Macromolecular
Rapid Communications
www.mrc-journal.de

pH and Thermo Dual-Responsive Fluorescent Hydrogel Actuator

Bao-Yi Wu, Xiao-Xia Le, Yu-Kun Jian, Wei Lu, Zhen-Yu Yang, Zhi-Kun Zheng, Patrick Théato, Jia-Wei Zhang, Afang Zhang,* and Tao Chen**

As one of the most important smart materials, fluorescent hydrogel actuators can produce both color and shape changes under external stimuli. In the present work, an effective approach to develop a novel fluorescent hydrogel actuator with pH and thermo dual responsiveness is proposed. Through incorporating pH-responsive perylene tetracarboxylic acid (PTCA), which is a typical fluorescent moiety with aggregation-caused quenching (ACQ) effect, into an anisotropic poly(*N*-isopropylacrylamide)–polyacrylamide (PNIPAm-PAAm) structure, the obtained hydrogel exhibits stable thermoresponsive shape deformation and switchable fluorescence performance upon a pH trigger. Therefore, fluorescence-quenching-based and actuation-based information can be revealed when exposed to UV light and immersed into warm water, respectively. Moreover, the thermoresponsive actuating behavior can be applied to further hide the fluorescence-quenching-based images. The present work may provide new insights into the design and preparation of novel stimuli-responsive hydrogel actuators.

As one of the most important intelligent materials, stimuli-responsive hydrogels[1–6] have the ability to generate reversible shape deformation, color change, or variation of mechanical properties upon the trigger of certain stimuli.[7–12] Conventional hydrogels only have single-performance alternation in response to environmental stimuli.[13–18] Hydrogels that could change two or more properties triggered by external conditions will own a wider range of potential applications; therefore, it is significantly important to develop hydrogels that could alter multiple properties upon external trigger. Inspired by some animals that could change their body colors during movement,[19–21] considerable efforts have been devoted to explore hydrogel actuators with fluorescence properties.[22,23] For example, Gong et al. have developed an inhomogeneous hydrogel with the ability to change the structure and color under controlled stress/strain.[22] We have designed a bilayer hydrogel actuator with integrated fluorescence color-changing functions and complex shape deformation properties.[23] However, most of the previous reports about fluorescent hydrogel actuators are concentrated on their fluorescence adjustment and actuating performances; the potential applications are rarely mentioned.

Herein, we present a novel hydrogel with pH-responsive fluorescence and thermally induced actuating behavior. First of all, pH-responsive fluorescent molecule perylene tetracarboxylic acid (PTCA) was grafted to gelatin chain. Then, PNIPAm-PAAm-PTCA hydrogel with heterogeneous structure was obtained by stepwise polymerization of isopropyl acrylamide (NIPAm) and acrylamide (AAm) in the presence of PTCA-modified gelatin (Scheme S1, Supporting Information). As shown in **Scheme 1**, information (a “love” pattern) could be loaded onto the surface of the hydrogel through contact with a filter paper containing OH^-, and strong fluorescence could be observed under UV light on the contacting area because of the deprotonation of the PTCA moieties, realizing fluorescence quenching–based information loading. Various information such as English letters, Chinese characters, and pictures could be printed onto the surface of the fluorescence hydrogel using the same method. Moreover, density of PAAm in the UV irradiation side of the hydrogel network was higher than that of the opposite side, resulting in a Janus structure in thickness direction; therefore, the hydrogel could generate shape deformation upon the trigger of heat due to the asymmetric swelling and deswelling behavior. As a result, the fluorescence quenching–based images above could be further covered by actuating. The

B.-Y. Wu, Prof. A. Zhang
Department of Polymer Materials
College of Materials Science and Engineering
Shanghai University
Nanchen Road 333, Shanghai 200444, China
E-mail: azhang@shu.edu.cn

B.-Y. Wu, X.-X. Le, Y.-K. Jian, Prof. W. Lu, Prof. J.-W. Zhang, Prof. T. Chen
Key Laboratory of Bio-based Polymeric Materials Technology
and Application of Zhejiang Province
Ningbo Institute of Material Technology and Engineering
Chinese Academy of Sciences
Ningbo 315201, China
E-mail: zhangjiawei@nimte.ac.cn; tao.chen@nimte.ac.cn

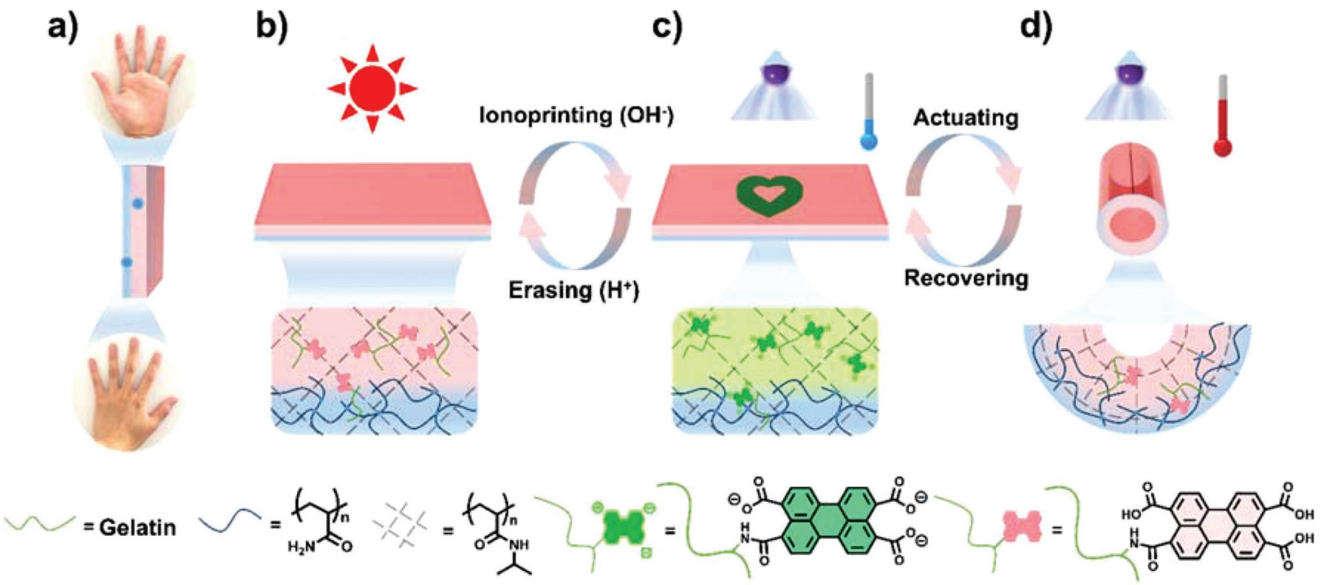
X.-X. Le, Y.-K. Jian, Prof. W. Lu, Prof. J.-W. Zhang, Prof. T. Chen
University of Chinese Academy of Sciences
19A Yuquan Road, Beijing 100049, China

Prof. Z.-Y. Yang, Prof. Z.-K. Zheng
School of Chemistry
Sun Yat-sen University
Xin Gang Xi Road 135#, Guangzhou, Guangdong 510275, China

Prof. P. Théato
Karlsruhe Institute of Technology
Engesser Str. 18, Gebaude 11.23, D-76131 Karlsruhe, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.201800648.

DOI: 10.1002/marc.201800648



Scheme 1. Schematic illustration of fluorescent hydrogel actuator with pH and thermo dual responsiveness. a) The hydrogel with Janus structure is similar to a human hand. b) Through an ionoprinting method, in which wet filter paper (contains OH$^-$) will be contacted with hydrogel to let OH$^-$ diffuse from paper to hydrogel, information will be presented on the surface of the hydrogel. c) The information load before is hidden by actuating in warm water (45 °C).

strategy have combined fluorescence and actuating performances in one system, which may provide new ideas for the design and fabrication of novel stimuli-responsive hydrogels.

First of all, PTCA was grafted onto gelatin according to a reported procedure (Figure S1, Supporting Information).[24,25]

As shown in **Figure 1**a, the aqueous solution of PTCA–gelatin (5 mg mL^{-1}) shows no fluorescence in acidic condition (0.1 M HCl). If the solution is adjusted to alkaline by adding NaOH (0.1 M), it shows a strong green fluorescence under UV irradiation (365 nm). The attachment of PTCA onto gelatin is

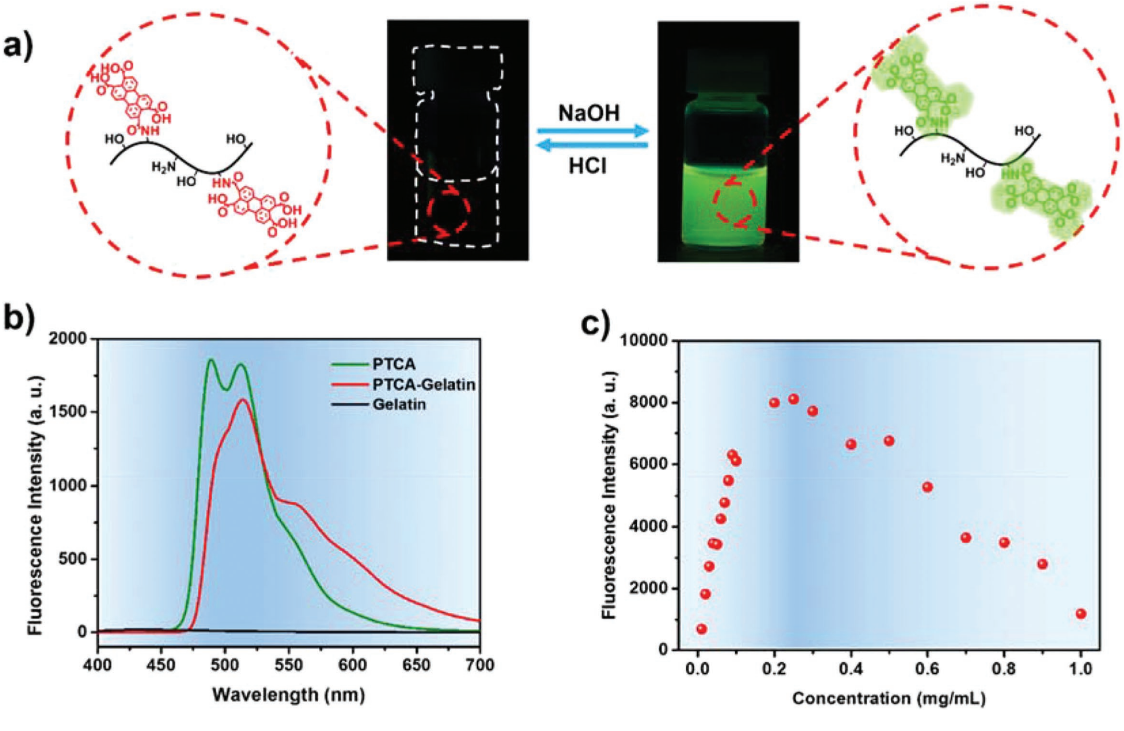


Figure 1. a) Reversible pH responsiveness of PTCA–gelatin solution. b) Fluorescence spectra of PTCA solution (0.02 mg mL^{-1}), PTCA–gelatin solution (5 mg mL^{-1}), and gelatin solution (5 mg mL^{-1}). c) Variation of the fluorescence intensities of PTCA solutions as a function of concentration.

confirmed by UV–vis spectra. Pure gelatin solution shows no fluorescence, while the aqueous solution of PTCA–gelatin shows a strong absorbance at around 400–600 nm (Figure 1b), just like the fluorescence behavior of pure PTCA solution, which indicates PTCA moieties have been successfully attached onto gelatin. In order to calculate the content of PTCA on gelatin, the relationship between the concentration of PTCA solution and corresponding fluorescence intensity have been investigated (Figure 1c). In a lower concentration (<0.25 mg mL^{-1}), the deprotonation of the carboxyl groups will bring electrostatic together, and the fluorescence intensity will increase with concentration of PTCA (Figure S2, Supporting Information). However, π–π stacking interactions between PTCA groups will strengthen with increasing concentration of PTCA, and the electrostatic repulsion will make less and less influence. Therefore, the PTCA moieties will finally aggregate together, and the fluorescence intensity will decrease because of the aggregation-induced fluorescence quenching. The fluorescence intensity of PTCA–gelatin (5 mg mL^{-1}) is approximately 1600, which corresponds to a high (0.9 mg mL^{-1}) or a low (0.02 mg mL^{-1}) concentration of PTCA. In order to precisely predict the graft ratio of PTCA, the PTCA–gelatin solution was gradually diluted and the corresponding fluorescence spectrum was recorded (Figure S3, Supporting Information). The fluorescence intensity decreases with decreasing concentration of PTCA–gelatin, which suggests that the PTCA–gelatin (5 mg mL^{-1}) corresponds to the low concentration of PTCA (0.02 mg mL^{-1}), and the concentration of PTCA in gelatin is calculated to be about 4 mg g^{-1}.

A homogenous PNIPAm hydrogel was prepared in the presence of PTCA–gelatin. Then PAAm network was introduced via UV-initiated polymerization. In visible light, the obtained PNIPAm-PAAm-PTCA hydrogel is light pink and has a superior light transmittance. After soaking in alkaline solution, the hydrogel turns to transparent green (Figure S4, Supporting Information). The fluorescence behavior of the hydrogel is more prominent, the just prepared hydrogel shows no fluorescence, and a strong green fluorescence is observed after it is treated with alkaline solution. In addition, the pH-responsive fluorescence of PNIPAm-PAAm-PTCA hydrogel is fully reversible and

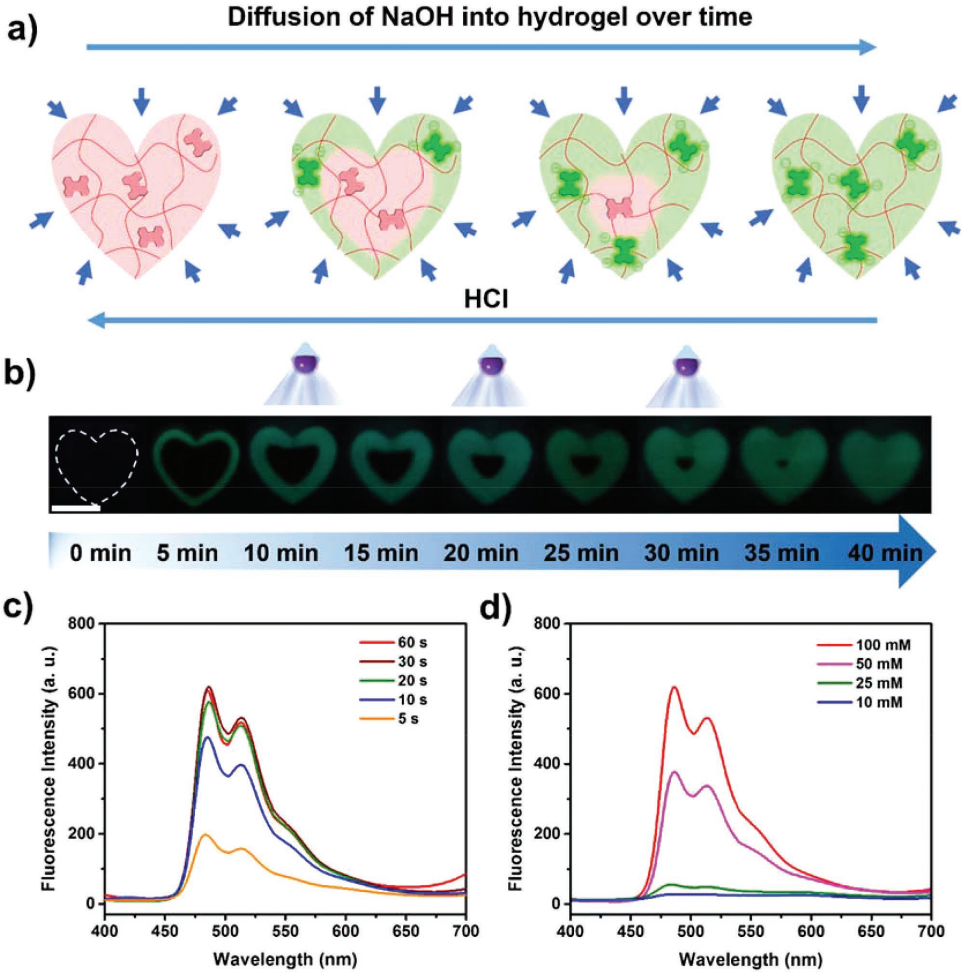


Figure 2. a) Illustration showing the time-dependent fluorescence of PNIPAm-PAAm-PTCA hydrogel in NaOH aqueous solution (100 mM). b) Images showing the time-dependent fluorescence of PNIPAm-PAAm-PTCA hydrogel in NaOH aqueous solution (100 mM) (Photos were taken under 365 nm UV light). c) Fluorescence spectra of the hydrogel upon treatment with filter paper containing NaOH for different contacting times. d) Fluorescence spectra of the hydrogel upon treatment with filter paper containing different content of OH^{-}. Scale bar: 1 cm.

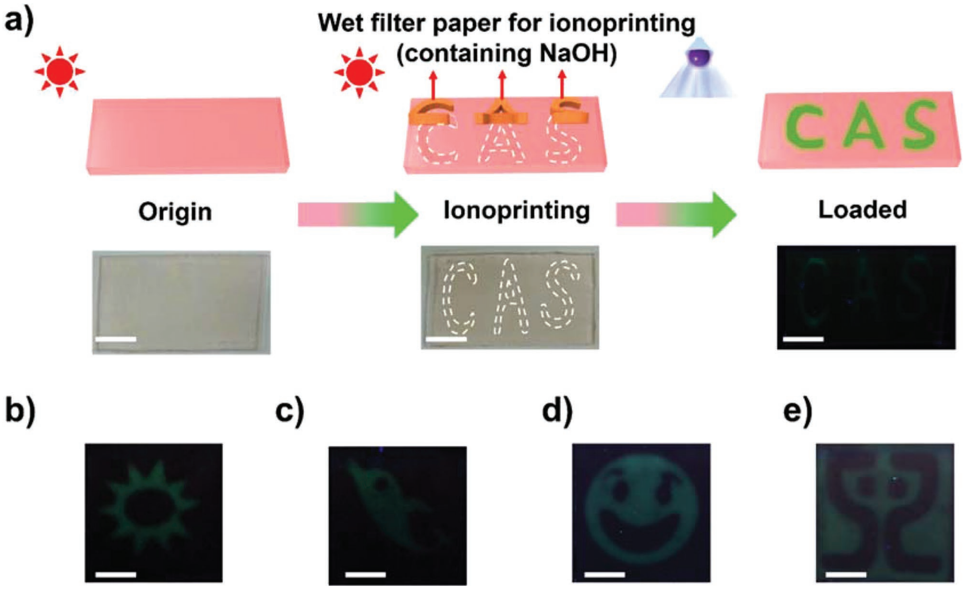


Figure 3. Fluorescence quenching–based information storage; hidden images are visible under UV light. a) Illustration and pictures of the ionoprinting process; English word "CAS" is observed under UV light. b–e) Images of the sun, dolphin, smiley face, and the logo of our group were obtained via ionoprinting onto the surface of hydrogel by four different seals containing OH^-. Scale bar: 1 cm.

can be preserved for at least 3 months (Figures S5 and S6, Supporting Information). The reason for the fluorescence change are presumed as follows: Though PTCA is grafted onto gelatin with a low grafting ratio and then introduced into hydrogels, the strong π–π stacking interactions and hydrogen bonding between PTCA moieties still make them aggregate; therefore, the fluorescence of the just prepared hydrogel is quenched. After treating with alkaline solution, the carboxyl groups of PTCA will be deprotonated. As a result, the hydrogen bonding of carboxyl groups will be weakened, and the electrostatic repulsion between negatively charged carboxylate ions will effectively hinder the PTCA groups from getting together. Therefore, the fluorescence emission of the hydrogel will be significantly enhanced. Fluorescence of the hydrogel is determined by the deprotonation of PTCA groups; therefore, the fluorescence of the hydrogel is related to the diffusion of OH^- into hydrogels. In order to visualize this process, a flat hydrogel sheet is clamped by two transparent glass plates and then immersed into NaOH aqueous solution, so NaOH can only penetrate from the edge of the hydrogel sheet to the center. As shown in the illustration and images (**Figure 2**a,b), green fluorescence appears from the perimeter of the heart-shaped hydrogel and gradually diffuses to the center with the increase in immersion time into NaOH aqueous solution, which indicates that NaOH permeates into the hydrogel and the PTCA groups disaggregate because of deprotonation of the carboxyl groups. Moreover, the fluorescence of the hydrogel can be manipulated by ionoprinting method. For ionoprinting, filter papers containing different amounts of OH^- are prepared by immersing blank filter papers into NaOH solution. Then, the filter papers are brought into contact with the surface of hydrogels. As shown in Figure 2c, the fluorescence intensity of the hydrogel increases with the increment in contacting time. If the contacting time is fixed, the fluorescence intensity enhances with the increase in concentration of NaOH solution (Figure 2d). The notable change in the fluorescence intensity is caused by the reduced ACQ effect between the PTCA moieties in alkaline condition.

Since the diffusion of NaOH into hydrogel can be observed under UV irradiation, it encourages us to explore fluorescence quenching–based information loading. As shown in **Figure 3**a, through ionoprinting method, the English word "CAS," abbreviation of Chinese Academy of Sciences, was imprinted onto the surface of hydrogel, and the word "CAS" was only visible under UV light. Besides simple letters, images such as the Sun, dolphin, smiley face, and the logo of our group could be loaded onto the surface of hydrogel using the same method (Figure 3b–e).

Because of the limited penetration of UV light, the obtained PNIPAm-PAAm-PTCA hydrogel exhibits an anisotropic structure with inhomogeneous PAAm network across the thickness direction (**Figure 4**a). As shown in Figure 4b, the hydrogel exhibits a gradient polymer concentration, with higher density in the UV irradiation side than that of the opposite side, which suggests that the distribution of polymer chains in the hydrogel is not homogenous. Therefore, if the hydrogel was immersed into warm water (45 °C), higher than the LCST of PNIPAm, the PNIPAm network would shrink and the clear hydrogel would become opaque gradually and bend to the side with less PAAm due to the unbalanced contraction. As shown in Figure 4c, a hydrogel strip turns into a circle and reaches equilibrium in about 55 s in warm water (45 °C). If the deformed hydrogel is then transferred to cool water (25 °C), it will recover to the original state because of the hydration of PNIPAM network.

Since there is a distinct difference in deswelling kinetics between the PNIPAM part and the PNIPAM/PAAm part in warm water, various deformed shapes could be designed and obtained by adjusting UV light-irradiated regions during the second polymerization process. As presented in **Figure 5**a, if the PAAm network was introduced as two separated domains, the hydrogel strip would bend toward the opposite of UV

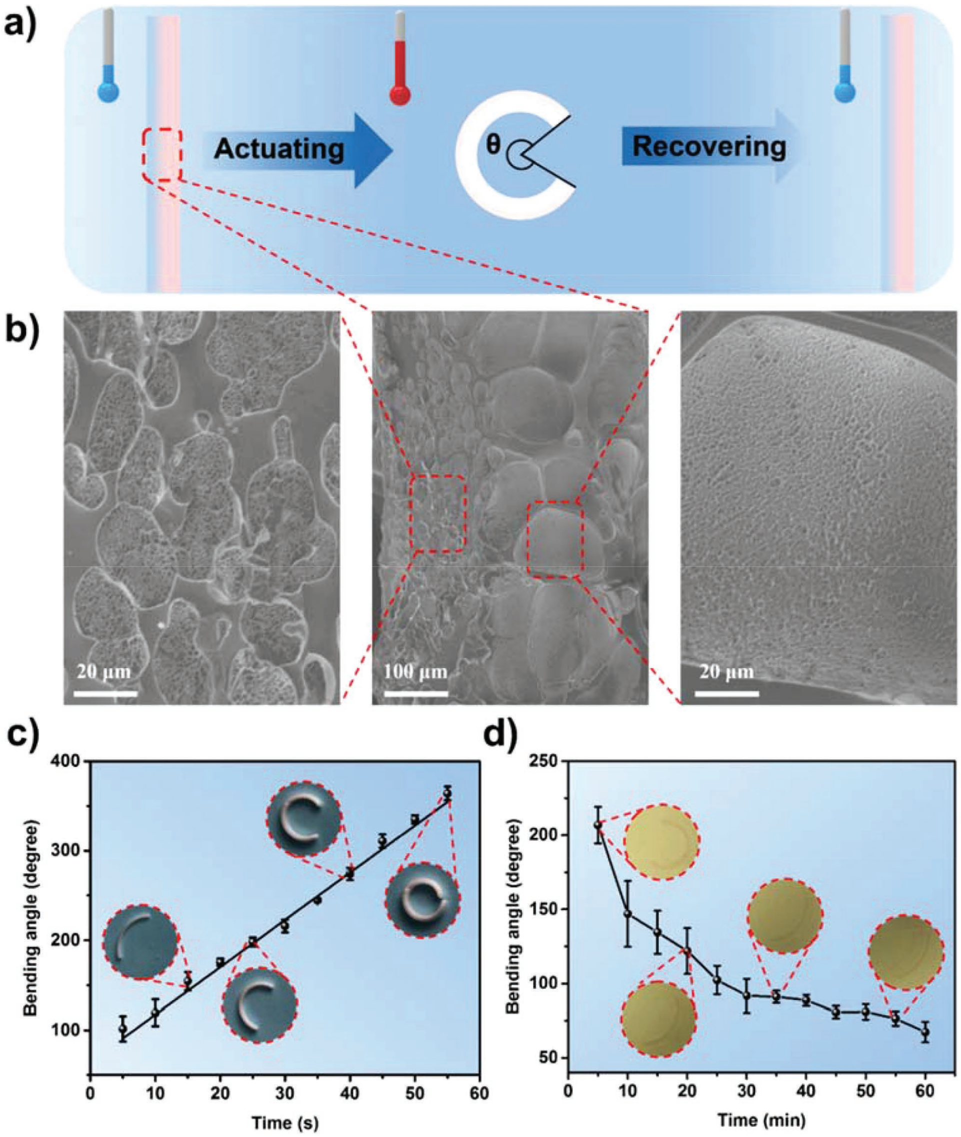


Figure 4. a) Illustration showing the actuating and recovering process of PNIPAm-PAAm-PTCA hydrogel. b) The cross section SEM image of PNIPAm-PAAm-PTCA hydrogel. c,d) The bending angle of hydrogel strip against time in 45 and 25 °C PBS aqueous solution.

irradiation side to form a “C” shape upon immersing into warm water; therefore, different information could be loaded onto the hydrogel strip and displayed through thermo-induced shape deformation. Similarly, straight hydrogels could form the numbers such as “1”, “2”, “3”, “4”, “5”, “6”, “7”, “8”, and “9” when immersed in 45 °C warm water as a result of the Janus structure across the thickness direction (Figure 5c). In addition, the shape deformation is reversible (Figures S8 and S9, Supporting Information).

The actuating performance of our hydrogel could be used not only for generating information, but also for covering the fluorescence quenching–based information. As shown in **Figure 6**a, a hand can hide the heart-shaped paper by making a fist. Inspired by this process, a hand-shaped hydrogel was prepared by laser cutting machine, and a heart pattern was loaded onto the palm of the hydrogel hand by ionoprinting (Figure 6b). Then the hydrogel hand was exposed to 45 °C warm water. The hydrogel hand could bend and form a fist because of the volume-phase transition of PNIPAm network, and the heart-shaped information on the palm could be completely wrapped. Through introducing two stimuli (cold water and UV light), the heart pattern on the palm could be revealed. Moreover, the actuating behavior of the hydrogel could be used for information destruction and reorganization. As shown in Figure 6c, a smart hydrogel window with a loaded Chinese character “中” was fabricated. As the hydrogel was treated with warm water, the window would open, leading to destruction of the information. When the temperature recovered, the window would close, resulting in reorganization of the information.

In summary, we have presented a novel fluorescent hydrogel actuator with pH and thermo dual responsiveness. The fluorescent hydrogel was fabricated by incorporating pH-responsive

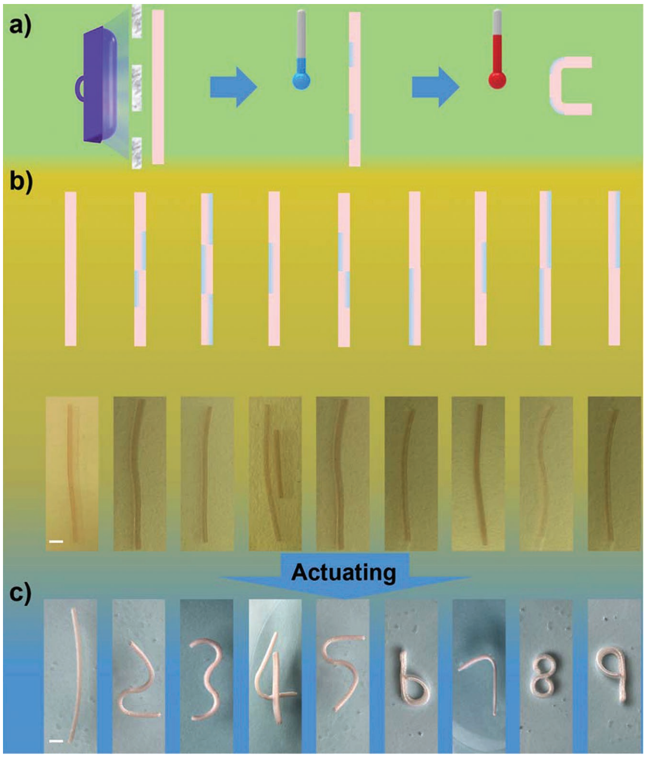


Figure 5. a) Illustration showing the thermo-induced actuating process. b,c) Shape deformation behavior: By changing the UV-irradiated domains of straight hydrogels and putting the hydrogels into warm water, different numbers—"1", "2", "3", "4", "5", "6", "7", "8", and "9"—can be achieved. Scale bar: 1 cm.

fluorescent moieties PTCA into anisotropic PNIPAm-PAAm hydrogel, realizing pH-responsive fluorescence performance and thermoresponsive actuating behavior. In addition, the images printed via fluorescence quenching could be further covered by shape deformation. We believe the present work will shed light on the design and preparation of novel, smart materials.

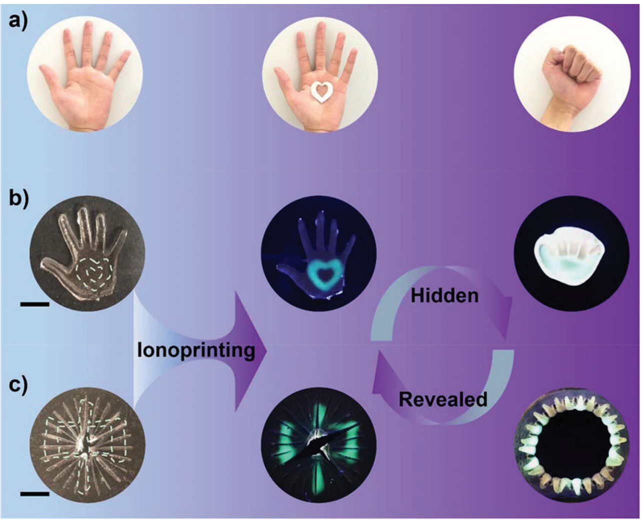


Figure 6. a–c) Illustration and images showing integrated fluorescence quenching and actuating behaviors. After ionoprinting, the loaded information could be further hidden through the thermally induced actuating performance, and the loaded information could be displayed by exposure to cold water and UV light. Scale bar: 1 cm.

Supporting Information

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

Acknowledgements

This work was supported by National Key R&D Program of China (2018YFB1105100),National Natural Science Foundation of China (51873223, 21774138, 51773215), Key Research Program of Frontier Science, Chinese Academy of Sciences (QYZDB-SSW-SLH036), Natural science foundation of Zhejiang (LY17B040003), and Youth Innovation Promotion Association of Chinese Academy of Sciences (2017337). Xinchen Jiang from HD Ningbo School is acknowledged for experimental assistant.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

anisotropic structures, fluorescence quenching, hydrogel actuators, shape deformation

Received: August 31, 2018
Revised: November 15, 2018
Published online: November 28, 2018

---

[1] X. Z. Yan, F. Wang, B. Zheng, F. H. Huang, *Chem. Soc. Rev.* **2012**, *41*, 6042.
[2] L. Ionov, *Mater. Today* **2014**, *17*, 494.
[3] R. C. Luo, J. Wu, N. D. Dinh, C. H. Chen, *Adv. Funct. Mater.* **2015**, *25*, 7272.
[4] M. H. Liao, P. B. Wan, J. R. Wen, M. Gong, X. X. Wu, Y. G. Wang, R. Shi, L. Q. Zhang, *Adv. Funct. Mater.* **2017**, *27*, 1703852.
[5] C. Ma, X. Le, X. Tang, J. He, P. Xiao, J. Zheng, H. Xiao, W. Lu, J. Zhang, Y. Huang, T. Chen, *Adv. Funct. Mater.* **2016**, *26*, 8670.
[6] E. Wang, M. S. Desai, S.-W. Lee, *Nano Lett.* **2013**, *13*, 2826.
[7] L. Zhao, J. H. Huang, Y. C. Zhang, T. Wang, W. X. Sun, Z. Tong, *ACS Appl. Mater. Interfaces* **2017**, *9*, 11866.
[8] S. Xiao, Y. Yang, M. Zhong, H. Chen, Y. Zhang, J. Yang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 20843.
[9] H. Chen, F. Yang, Q. Chen, J. Zheng, *Adv. Mater.* **2017**, *29*, 1606900.
[10] C. Yao, Z. Liu, C. Yang, W. Wang, X. J. Ju, R. Xie, L. Y. Chu, *Adv. Funct. Mater.* **2015**, *25*, 2980.
[11] A. S. Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan, J. A. Lewis, *Nat. Mater.* **2016**, *15*, 413.
[12] C. Ma, T. Li, Q. Zhao, X. Yang, J. Wu, Y. Luo, T. Xie, *Adv. Mater.* **2014**, *26*, 5665.
[13] S. J. Kim, M. S. Kim, S. I. Kim, G. M. Spinks, B. C. Kim, G. G. Wallace, *Chem. Mater.* **2006**, *18*, 5805.
[14] L. Ionov, *Adv. Funct. Mater.* **2013**, *23*, 4555.

[15] Y. Liu, K. Zhang, J. Ma, G. J. Vancso, *ACS Appl. Mater. Interfaces* **2017**, *9*, 901.
[16] Z. Wu, M. Moshe, J. Z. Greener, *Nat. Commun.* **2013**, *4*, 1586.
[17] R. Takahashi, Z. Wu, M. Arifuzzaman, T. Nonoyama, T. Nakajima, T. Kurokawa, J. Gong, *Nat. Commun.* **2014**, *5*, 4490.
[18] C. Qin, Y. Feng, W. Luo, C. Cao, W. Hu, W. Feng, *J. Mater. Chem. A* **2015**, *3*, 16453.
[19] P. Vukusic, J. R. Sambles, *Nature* **2003**, *424*, 852.
[20] L. M. Mathger, S. L. Senft, M. Gao, S. Karaveli, G. R. R. Bell, R. Zia, A. M. Kuzirian, P. B. Dennis, W. J. Crookes-Goodson, R. R. Naik, G. W. Kattawar, R. T. Hanlon, *Adv. Funct. Mater.* **2013**, *23*, 3980.
[21] J. Teyssier, S. V. Saenko, D. van der Marel, M. C. Milinkovitch, *Nat. Commun.* **2015**, *6*, 6368.
[22] B. M. A. Haque, G. Kamita, T. Kurokawa, K. Tsujii, J. Gong, *Adv. Mater.* **2010**, *22*, 5110.
[23] C. Ma, W. Lu, X. Yang, J. He, X. Le, L. Wang, J. Zhang, M. J. Serpe, Y. Huang, T. Chen, *Adv. Funct. Mater.* **2018**, *28*, 1704568.
[24] W. Tian, J. Zhang, J. Yu, J. Wu, H. Nawaz, J. Zhang, J. He, F. Wang, *Adv. Opt. Mater.* **2016**, *4*, 2044.
[25] D. Loessner, C. Meinert, E. Kaemmerer, L. C. Martine, K. Yue, P. A. Levett, T. J. Klein, F. P. W. Melchels, A. Khademhosseini, D. W. Hutmacher, *Nat. Protoc.* **2016**, *11*, 727.