne click polymerization. Interestingly, the fluorescent photoinduced actuators with single-layered janus structure were successfully obtained with UV cause photo-crosslinking. Due to the photothermal effect, the photoresponsive polyimide film exhibited quickly bending deformation behaviours, causing diverse actuators. These contribute to the development of photo-driven actuating materials, which merits publication in NC after considering the following possible revisions.

Response: We thank the reviewer for the high recognition and positive comments. This manuscript has been carefully improved base on the following constructive suggestions. Thanks again!

Specific Comments:

1. What is the highest resolution of the present PI obtained upon photopatterning?

Response: We thank Reviewer 3 for raising this query. Photosensitive polyimide (PSPI) is a kind of material sensitive to high energy radiation such as ultraviolet light, X-rays, etc. According to the difference in photolithographic patterns after exposure and development, it can be divided into negative photosensitive polyimide (n-PSPI) and positive photosensitive polyimide (p-PSPI). When n-PSPI is exposed, the exposure region is photocrosslinked, reducing the solubility of the polymers and is preserved. The unexposed region is dissolved in the developing solution and the resulting pattern is the opposite of the mask plate pattern. n-PSPI has the advantages of high sensitivity, good adhesion to silicon wafers and low cost, but it also has the defects of low resolution. We are working to improve the resolution of n-PSPI. The resolution of n-PSPI reported so far is generally above 5 μm . For example, Yang et al. (*Eur. Polym. J.* 2023, 192, 112071) reported a series of n-PSPI showing high transparency and good photolithographic performance with resolution of 8 μm (via) and 7 μm (line). To the best of our knowledge, Hsu et al. (*Polym. Adv. Technol.* 2021, 32, 663–669) reported low-temperature curable, alkaline-developable n-PSPI with the highest resolution up to 2 μm . Unfortunately, due to the reabsorption through the charge transfer effect in PI chains, these reported negative patterns usually show non-fluorescence. In this work, we simultaneously introduced AIEgen (aggregation-induced emission luminogens) and photosensitive double bonds into PI, which can form a clear negative pattern of about 5 μm by UV photo-crosslinking and development (Fig. 2i and j). Importantly, the photocrosslinking also leads to a further increase in fluorescence intensity, thus obtaining both 2D and 3D fluorescence patterns (Fig. 2l-n).

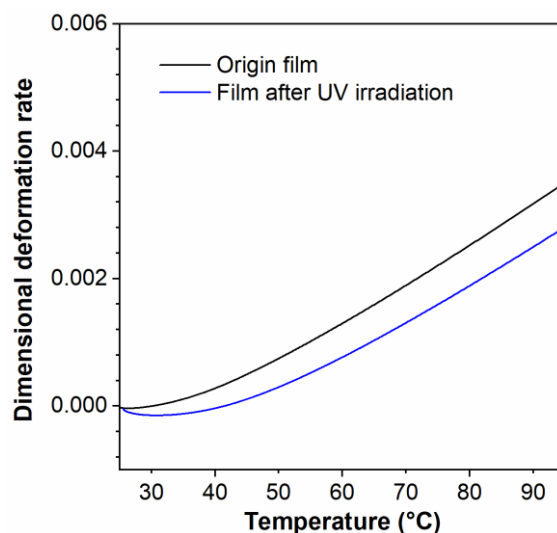
2. In Figure 3f, I cannot understand that why microtraces appeared after UV irradiation of the PI film? Generally, only the photo cross-linking cannot induce microscopic deformation of photoresists?

Response: We thank Reviewer 3 for raising this query. In the preparation process of n-PSPI, the spin-coated film containing resins with high sensitivity groups, photoinitiators, photocrosslinkers, polymerization inhibitor and adhesion promoter etc. is usually exposed to ultraviolet light under low exposure doses ranging from 0–200 mJ/cm^2 , which can't induce the microscopic deformation. However, the PI films reported in this work contain intrinsic photosensitive double bonds. In the absence of other additives, the construction of heterogeneous actuators requires the film to be exposed to ultraviolet light with an extremely high exposure dose of 180 J/cm^2 , which is much

higher than the exposure doses of photoresist preparation. It is known to us that most photochemical reactions induced by the strong UV irradiation initiate at the surface, thus causing morphological and chemical differences in the materials' surface (*Macromolecules* 2024, 57, 1266–1276). Zhang et al. (*Macromolecules* 2024, 57, 1266–1276) reported new intrinsically UV-resistant PI films with greatly enhanced mechanical stability by copolymerization with UV-absorbing diamine. Prior to UV irradiation, all PI films showed smooth and flat surfaces without visual defects. However, after UV irradiation, numerous cracks could be clearly observed on the surface of PI without UV-absorbing groups, representing the defects derived from the chain cleavage. However, the PI films with UV-absorbing groups displayed a “dotted patch” structure. Zhang et al. believed that this phenomenon arises from the cross-linking reactions of UV-absorbing groups occurring on the surface with exposure to UV irradiation. Similarly, in this work, the cross-linking reactions of photosensitive double bonds occur on the surface with exposure to strong UV irradiation and therefore the morphology of the irradiated side will inevitably change.

3. What is the thermal expansion efficiency of the PI film with and without UV irradiation? This is very important for explaining the photomechanical deformation behaviours.

Response: We thank reviewer 3 for providing this important and constructive suggestion. In the current study, we have prepared fluorescent robust photoactuators via photo-crosslinking induced single-layered Janus PI films, exhibiting reversible response driven by a pronounced mismatch in expansion between the front and back sides of the films. With the reviewer's comments, tests of thermal expansion were performed on the films before and after UV treatment to better demonstrate the driving behavior. Since the actuator obtained by irradiating only one side of the film also responds to heat, the irradiated film can be driven during the heating process, which affects the test results. Based on this consideration, both sides of the PI film were irradiated by the same condition (UV irradiation for 30min, 100 mW/cm²) to obtain the irradiated film. Then these films were heat treated, followed by thermal mechanical analysis (TMA) test and the results were shown in Supplementary Fig. 39. It can be seen that the original film gradually began to expand as the temperature increased from room temperature, while the irradiated film did not expand significantly from 25 °C to about 45 °C. At about 45 °C, the dimensional deformation rate of the untreated film was nearly 5 times that of the irradiated film, thus resulting in obvious photomechanical deformation behavior.



Supplementary Fig. 39 | The thermal expansion curves of the 6FDA-PI films before and after UV irradiation.

4. The leaping polymer is interesting. What is the stored energy upon UV irradiation to escape from the adhesive?

Response: We thank Reviewer 3 for raising this query. The PI films bent upwards when exposed to UV light and using a small amount of adhesive can store the energy generated by light. When the driving force for upward bending is larger than the adhesive force, the stored energy is suddenly released, achieving a jump. At this moment, the stored energy is converted into kinetic energy. Based on the maximum take-off velocity ($v = 0.60 \text{ m s}^{-1}$) and the mass ($m = 5.0 \text{ mg}$) of the actuator, the kinetic energy ($E_k = 0.5 mv^2$) of the soft jumping robot at take-off was calculated to be approximately $0.9 \mu\text{J}$.

5. In Line 67, “Achieving reversible actuation requires the operation of dual wavelength (UV and visible light) and typically exhibits slow response time.” It is not true since the reversible actuation can be obtained by lamellar or composite ways using only one beam of UV light. Please refer to *Angew. Chem. Int. Ed.* 2019, 58, 2655-2659; *Nano Energy*, 2021, 87, 106207; *ACS Applied Materials & Interfaces* 2022, 14, 15632-15640

Response: Thank you for the kind suggestion. We have cited the references on actuators via lamellar or composite ways mentioned by referee 3 as ref. 29-31 and revised the introduction to better present the difficulties in this field. With the reviewer’s comments, we added the following description to the second paragraph of page 2 in the revised manuscript:

“Yet, azobenzene-containing single materials always require the operation of dual wavelength (UV and visible light) for reversible actuation, showing poor driving performance when compared to lamellar or composite actuators using only one beam of UV light.”

6. Since TPE is importance in the AIE performance, why not using TPE to replace the 6FDA to prepare full TPE-containing PIs?

Response: Thank the reviewer for the valuable suggestion. Polyimides have poor solubility in common organic solvents, especially THF, due to their rigid molecular chains and strong interchain interactions. In our system, the optimal solvent selected for polymerization is THF, so how to design the structure of alkyne and dithiol monomers to ensure that the PI during polymerization in THF will not precipitate early and lead to low molecular weight is a key problem. In our previous study (*Macromolecules* 2021, 54, 11256–11268), commercial dithiols 4,4'-thiobisbenzenethiol (TBT) and 4,4'-biphenyldithiol (BPT) were used to prepare PIs. It was found that when BPT with poor solubility was polymerized with BPADA-APA, the polymer precipitated early and a high molecular weight polymer could not be obtained. However, using TBT could avoid this situation. Therefore, the rational design of the structure of dithiol is very important for successful polymerization.

A large number of studies have shown that the introduction of CF₃ in PI is conducive to improving the solubility of PIs, so 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) is the most popular dianhydride for the preparation of soluble PIs. Therefore, based on this consideration, we use 4-aminothiophenol and 6FDA to prepare CF₃-containing dithiol, so that polymerization with other kinds of dialkynes can effectively avoid the precipitation of PIs, thus producing high molecular weight polymers and tough films. However, we found that the prepared TPE dianhydride was less soluble than 6FDA. In order to avoid the precipitation of the PI during polymerization, TPE structure was not used to prepare TPE-containing dithiol to obtain full TPE-containing PIs. In future, we will modify TPE-based dianhydride, such as introducing CF₃ to further improve solubility, so as to prepare full TPE-based PI.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

now this manuscript can be accepted.

Reviewer #2 (Remarks to the Author):

All my concerns have been well addressed. I suggest the publication of this manuscript.

Reviewer #3 (Remarks to the Author):

after carefully reading the reponse to reviewers, I suggest acceptance of the revised manuscript at the present format since all my concerned issues have been addressed.