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Bioinspired Anisotropic Hydrogel Actuators with On–Off Switchable and Color-Tunable Fluorescence Behaviors

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An effective approach to develop a novel macroscopic anisotropic bilayer hydrogel actuator with on–off switchable fluorescent color-changing function is reported. Through combining a collapsed thermoresponsive graphene oxide-poly(*N*-isopropylacrylamide) (GO-PNIPAM) hydrogel layer with a pH-responsive perylene bisimide-functionalized hyperbranched polyethylenimine (PBI-HPEI) hydrogel layer via macroscopic supramolecular assembly, a bilayer hydrogel is obtained that can be tailored and reswells to form a 3D hydrogel actuator. The actuator can undergo complex shape deformation caused by the PNIPAM outside layer, then the PBI-HPEI hydrogel inside layer can be unfolded to trigger the on–off switch of the pH-responsive fluorescence under the green light irradiation. This work will inspire the design and fabrication of novel biomimetic smart materials with synergistic functions.

1. Introduction

Nature is a perpetual source of inspiration for exploring artificial intelligent materials that can adapt and actuate in response to environmental stimuli.[1] In particular, polymeric hydrogel actuators that are able to transfer various external stimuli to controllable mechanical deformations such as swelling/shrinking,[2] bending,[3] and buckling,[4] have attracted tremendous interest and can be used as switches,[5] microrobots,[6] artificial muscles,[7] and motors.[8] In order to expand the utility and functionality of polymeric hydrogel actuators, it is advantageous to develop hydrogels that can respond to multiple stimuli and mimic the living systems for yielding new applications.

It is well known that many animals/plants found in nature, such as chameleons, octopuses, and honeysuckles, can tune their body colors to camouflage or communicate in specific surroundings. These color changes of in vivo tissues are caused by various complex movements/deformations and the transformation of optical properties including reflection, scattering, absorption, refraction, and even luminescence, triggered by environmental stimuli.[9] Inspired by the biological color-changing capacity, considerable progress has been achieved in fabricating polymeric hydrogels with color-tunable behavior upon the external trigger. For instance, Gong[10] et al. developed an anisotropic poly(dodecylglyceryl itaconate)/polyacrylamide hydrogel with unidirectional orientation of lamellar bilayers, which could provide reversibly tunable structural color under a controlled stress/strain. Würthner[11] et al. explored thermoresponsive supramolecular hydrogels that change color between dark red and bright orange based on the self-assembly of perylene bisimide chromophores bearing oligo ethylene glycol. We have designed a triphenylmethane leucohydroxide-modified poly(*N*-isopropylacrylamide) (PNIPAM) microgel-based etalon with multi-responsive color tunability induced by the swelling or shrinking of microgel photonic crystals via external stimuli.[12] These color-changing polymeric hydrogels hold great potential applications to explore intelligent visual detection/display systems including monitors, sensors and some biomimetic color-changing systems.[13] However, compared with living organisms in nature, the currently investigated color-tunable hydrogels can only provide simple swelling/shrinking deformation, as it is challenging to integrate color-changing and complex shape deformation abilities in one system.

Herein, we present a macroscopic anisotropic composite polymeric hydrogel with synergistic shape deformation and color-changing functions (**Scheme 1**a). To accomplish this, a thermoresponsive graphene oxide-PNIPAM (GO-PNIPAM) hydrogel sheet and a pH-responsive perylene bisimide-functionalized hyperbranched polyethylenimine (PBI-HPEI) fluorescent hydrogel sheet were prepared. The GO-PNIPAM

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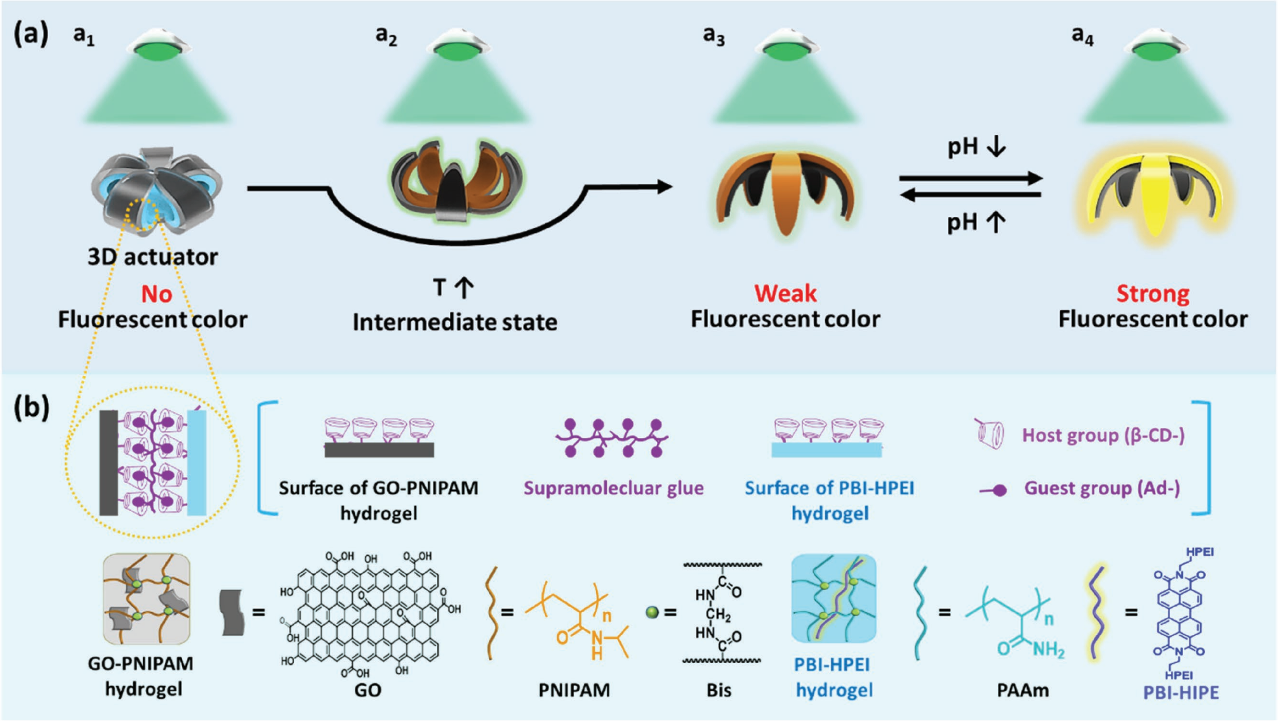

Scheme 1. a) The fluorescent color change and 3D complex shape change of the macroscopically anisotropic stimuli-responsive polymer hydrogels (MA-SPH). (The exciting light was 532 nm green laser, the fluorescent color change was observed and taken photos through an optical filter which can filtrate the exciting light.) b) Principle of the adhesion between the GO-PNIPAM hydrogel and the PBI-HPEI hydrogel based on the host–guest interaction.

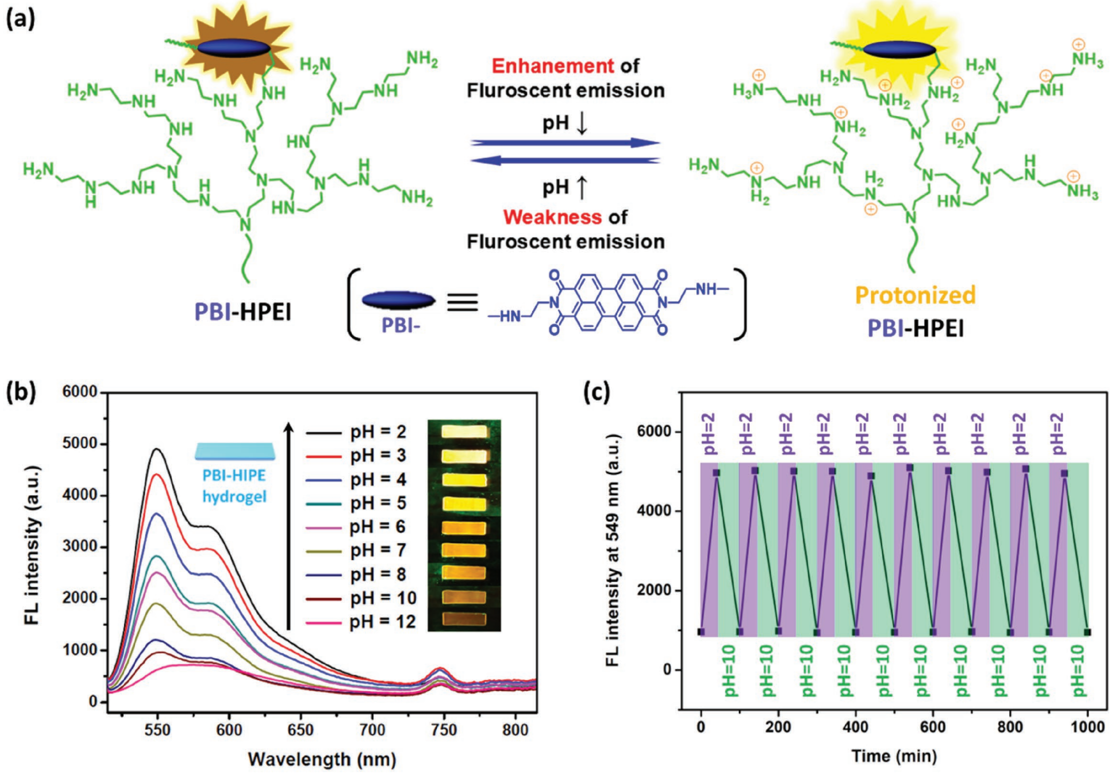

Figure 1. a) The pH-responsive fluorescent color changing principle of the PBI-HPEI hydrogel. b) The pH-dependent fluorescence emission spectra of PBI-HPEI hydrogel ($\lambda_{ex} = 532$ nm). (The fluorescent color change was observed and taken photos through an optical filter which can only let 550–1100 nm light pass through.) c) Cyclic reversible fluorescence emission behavior of the PBI-HPEI hydrogel as the solution pH is varied between 10 and 2 at 40 °C.

hydrogel in its collapsed state was bonded with the PBI-HPEI hydrogel via a supramolecular glue based on host–guest interactions[14] to obtain a bilayer hydrogel (Scheme 1b; Figure S1, Supporting Information). The bilayer hydrogel was tailored into a star shape, and then transferred into cold environment to induce the swell of the PNIPAM layer caused by the extension of the PNIPAM network, a 3D hydrogel actuator can thus be achieved. At low temperature, the PBI-HPEI layer is covered by the GO-PNIPAM layer, which blocks most of the excitation light, therefore no fluorescence is observed from the PBI-HPEI layer (Scheme 1a_1). If the actuator is exposed to warm environment, the GO-PNIPAM layer will shrink due to the collapse of the PNIPAM network and lead to an unfolding of the actuator that allows the PBI-HPEI inside layer to be exposed to light, and triggers the off–on switch of fluorescence (Scheme 1a_2,a_3). Moreover, the fluorescence will be enhanced by decreasing the pH of the environment (Scheme 1a_3,a_4). To integrate shape deformation and fluorescence color-changing properties into one hydrogel system, our strategy may provide new insights in the design of biomimetic intelligent systems with synergistic multiple functions.

2. Results and Discussion

2.1. Fabrication of Bilayer Anisotropic Hydrogel Actuator

An effective strategy to produce smart fluorescent hydrogels can be the embedding pH-responsive fluorescent polymers into chemically crosslinked polymeric matrix, which can avoid fatigue and complex preparation process. Here, the pH-responsive PBI-HPEI was synthesized and physically incorporated into a polyacrylamide hydrogel to produce the PBI-HPEI hydrogel with semiinterpenetrating polymer network structure and pH-responsive color-tunable fluorescence behavior. As shown in **Figure 1**a, the obtained PBI-HPEI hydrogel can undergo a clear and instant pH-responsive fluorescence color change from dark to yellow under green-light irradiation (532 nm), as is evidenced by the fact that its fluorescence intensity at 549 nm is enhanced by 10 times when the hydrogel is immersed into different solutions with pH value changes from 12 to 2. This remarkable fluorescence color change is due to the reduced photoinduced electron transfer (PET) process between amino groups and PBI fluorophores at acidic condition.[15] The pH-responsive fluorescence of the PBI-HPEI hydrogel was proven to be fully reversible

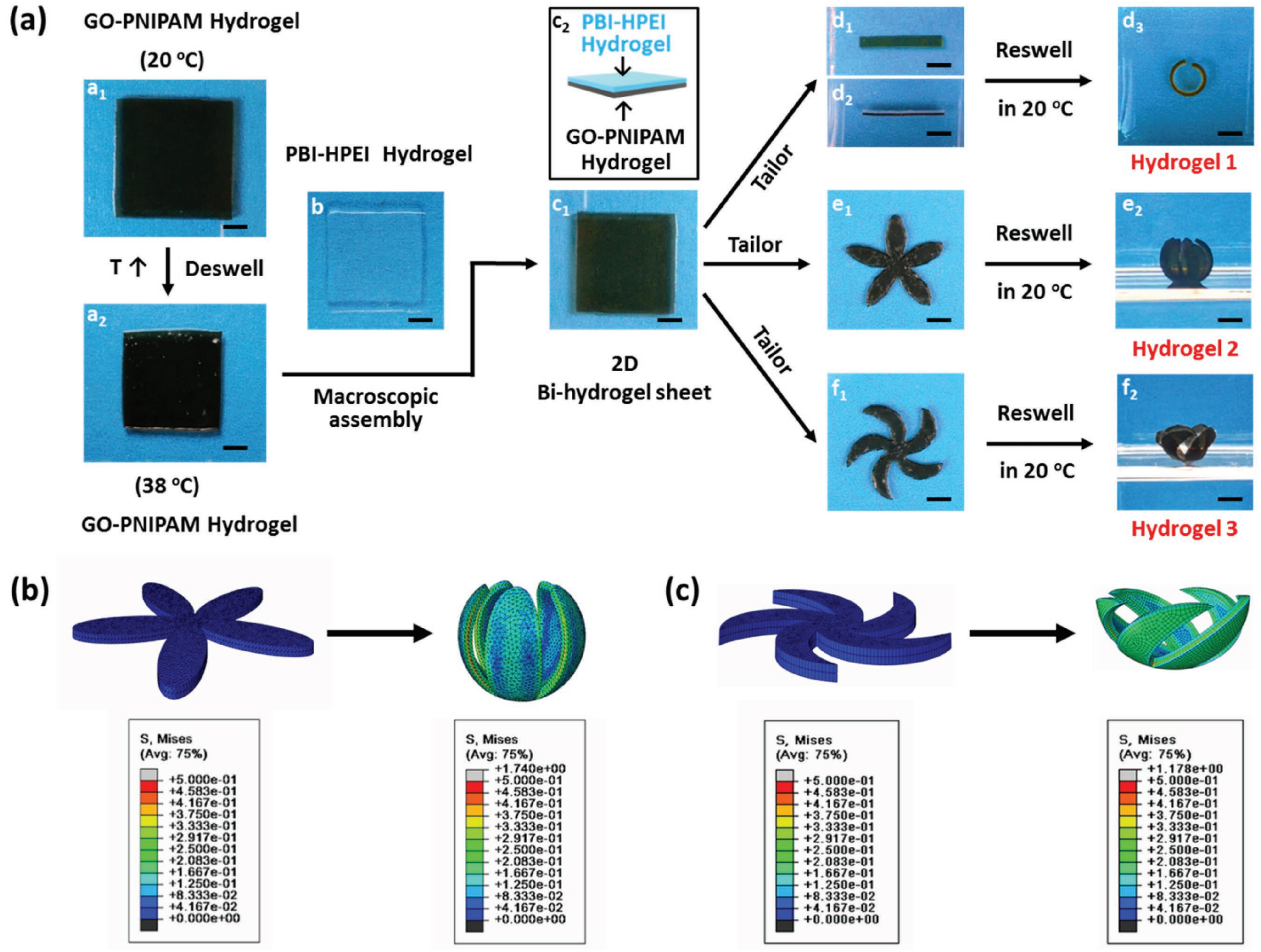

Figure 2. a) The process of integrating two different hydrogel sheets into bilayer hydrogels based on macroscopic assembly through the supramolecular glue. (Scale bars, 5 mm.) b) Finite element modeling of forming the actuator 2. c) Finite element modeling of forming the actuator 3.

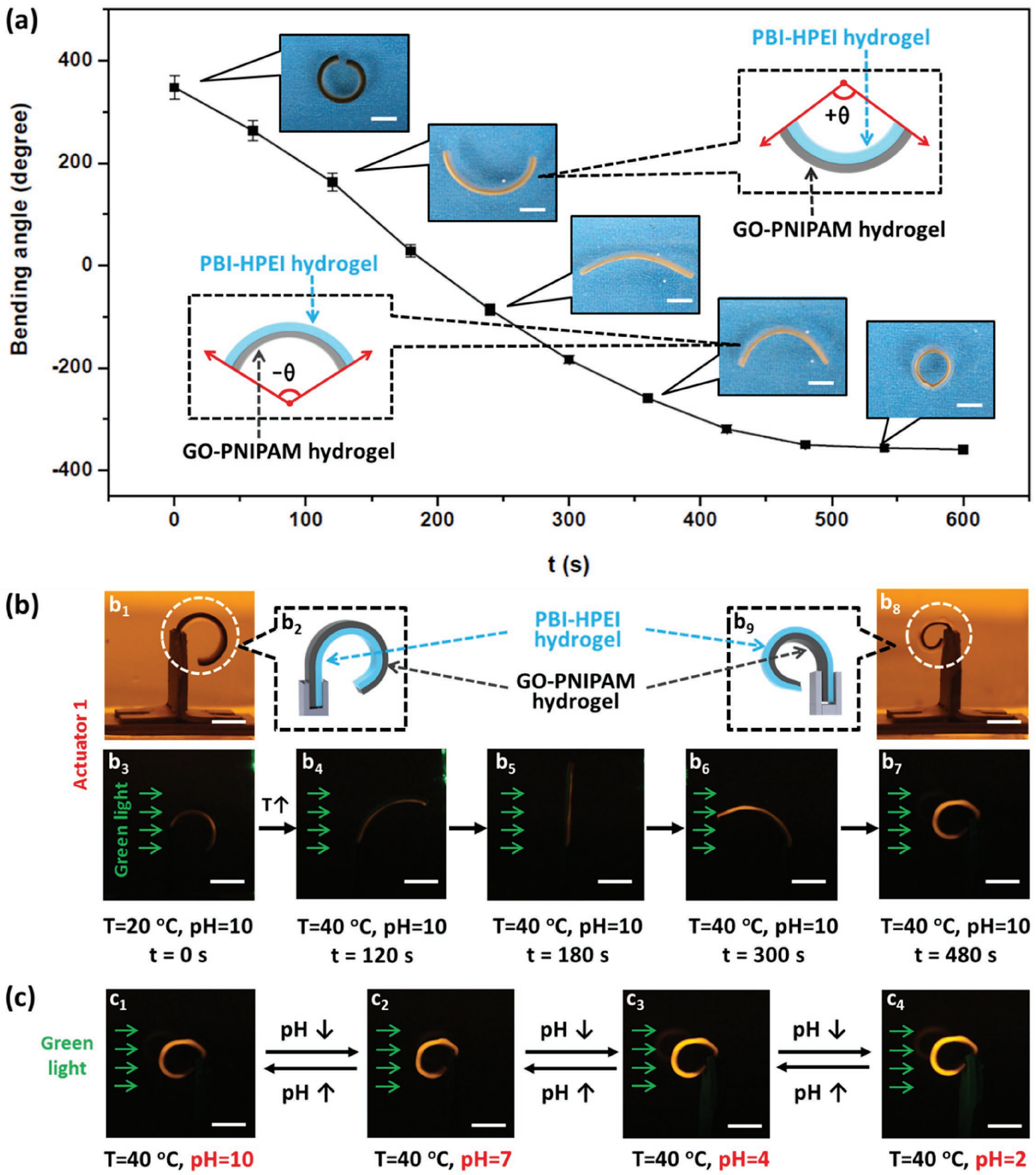

Figure 3. The shape deformation and color change of actuator 1. a) Thermoresponsive bending upon the temperature changing from 20 to 40 °C. b) Thermoresponsive bending and shape-depended color changing. c) The pH-responsive fluorescent color changing after shape deformation. (Photos were taken after filtering the exciting light through an optical filter which can only let 550–1100 nm light pass through. Scale bars, 5 mm.)

(Figure 1b), indicating they are devoid of fluorescence fatigue. Moreover, no noticeable fluorescence spectra change of the PBI-HPEI hydrogel was observed when the environment temperature increased from 20 to 50 °C (Figure S2, Supporting Information), demonstrating its excellent photoluminescence stability. Taken together, all of these results make the PBI-HPEI hydrogel excellent fluorescent functional material.

The thermoresponsive GO-PNIPAM hydrogel was prepared according to our previous report.[16] There are two considerations to composite GOs in the PNIPAM networks: (1) GO-PNIPAM hydrogel sheet could block most of the 532 nm exciting light (Figure S4a, Supporting Information), because the transmittance of the GO-PNIPAM hydrogel sheet is only ≈15% at 532 nm (Figure S4b, Supporting Information); (2) The decreasing of the size of GO-PNIPAM hydrogel as a function of temperature is much slower than that of the PNIPAM hydrogel (Figure S4c, Supporting Information), therefore the shrinkage degree of GO-PNIPAM hydrogel could be controlled precisely through adjusting the environmental temperature.

After shrinking in warm water (38 °C), the GO-PNIPAM hydrogel was taken out and firmly bonded with the PBI-HPEI hydrogel modified with a supramolecular glue (the poly(AAm-*co*-Ad-AAm aqueous solution) based on macroscopic supramolecular assembly (**Figure 2**a; Figure S1, Supporting Information).[14c] The shape of the planar bilayer hydrogel sheet can be tailored arbitrarily to achieve different patterns, and after the GO-PNIPAM hydrogel reswells in cool water (20 °C), the 2D sheet can transform into various programmable 2D and 3D shapes (Figure 2a), which can be simulated and predicted by forming a finite element modeling of the shape transformation (Figure 2b,c; Movies S1 and S2, Supporting Information).

2.2. On–Off Switchable and Color-Tunable Fluorescence Behaviors

The bilayer hydrogel actuators show synergetic shape deformation and color-changing properties. Taking actuator 1 for example, it shows original arc-shape toward the PBI-HPEI hydrogel side (positive bending angle) at 20 °C (**Figure 3**a; Figure S5a, Supporting Information). When the environmental temperature increases to 40 °C, it becomes straight gradually, and then bends toward the GO-PNIPAM side (negative bending angle) (Figure 3a; Figure S5b, Supporting Information). Additionally, the bilayer hydrogel actuators own excellent multicycle reversibility (Figure S6, Supporting Information). As a result, the PBI-HPEI hydrogel can be exposed the excitation light and fluorescence will be observed (Figure 3b). Moreover, with the decrease of pH value from 10 to 2, the intensity of fluorescence emission will be enhanced, and the color of actuator 1 will reversibly change from dark brown to bright yellow (Figure 3c). The integrate shape deformation and color-changing behaviors can be applied to design double-control smart devices: before shape deformation, almost no fluorescence of the PBI-HPEI hydrogel layer could be observed, because most of the exciting light was shielded by the GO-PNIPAM layer. Only when the temperature is high enough, the actuator bends toward the opposite side, the fluorescence would be visually detected and then tuned by changing the pH.

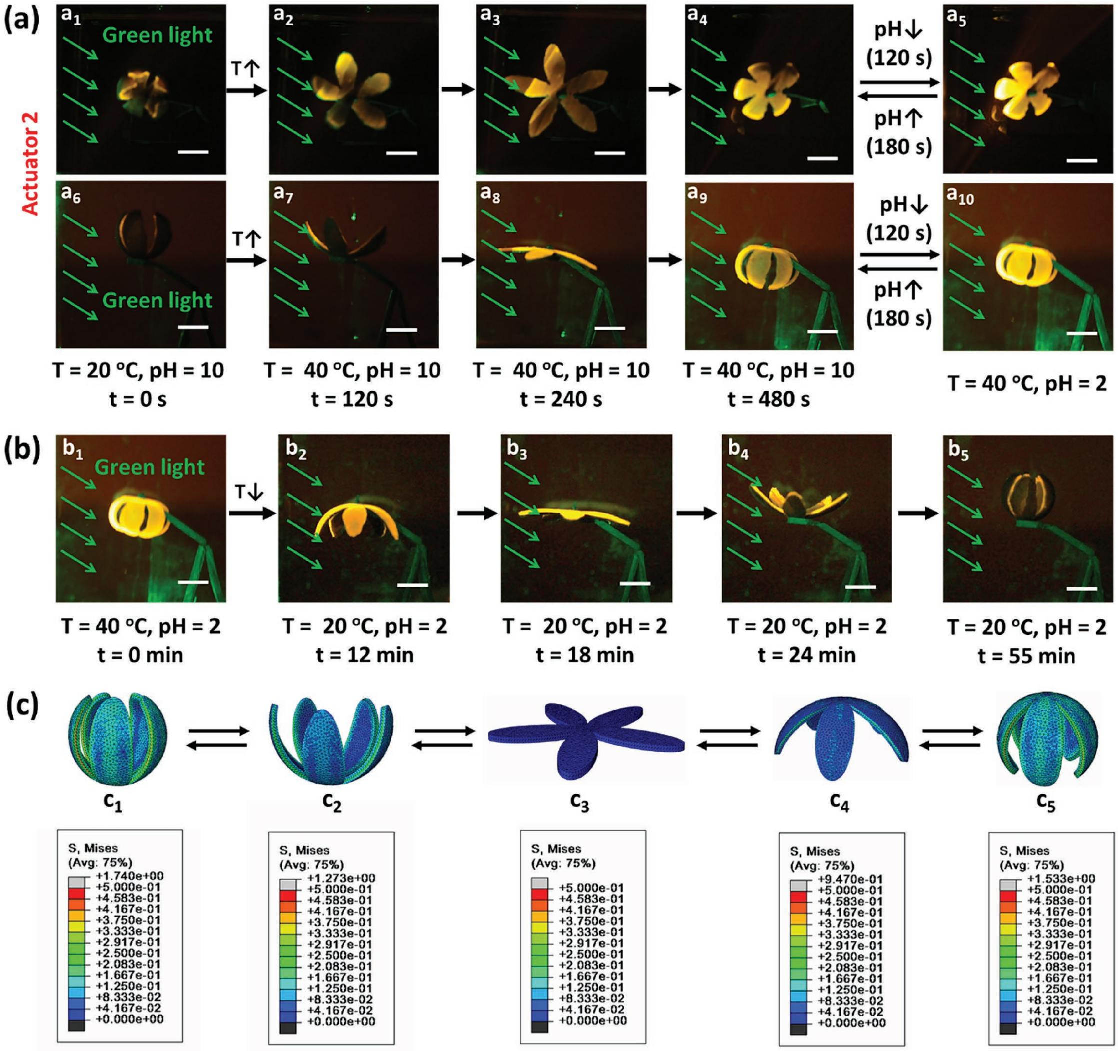

Figure 4. Thermoresponsive complex shape deformation and fluorescent color displaying of actuator 2. a) a_1–a_5 are plane views, a_6–a_{10} are flat views. b) b_1–b_5 are flat views. (Photos were taken after filtering the exciting light through an optical filter which can only let 550–1100 nm light pass through. Scale bars, 5 mm). c) Finite element modeling of the shape transformation corresponding to actuator 2.

Besides simple shape deformation, actuators with complex shape transformation could also be constructed on the basis of the same strategy. As shown in **Figure 4**a, the PBI-HPEI hydrogel layer of actuator 2 is closed by the GO-PNIPAM hydrogel layer and cannot be exposed to the exciting green light at 20 °C. After a change of temperature from 20 to 40 °C, the petals of actuator 2 will deform and lead to the uncovering of the PBI-HPEI layer, then the actuator could display pH-responsive fluorescent color change (Figure 4b). Both of the thermoresponsive shape-change and pH-responsive fluorescent color change are reversible over many cycles (Figure 4a,b). The finite element analysis was conducted to simulate and predict 3D complex shape transformation of actuator 2 (Figure 4c; Movie S3, Supporting Information). Through the finite element analysis, various biomimetic actuators with 3D complex shape deformation can be designed and fabricated conveniently (Figure S7 and Movie S4, Supporting Information). These hydrogel actuators with programmable shape deformation and color-changing performances could mimic some natural creatures that not only could move but also adjust their body color.

3. Conclusion

In conclusion, we have developed a convenient and general applicable strategy to fabricate an anisotropic hydrogel actuator with on–off switchable and color-tunable fluorescence behaviors. The pH-responsive color-changing PBI-HPEI hydrogel and the shrunk thermoresponsive shape-changing GO-PNIPAM hydrogel can be bonded to obtain planar sheet based on the macroscopic supramolecular assembly, then hydrogel actuator with various shapes could be obtained through tailoring and reswelling. The shape of the actuator could be deformed via thermostimulus, which could control the on–off fluorescence behavior of the actuator. Moreover, the fluorescence color could be tuned through adjusting the pH. Therefore, shape deformation and fluorescence color-changing functions are integrated and optimized in one system. This method may provide some new strategies to explore smarter biomimetic systems coupling synergistic visually detecting and complexly actuating functions. In addition, whereas this study is focused on synergistic actuating and detecting functions based on hydrogel, our method has a potential application to create new smart materials and systems integrating more intelligent functions, including shape memory, self-adaptive, self-healing, and so on.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anisotropic structures, color-changing materials, macroscopic supramolecular assembly, polymeric hydrogel actuators, shape deformation

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