

# Rhodamine Mechanophore Functionalized Mechanochromic Double Network Hydrogels with High Sensitivity to Stress

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## Electronic Supplementary Information

**Abstract** Mechanochromic hydrogels, a new class of stimuli-responsive soft materials, have potential applications in a number of fields such as damage reporting and stress/strain sensing. We prepared a novel mechanochromic hydrogel using a strategy that has been developed to prepare dual-network (DN) hydrogels. A hydrophobic rhodamine derivative (Rh mechanophore) was covalently incorporated into a first network as a cross-linker. This first network embedded with Rh mechanophore within the DN hydrogel was pre-stretched. This guaranteed that the stress could be transferred extensively to the Rh-crosslinked first network once the hydrogel was under an applied force. Interestingly, we found that the threshold stress required to activate the mechanochromism of the hydrogel was less than 200 kPa, and much less than those in previous reports. Moreover, because of the excellent sensitivity of the hydrogel to stress, the DN hydrogel exhibited reversible freezing-induced mechanochromism. Benefiting from the sensitivity of Rh mechanophore to both pH and force, the DN hydrogel showed pH-regulated mechanochromic behavior. Our experimental results indicate that the preparation strategy we used introduces sensitive mechanochromism into the hydrogel and preserves the advantageous mechanical properties of the DN hydrogel. These results will be beneficial to the design and preparation of mechanochromic hydrogels with high stress sensitivity, and foster their practical applications in a number of fields such as damage reporting and stress/strain sensing.

**Keywords** Rhodamine mechanophore; Mechanochromic; Dual-network hydrogel; Freezing-induced mechanochromism; pH-regulated; Stress sensitivity

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## INTRODUCTION

Stimuli-responsive hydrogels are of high interest in soft matter science because of their versatile applications in sensors, actuators, tissue engineering, controlled drug release, processors, imaging, and more.<sup>[1–3]</sup> Recently, a variety of functional hydrogels have been developed that can respond to different physical, chemical, or mechanical external stimuli, including temperature,<sup>[4,5]</sup> light,<sup>[6,7]</sup> pH,<sup>[8,9]</sup> ionic strength,<sup>[10,11]</sup> magnetic fields,<sup>[12,13]</sup> chemical species,<sup>[14,15]</sup> and sonication.<sup>[16,17]</sup> Mechanochromic hydrogels, which are novel stimuli-responsive soft materials that show either adsorption (chromogenic) or emission (fluorochromic) color changes when subjected to an external force, have attracted wide attention. These hydrogels integrate mechano-responsiveness with the structural features of hydrogels (*i.e.*, high hydrophilicity and flexibility) and broaden the research scope for mechanical detection, particularly in biological systems, such as for sensing cell contractile force.<sup>[18,19]</sup>

Generally speaking, there are two main fabrication methods for these hydrogels. One is to fix the crystalline colloidal arrays of charged nanoparticles<sup>[20]</sup> or self-assembled lipid-like bilayer structures<sup>[21]</sup> into hydrogels. Under an applied force, the lengths of ordered nanoarchitectures commensurate with photons will vary, and a tunable structure color will emerge. For example, Gong *et al.*<sup>[21]</sup> fabricated mechanochromic hydrogels by immobilizing the lamellar structure of poly(dodecylglyceryl itaconate) (Poly-DGI) inside the polyacrylamide (PAAm) network. The hydrogel color could be reversibly tuned over a large spectral range. The second fabrication method is to use chromophores such as luminescent metal coordination compounds<sup>[17]</sup> or organic dye molecules.<sup>[22]</sup> Because the coordination interactions or aggregation states of the chromophores in hydrogels may vary dynamically under an applied force, the optical colors of the hydrogels can change. For example, Porfiri *et al.*<sup>[22]</sup> developed an interesting pyrene-functionalized mechanochromic hydrogel. The mechanochromism arose because the polymer chains could progressively unfold under stress, which gave rise to changes in the intermolecular distances of the pyrene molecules. Correspondingly, the excimer emission with respect to monomer emission varied and fluorescent color changes emerged under UV irradiation.

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An alternative possible strategy is incorporation of a mechanochromic "mechanophore", such as spiropyran (SP),<sup>[23]</sup> rhodamine (Rh),<sup>[24]</sup> diarylbibenzofuranone,<sup>[25]</sup> or hexaarylbiimidazole,<sup>[26]</sup> into the hydrophilic hydrogel network. However, because of the poor solubilities of mechanophores in aqueous solutions, there have been few reports on mechanochromic hydrogel preparation from specific mechanophores. Recently, novel micellar hydrogels that covalently incorporated hydrophobic mechanophores, such as SP or Rh, in the microsphere were developed. These hydrogels showed strong mechanochromic and mechanical properties.<sup>[27,28]</sup> The SP mechanophore-functionalized micellar hydrogel had good mechanochromism but poor mechanofluorescence,<sup>[28,29]</sup> whereas the Rh mechanophore-functionalized micellar hydrogel had good mechanochromic and mechanofluorescent properties.<sup>[28]</sup> To the best of our knowledge, hydrogels with mechanofluorescence, which is important for quantitative detection of stress/strain, have been rarely reported. Because of the stress relaxation induced by hydrophobic interactions in the microsphere and the unfavorable hydrophobic environment in which the mechanophores are embedded, the stress sensitivity of a Rh mechanophore-functionalized micellar hydrogel is limited.<sup>[28]</sup> An alternative strategy, which could greatly increase the mechanochromic and mechanofluorescent sensitivities of hydrogels, should be explored for both academic research and practical applications.

Rhodamine-based mechanophores can undergo a force-induced structure isomerization from a twisted spirolactam to a planar zwitterionic form; however, their mechanical sensitivities are very low.<sup>[24,29,30]</sup> When they were covalently incorporated into single network elastomers, mechano-activation did not occur until they were broken. While they were incorporated into a pre-stretched first network of a triple-network elastomer, the mechanical sensitivity obviously increased.<sup>[24,29]</sup> In fact, extensive pre-stretching of the first network in a multiple-network elastomer is important for increasing

the degree of mechanical response of the mechanophores, as shown in work by Creton *et al.*<sup>[31]</sup> Given that the first network in a dual-network (DN) hydrogel is highly swollen and pre-stretched<sup>[32,33]</sup> and water can make large contribution to the activation of the Rh mechanophore,<sup>[30]</sup> if the Rh mechanophore is embedded into the first network of the DN hydrogel, the stress sensitivity of the gel may be high.

Herein, we report a Rh mechanophore-functionalized mechanochromic and mechanofluorescent DN hydrogel system. To incorporate the hydrophobic Rh into the hydrogel, we adopted a solvent replacement method, and the Rh mechanophore was covalently incorporated as a cross-linker into the first network of the hydrogel (Fig. 1). Considering the high level of pre-stretching of the first network and the favorable activation of Rh in the presence of water, we expected the mechanochromism sensitivity would be high. The high stress sensitivity of the hydrogel was validated by evaluation of mechanoresponsiveness of the DN hydrogel upon stretching or freezing. To the best of our knowledge, this is the first example of a DN hydrogel that exhibits highly stress-sensitive, freezing-induced mechanochromic, and pH-regulated mechanochromic properties.

## EXPERIMENTAL

### Materials

2-Acrylamido-2-methylpropanesulfonic acid (AMPS, 99%, Aladdin) was recrystallized from methanol. Acrylamide (AAM, 97%, Sinopharm Chemical Reagent, Co., Ltd.) was recrystallized from chloroform. 4-Methoxyphenol (MEHQ, 99%, Aladdin) and *N,N'*-methylenebisacrylamide (MBAAm, 96%, Aladdin) were recrystallized from ethanol. Dimethylacrylamide (DMAAm), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (photoinitiator Irgacure 2959, 98%, Aladdin), 2-oxogultaric acid (97%, Aladdin), sodium hydroxide (NaOH), disodium phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), sodium dihydrogen phos-

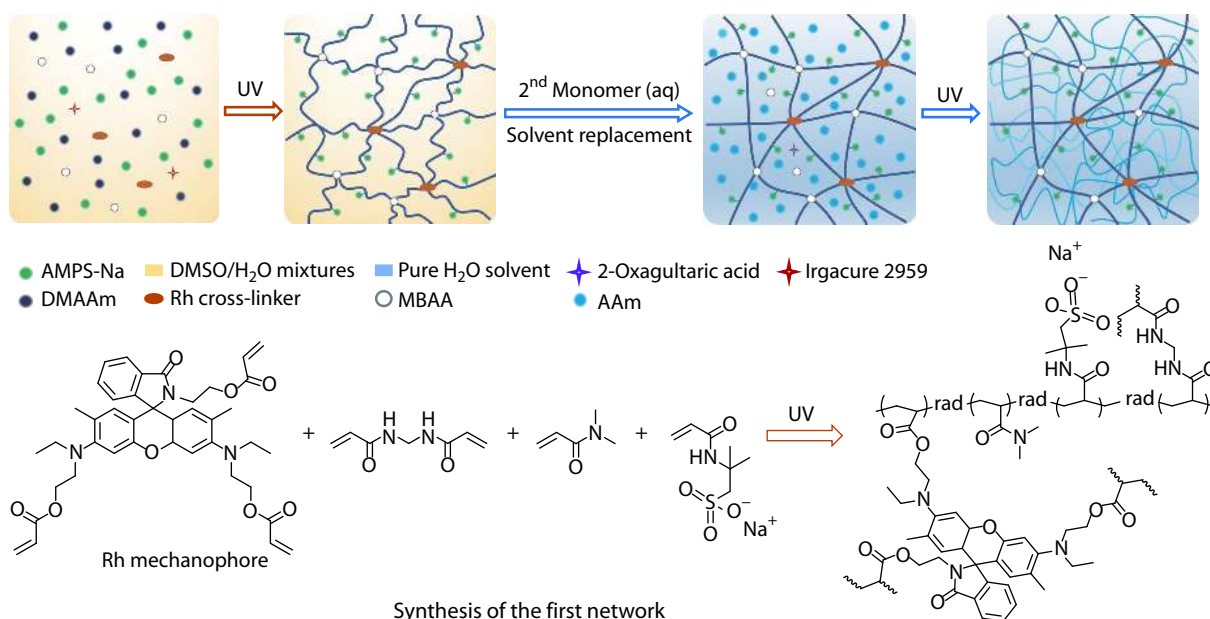


**Fig. 1** Schematic illustration of the preparation of the rhodamine mechanophore-functionalized dual-network hydrogel.

phate dihydrate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ), sodium tetraborate standard buffering agent (pH 9.18), and potassium hydrogen phthalate buffering agent (4.01) (AR, Sinopharm Chemical Reagent, Co., Ltd.) were used as received. A series of 20 or 80 mmol/L buffer solutions with different pH values (4.01, 6.0, 6.5, 7.0, 7.4, 8.0, 9.18, and 12.0) were prepared. Buffer solutions with pH values between 6.0 and 8.0 were prepared using the  $\text{Na}_2\text{HPO}_4$ - $\text{NaH}_2\text{PO}_4$  buffer system (PB), and the pH 12.0 solution was prepared using the  $\text{NaOH}$ - $\text{NaH}_2\text{PO}_4$  buffer system. A 200 mmol/L PB buffer solution with a pH of 7.0 was prepared as well. Water used in this work was purified using a Millipore water purification system with a resistivity of 18.2 M $\Omega$ -cm ( $\text{H}_2\text{O}$ , pH = 7.0). Soda-lime glass plates (thickness: 3 mm) were used for the gel synthesis. Glass molds were prepared from two glass plates with silicone rubber spacers (thickness: 1.0 or 1.5 mm).

## Synthesis and Preparation

### Synthesis of Rh cross-linkers

Three kinds of Rh cross-linkers, namely Rh mechanophore, control Rh molecule, and control mechanophore (Fig. S1, in electronic supplementary information, ESI), were synthesized via multi-step organic synthesis as reported previously.<sup>[29]</sup> Their chemical structures and purities were identified by  $^1\text{H}$ -NMR (Figs. S2–S4 in ESI).

### Preparation of 2-acrylamido-2-methylpropanesulfonic acid sodium (NaAMPS) solution (3 mol/L)

4.7 g of AMPS was dissolved in 3.62 g of deionized water in a flask, and the flask was sealed and kept in an ice-water bath. Then, 0.84 g of NaOH was gradually added into the solution while stirring. Finally, pH of the solution was adjusted to be 7.0, and 300 ppm of MEHQ as polymerization inhibitor was added. The final concentration of the NaAMPS solution was 3 mol/L.

### Synthesis of Rh mechanophore-crosslinked first network

Typically, as for the SN-1.5-0.5 gel (Table S1 in ESI), the preparation procedure was as follows: DMAAm (0.1 g, 1.04 mmol), MBAAm (4.65 mg,  $3 \times 10^{-2}$  mmol), Rh mechanophore (7.5 mg,  $1 \times 10^{-2}$  mmol), and Irgacure 2959 as photoinitiator (5 mg) were dissolved in DMSO (1.45 g). Then, 0.32 g of NaAMPS solution (0.96 mmol) was added, followed by uniform mixing. After bubbling with  $\text{N}_2$ , the mixture was injected into a glass mold with a 1.0 mm thick Teflon spacer and exposed to UV light (4 mW/cm $^2$ ). The gel would be formed after 4 h of photopolymerization. The obtained gels were removed from the mold and repeatedly washed with excess DMSO to remove unreacted materials.

### Synthesis of the second network

In a typical preparation process, the Rh mechanophore cross-linked first network gels were immersed in the second network precursor aqueous solution (pH adjusted to about 7.0) containing 2 mol/L AAm, 0.02 mol% MBAAm, and 0.01 mol% 2-oxoglutamic acid for about 12 h to remove DMSO. Then, the gels were immersed in fresh second network precursor aqueous solutions two more times before sandwiching between two glass plates. Next, photopolymerization was initiated under 365-nm UV irradiation (4 mW/cm $^2$ ) for 9 h to synthesize the second PAAm network within the Rh cross-linked gels in a  $\text{N}_2$  blanket. Finally, the poly(NaAMPS-co-DMAAm)/PAAm DN hydrogels (namely Rh mechanophore-functionalized hydrogels) were successfully obtained. Some of the obtained Rh cross-linked

DN hydrogels were immersed into pure water or PB (80 or 200 mmol/L) to prepare swollen hydrogels. The rest of the gels (as-prepared hydrogels) were used directly for testing. To obtain DN hydrogels with different pH values, the gels were first soaked in PB (80 mmol/L, pH 6.0–12.0) several times, and then put in the same environment to obtain dehydrated hydrogels with the same solid contents and almost the same sizes as the as-prepared hydrogels. Finally, we used gels with different pH values to investigate pH-regulated mechanochromism.

### Preparation of control DN hydrogels

The control DN hydrogels were prepared following the same procedure for Rh mechanophore-functionalized hydrogel except that the cross-linker used in the first networks was control Rh molecule for C2 DN hydrogel and control mechanophore for C3 DN hydrogel.

## Characterizations

### Mechanical characterization

Tensile tests of the hydrogels were conducted on an electrical universal material testing machine with a 500 N load cell (EZTest, SHIMADZU). The samples of SN and DN hydrogels were cut into long dumb bell shape with a gauge length of 13 mm, a width of 2.2 mm, and a thickness of 2.5 mm. And the crosshead velocity was kept at 100 mm/min during the normal tensile tests. In addition, silicone oil was coated on hydrogel surface during the tensile tests. When the tests finished, the tested hydrogels were coated with a layer of silicone oil, encased by the plastic wrap, and stored in sealed plastic pipe to avoid water volatilizing. All the measurements were carried out at room temperature (about 25  $^{\circ}\text{C}$ ).

### Fluorescence spectrometry

Fluorescence spectra were measured after removing stress immediately and the measurements were performed on a Shimadzu RF-5301PC spectrofluorophotometer. The excitation wavelength was 365 nm. Scan speed: 3000 nm/min. Scanning range: 400–700 nm. Variable-temperature (25,  $-3$ ,  $-15$ , and  $-30$   $^{\circ}\text{C}$ ) fluorescence measurements were carried out on a Shimadzu RF-5301PC spectrofluorophotometer, and the temperatures were controlled by a DR 502 Freeze-thaw test chamber ( $-50$   $^{\circ}\text{C}$  to 150  $^{\circ}\text{C}$ ). The fluorescence spectrum of  $-196$   $^{\circ}\text{C}$  was measured after freezing in liquid nitrogen.

### Digital image or video analysis

Optical images or videos were taken by a NIKON D7000 camera. The images of frozen gels were taken in the DR 502 Freeze-thaw test chamber below 0  $^{\circ}\text{C}$ .

### Swelling measurements

To calculate the swelling ratios of the prepared poly(NaAMPS-co-DMAAm) SN gels in the second monomer precursor solutions, volume swelling degrees ( $V/V_0$ ) were measured (Table S1 in ESI), where  $V$  is the volume of the swollen gel. The volumes were measured by taking the gels out of their solutions, removing excess solution from the gel surface, and measuring the dimensions.  $V_0$  is the volume of as-prepared SN gel. Additionally, before detection of the mechanochromic behaviors of the swollen DN gels, we measured the equilibrium swelling ratios of the DN gels in pure water or PB solutions. First, the as-prepared DN hydrogels were placed in pure water or PB solutions (200 or 80 mmol/L, pH 7.0) at room temperature on three occasions over 2 days, and the swelling ratios ( $Q$  values) of the DN gels

were calculated from the masses of the swollen and original gels as follows:  $Q = W_t/W_o \times 100$ , where  $W_t$  and  $W_o$  are the masses of swollen gels in the equilibrium swelling state and the original gels, respectively.

## RESULTS AND DISCUSSION

### Fabrication of Mechanochromic DN Hydrogel

The hydrogel was prepared as shown in Fig. 1. To fabricate the mechanochromic DN hydrogel, the Rh mechanophore needed to be incorporated into the hydrogel. However, the poor solubility of Rh mechanophore in aqueous solutions made it quite difficult to be directly incorporated into the highly hydrophilic network. To overcome this problem, we adopted a solvent replacement method. First, the Rh mechanophore, MBAAm, Irgacure 2959 (photoinitiator), and DMAAm were dissolved in DMSO. Then, a NaAMPS aqueous solution was added, followed by mixing until uniform and injection of the mixture into a glass mold. After 4 h of photopolymerization, we obtained an organogel. Importantly, by considering the poor solubility of NaAMPS in DMSO and to guarantee the homogeneity and integrity of the gel, DMAAm was introduced as a co-monomer. Next, the gel was soaked in the second network precursor aqueous solution three times. This completely replaced DMSO with H<sub>2</sub>O, and gave a very swollen hydrogel partially cross-linked with the Rh mechanophore (Fig. S5 in ESI). After another photopolymerization, the second network of neutral PAAm gel was synthesized in the presence of the first network gel. The solid mass fraction of the as-prepared DN hydrogel was as low as 22%. Almost all components in the gel were hydrophilic, which endowed the gel with good water retention ability.

Fig. S6 (in ESI) shows the FTIR spectra of the first network hydrogel and DN hydrogel. In the spectrum of the first network gel, bands associated with NaAMPS, DMAAm, and MBAAm were observed at about 1648 cm<sup>-1</sup> (amide C=O (amide I)), and 3438 cm<sup>-1</sup> (—NH stretching); bands at about 1199 and 1038 cm<sup>-1</sup> corresponded to the asymmetric and symmetric S—O stretching of the —SO<sub>3</sub><sup>-</sup> in NaAMPS. These characteristic bands could also be observed in the spectrum of DN gel, which strongly suggested the existence of the first network (poly(NaAMPS-co-DMAAm)) in the DN gel. A small characteristic band at 1616 cm<sup>-1</sup> corresponding to —NH<sub>2</sub> bending (amide II) from AAm was only observed in the spectrum of DN gel, indicating that PAAm network was also

presented in the DN gel. These results demonstrated that both the poly(NaAMPS-co-DMAAm) network and PAAm network were present in the DN hydrogel.

Successful incorporation of the Rh mechanophore was verified by obvious optical changes of the DN hydrogel under force or acid/alkali conditions. These changes occurred because the Rh mechanophore can undergo force- or acid-induced structure isomerization from a colorless spirocyclic form to a colored open-cycle form (Fig. S7 in ESI), which produces a change in the visible or fluorescent color of the material.<sup>[24,29,34,35]</sup> The DN hydrogel we fabricated was mechanochromic (Fig. 2). The original colorless gel turned rose red after stretching, and the corresponding fluorescent color changed from pale yellow to orange-red under UV irradiation (Fig. 2a). Moreover, when the gel was mechanically stamped by a “USTC60” mold, the letters had a distinct rose red color and could be observed by naked eye. Under UV irradiation, the letters were orange-red and clearly in contrast to the pale yellow background (Fig. 2b). These visible and fluorescent color changes substantiated the mechanoactivation of the Rh mechanophore cross-linked in the DN gel. After removing the stress, the rose red color and orange-red fluorescence faded gradually, and the initial colorless state or pale yellow fluorescence state of the gel was fully restored within about 1 h at room temperature (Figs. 2a and 2b). The gel was also acidochromic. After soaking in an acidic buffer solution, the gel showed a visible color change from colorless to red, and the fluorescent color changed from pale yellow to bright yellow under UV irradiation (Fig. 2c). After soaking the colored gel into an alkaline buffer solution, the visible color of the gel returned to the original colorless state, and the fluorescent color changed to blue (Fig. 2c).

In a word, based on the conventional preparation method of DN hydrogels and in virtue of the solvent replacement strategy, hydrophobic Rh mechanophore was successfully incorporated into the hydrogel. As a result, we obtained the mechanochromic DN hydrogel.

### Mechanical Properties of the DN Hydrogel

Because DN hydrogels usually have high mechanical strength, and some even exhibit good stretchability, we aimed to produce a mechanochromic DN hydrogel with high tensile strength and good stretchability. To do so, we prepared a series of organogels as the first networks, which contained different total concentrations of cross-linkers (including Rh mechanophore

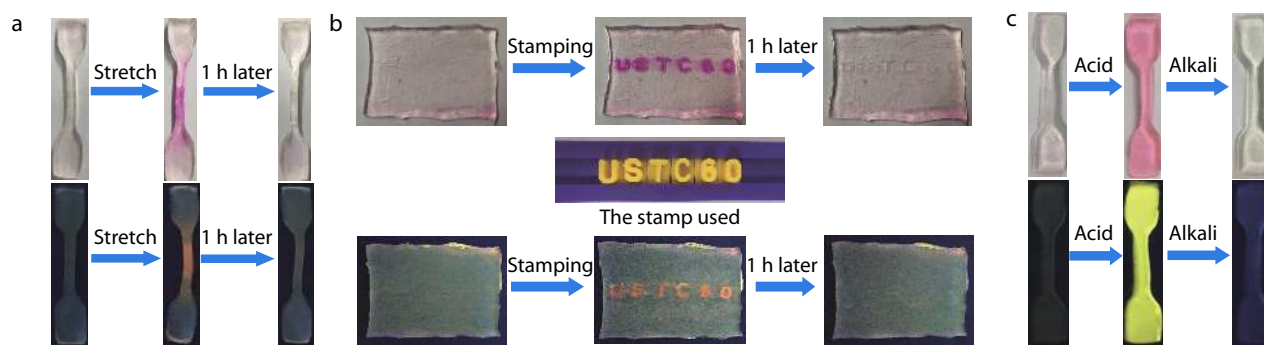


**Fig. 2** Optical (upper) and fluorescent (lower) images of (a) a dumbbell-shaped DN hydrogel after stretching, (b) a quadrate DN hydrogel after stamping with letters, and (c) the DN hydrogel after treatment with acid or alkali.

and MBAAm) or various concentrations of Rh mechanophore while the total concentration of cross-linkers was held constant. After soaking them in the second network precursor aqueous solution, followed by photo-polymerization of the swollen gels, a series of DN hydrogels were obtained. We first examined the mechanical properties of the first network gels. The tensile strengths and fracture strains of the organogels were all very low (Fig. 3a), and the swollen gels were too brittle to be tested on the tensile machine. Then, we investigated their mechano-responsive properties, and no color change was observed, even after breaking (Fig. S8 in ESI). These results demonstrate the Rh mechanophore cross-linked in the first network gel cannot be activated by force, probably due to the low mechanical strength. Next, we examined the mechanical properties of the DN hydrogels. Their mechanical properties were enhanced markedly compared with those of the first network gels (Fig. 3). Since the DN hydrogels fabricated here were similar to the conventional DN hydrogel first developed by Gong,<sup>[33]</sup> the enhancement of tensile mechanical properties was supposed to be attributed to the sacrifice of the first network. To confirm it, successive cyclic loading-unloading experiments were performed. As shown in Fig. S9 (in ESI), a large hysteresis loop and energy loss were observed in the first loading-unloading cycle, suggesting that DN gels dissipated energy effectively. By com-

parison, in the 2<sup>nd</sup>–4<sup>th</sup> cycles, the gels exhibited much smaller hysteresis loop and lower energy loss, indicating the irreversible rupture of the first network occurred in the DN gels, leading to softening. Although the mechanical strengths of the DN hydrogels were much higher than those of the first network gels, their mechanical properties were quite different (Fig. 3 and Table S2 in ESI). We inferred that the total concentration of cross-linkers or the concentration of Rh mechanophore in the first network had great effect on the tensile mechanical properties of the DN hydrogels.

Then, we investigated the effect of the total concentration of cross-linkers (Fig. 3b). As the concentration of total cross-linkers increased from 2 mol% to 3 mol% of total monomer concentration in the first network, and the concentration of Rh mechanophore was held constant, the volume swelling ratio of the first network decreased monotonically from 24.5 to 9.7 (Table S1 in ESI). As a result, the molar ratio of the first to the second network in the DN gel increased. In fact, the rigid and brittle first network of DN gels usually serves as a sacrificial bond which fractures at an early stage of deformation, while the soft and ductile second network maintains the integrity of the DN gels and offers extensibility.<sup>[33,36]</sup> As the molar ratio of the first to the second network increased, the gels would become more brittle. Thus, with increasing total con-

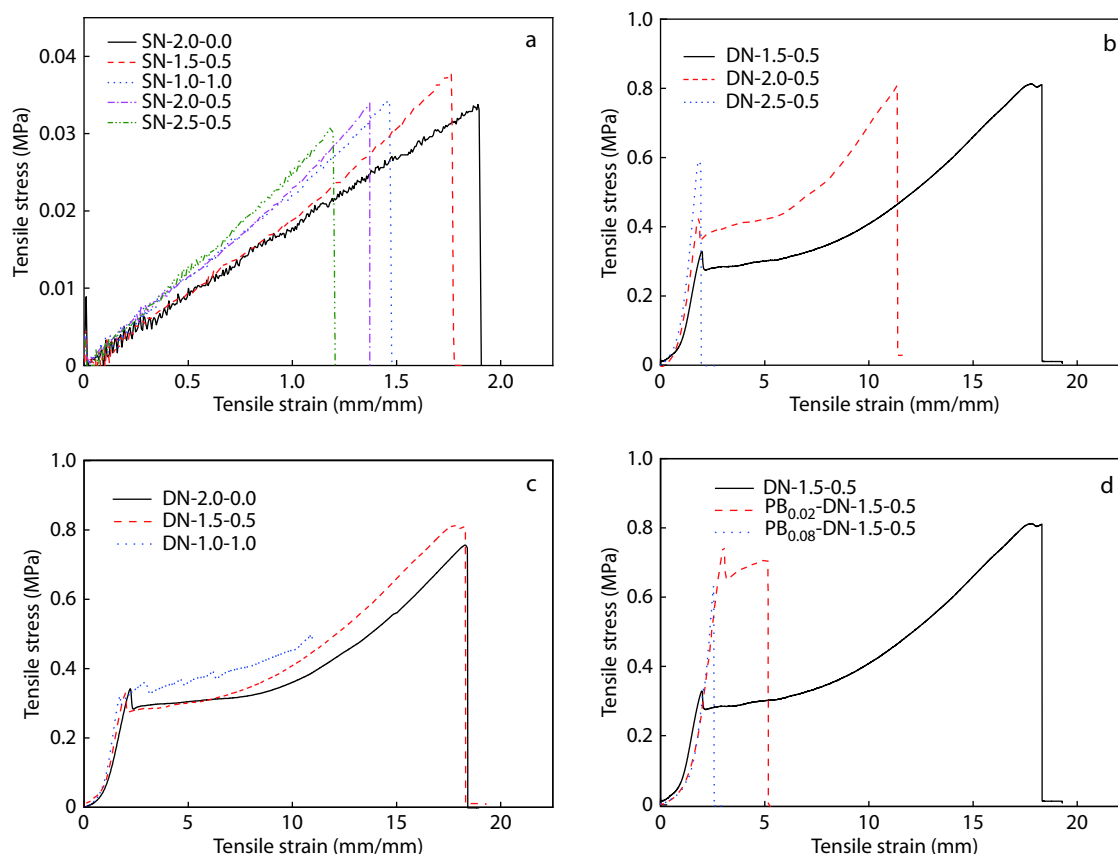


**Fig. 3** (a) Tensile stress-strain curves of poly(NaAMPS-co-DMAAm) SN gels with different total concentrations of cross-linkers or different concentrations of Rh mechanophore; Tensile stress-strain curves of the corresponding DN hydrogels (b) with different total concentrations of cross-linkers for the first network, (c) with different concentrations of Rh mechanophore for the first network, and (d) prepared in PB solutions with different concentrations. In DN-X-Y and PB<sub>z</sub>-DN-X-Y: PB stands for phosphate buffer, z is the concentration of PB, DN stands for dual network gel, X represents the cross-linker concentration of MBAAm (mol%), and Y represents the cross-linker concentration of Rh mechanophore (mol%).

centrations of cross-linkers, the tensile fracture strain of the gel decreased dramatically from 17.8 to 1.87. Meanwhile, the elastic modulus of the gel increased greatly from 270 kPa to 530 kPa, which was essentially associated with the increase in cross-linking density of the first network. In addition, with increasing total concentrations of cross-linkers, the yielding stress of the gel increased, whereas the “necking” or “hardening” process got weaker and the fracture stress decreased (Fig. 3b and Table S2 in ESI). We concluded that when the first network of the DN hydrogel had a low cross-linking density, that is, a low cross-linker concentration (2 mol%), the DN hydrogel showed better tensile mechanical properties, including high toughness ( $\epsilon_f = 17.8$ ), high strength ( $\sigma_f = 0.81$  MPa), and an outstanding yielding-like phenomenon.

We also studied the effect of Rh mechanophore concentration. The total concentration of cross-linkers remained the same (2 mol%), while the concentration of Rh mechanophore was varied from 0 to 1 mol%. As the concentration of Rh mechanophore increased, the swelling ratio of the first network decreased gradually (Table S1 in ESI). This was mainly ascribed to the small increase of total cross-linking density that occurred because Rh mechanophore has three cross-linking junctions whereas MBAAm has two. Accordingly, the molar ratio of the first to the second network in the DN gel increased by degrees, and the tensile fracture strains of the hydrogels decreased to different degrees (Fig. 3c and Table S2 in ESI). Additionally, the (primary) yielding stress and yielding strain of the gels decreased gradually as the Rh concentration increased (Table S2 in ESI). In parallel, the tensile stress-strain curves corresponding to the “necking” regions gradually became less smooth. When the Rh concentration was increased to 1 mol%, several yielding points emerged, resulting in irregular tensile mechanical behavior (Fig. 3c). These results suggest catastrophic internal fracture will occur more easily with the increasing concentration of Rh. Fortunately, when the concentration of Rh mechanophore was 0.5 mol%, the tensile stress-strain curve of the hydrogel showed only one yielding point, and it also exhibited high mechanical strength and a large fracture strain.

Interestingly, the concentration of salt in the second network precursor aqueous solution also influenced the tensile mechanical properties of the DN hydrogels. Although all the first network gels had the same composition, after soaking them in the second network precursor aqueous solutions, which contained different concentrations of phosphate buffer (PB; 0, 20, and 80 mmol/L), their swelling ratios were different (Table S3 in ESI). Moreover, after examining the mechanical properties of the corresponding DN hydrogels, we found the tensile fracture strain of the gel decreased dramatically with increases in the salt concentration (Fig. 3d). This occurred mainly because the ions in saline solutions can weaken the repulsive interactions of the anionic groups of Na-AMPS units, resulting in a decrease in the swelling ratio of the first network<sup>[10,37]</sup> (Table S3 in ESI). Thus, the molar ratio of the first to the second network in the DN gels increased, and as a result, the gels became more brittle. These results indicate that the DN hydrogels fabricated in saline solutions like PB will be more brittle and less tough than those fabricated in pure water. To obtain a DN hydrogel with both mechanore-

sponsive performance and good tensile mechanical properties, saline solutions should not be used during the preparation process.

From the above arguments, we concluded that when the first network of the DN hydrogel had a low total concentration of cross-linkers (2 mol%) and a moderate concentration of Rh mechanophore (0.5 mol%), the corresponding DN hydrogel (DN-1.5-0.5) fabricated in pure water would exhibit regular and good tensile mechanical properties, including high toughness, high strength, and one yielding point (Fig. 3).

Additionally, we also examined the mechanical properties of the control DN hydrogels functionalized with control Rh molecule or control mechanophore. The hydrogels exhibit regular and good tensile mechanical properties (Fig. S10 in ESI).

### Mechanoactivation of Rh Mechanophore in the DN Hydrogel upon Stretching

Mechanoactivation of the Rh mechanophore was studied mainly using the DN-1.5-0.5 hydrogel. Because mechanoactivation of the Rh mechanophore can be reflected by the mechanochromic and mechanofluorescent properties of the materials,<sup>[24,29]</sup> we first examined the mechanochromic and mechanofluorescent behaviors of the hydrogel, which are presented in dynamic optical images and videos taken during the uniaxial tensile tests (Figs. 4a and 4b). In the early stages of elongation, the hydrogel was uniformly elongated (Figs. 4a and 4b). When the strain ratio reached about 150%, both fluorescent and visible color changes began to emerge in the narrow part of the stretched gel. Once the applied stress reached a critical value of  $\sigma_c$  (about 330 kPa), the strain ratio reached about 198% (Fig. 4d) and the necking region appeared in the central part of the gel. Meanwhile, the necked region turned rose red and emitted red fluorescence. Notably, the force-induced color change in the necked region was more apparent than that in the un-necked region. Upon further elongation, the necked region described above extended, which reduced the size of the un-necked region located in the middle of the gel. When the strain ratio reached 800%, the un-necked region almost disappeared, and at the same time, the gel showed obvious fluorescence and visible red coloration throughout the whole necked region. This demonstrated that mechanoactivation of the Rh mechanophore cross-linked in the first network began to take place before the gel yielded. Subsequently, the amount of Rh mechanophore activated by force increased obviously in the necked region because apparent catastrophic fracture occurred, which greatly promoted mechanoactivation of the Rh mechanophore. Later, with propagation of the necked region, the dominant first network fragmented into small clusters, and as a result, the amount of the Rh mechanophore activated by force increased progressively (Fig. 5). By using the Rh mechanophore, we can directly see where and when sacrificial bonds break as the gel is deformed, which is beneficial for us to understanding the yielding process of the DN hydrogel. It should be noticeable that the Rh mechanophore can emit three-primary-color fluorescence under the stimulus of force.<sup>[29]</sup> Therefore, upon stretching, the Rh-functionalized DN-1.5-0.5 hydrogel emitted red fluorescence (Fig. 4b). After unloading, the fluorescence color turned from red to yellow (Fig. 2a). The mechanochromic behavior of the DN-1.0-1.0 hydrogel is also shown in dynamic images or videos (Fig. S11 in ESI). No-

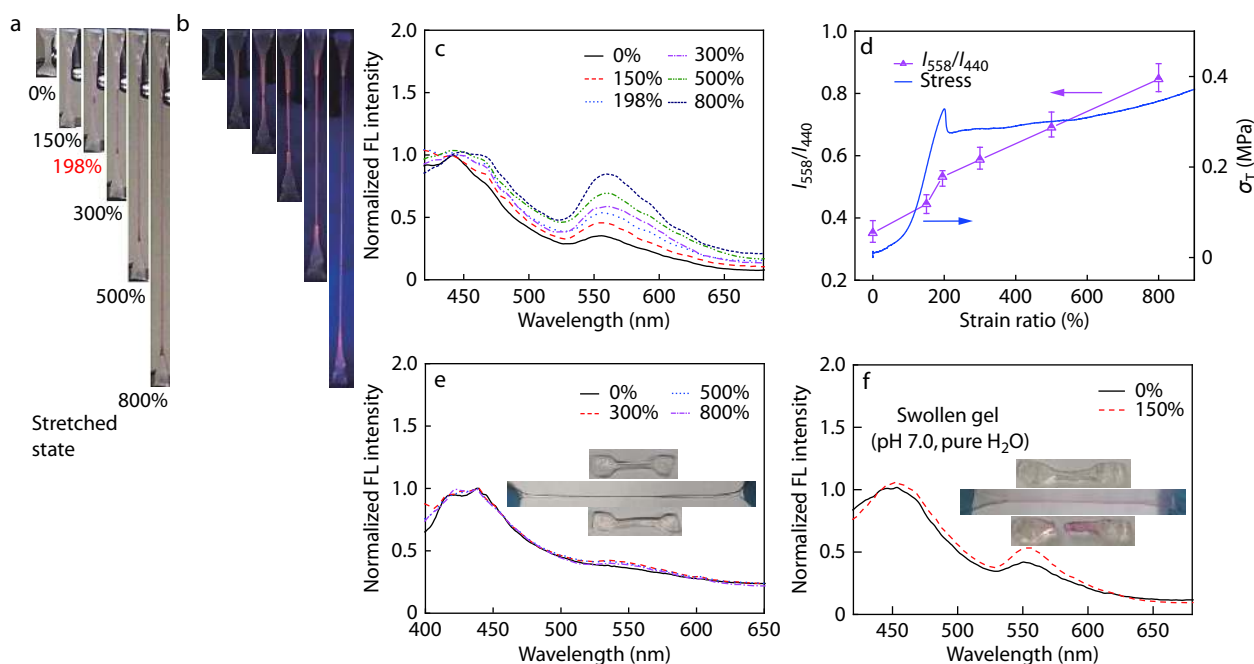


**Fig. 4** Strain-induced dynamic (a) visible color changes and (b) fluorescent color changes of the as-prepared Rh-mechanophore-functionalized DN hydrogel (DN-1.5-0.5 gel, stretch ratios of 0%-800%); (c) Fluorescence emission spectra of the as-prepared DN-1.5-0.5 gel with different strain ratios; (d) The stress/fluorescence intensity ratio of  $I_{558}/I_{440}$  as a function of stretch ratio for the as-prepared DN-1.5-0.5 gel; (e) Fluorescence emission spectra of the control Rh molecule-functionalized DN hydrogel (C2 DN-1.5-0.5 gel) with different strain ratios; (f) Fluorescence emission spectra of the DN-1.5-0.5 gel with different strain ratios for gel swollen in pure water until it reached its equilibrium state. (The insets show the images of corresponding hydrogels before and after mechanical stretching. The strain ratio was ~500% for e and ~200% for d.)

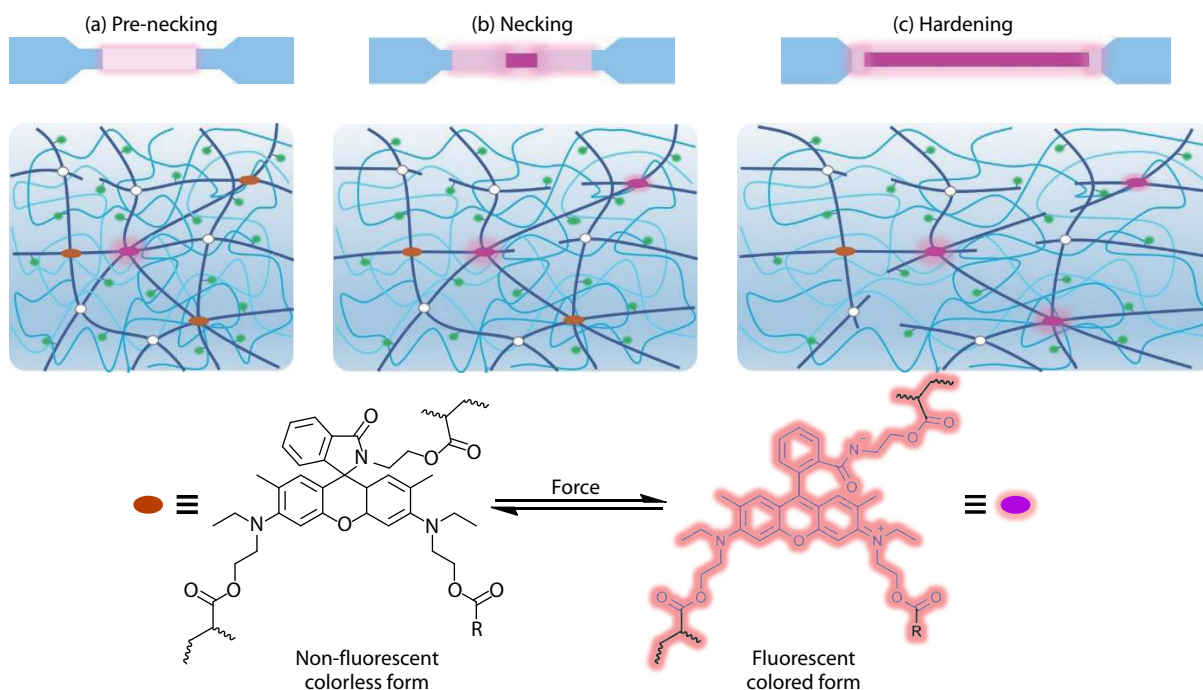


**Fig. 5** The mechanochromic/mechanofluorescent performance of the Rh mechanophore-functionalized DN hydrogel in accordance with the internal stretched state or fracture process in pre-necking, necking, and hardening regions. "R" in the chemical structures presents a polymer chain or polymerizable double bond.

tably, the color change of this gel induced by force seemed more obvious than that of DN-1.5-0.5 gel, which was because the concentration of Rh mechanophore in this gel was higher

than that in DN-1.5-0.5 gel. Unfortunately, this gel showed unfavorable mechanical behavior, namely multiple yielding points (Fig. S11 in ESI).

To gain further insight into mechanoactivation of the Rh mechanophore in the DN hydrogel upon stretching, we investigated the dependence of fluorescence intensity on the strain ratios (Fig. 4c). The fluorescence intensity is easy to quantify and is often consistent with changes in visible or fluorescent color. The hydrogel initially showed two emission bands, at 440 and 558 nm, which originated from the ring-closed form and the corresponding ring-opened form of the Rh mechanophore, respectively (Fig. 4c). We suspected that the small amount of ring-opened Rh in the original gel might stem from mechanoactivation of ring-closed Rh, which was induced by high swelling of the first network. Upon stretching and with increases in the strain ratio, fluorescence intensity of the emission band at 558 nm increased gradually, which meant more and more Rh moieties were activated. Furthermore, the relationship of the fluorescence intensity ratio,  $I_{558}/I_{440}$ , to the stress and strain ratio was plotted (Fig. 4d) and used to evaluate the influence of stress/strain on mechanoactivation of Rh mechanophore. When the strain ratio reached about 150%, a small amount of the Rh moiety was activated by force, and the stress the gel endured was less than 200 kPa (Fig. 4d). In particular, when the gel began to yield, the amount of activated Rh mechanophore increased, whereas the corresponding stress was only 330 kPa. With any further increase in the strain ratio, the amount of activated Rh mechanophore increased gradually and the corresponding stress first decreased and then increased. Even when the strain ratio reached 800%, the corresponding stress was still less than 400 kPa. Compared with previously reported Rh mechanophore-functionalized elastomers or hydrogels, which required a high level of stress for activation (i.e., 800 kPa),<sup>[28,29]</sup> the detectable activation stress for this DN hydrogel was much smaller. This demonstrates that the stress sensitivity of this DN hydrogel is high. We supposed that both the hydrophilic environment Rh located and the advantages of dual network structure would be beneficial to high stress sensitivity. Firstly, water indeed helped to enhance the mechanical sensitivity of Rh, and it could promote the activation of Rh induced by force.<sup>[28,30]</sup> Then, the highly swollen first network could render the Rh-cross-linked chains in a highly extended and pre-stretched state, guaranteeing the extensive transfer of stress to the Rh mechanophores and facilitating their activation.<sup>[29,31,38]</sup> The Rh-cross-linked chains in the first network could act as sacrificial bonds that fractured easily upon stretching, which could also promote activation of the Rh mechanophore.<sup>[31]</sup> In addition, it is important to recognize that the second network sustained the integrity of the gel.

To develop deeper insight, we investigated the mechano-responsive property of a control DN hydrogel, C2 DN-1.5-0.5, which was functionalized with control Rh molecule (Fig. 6a). Upon stretching, no color change was observed, and the fluorescent band at 558 nm almost remained the same with increases in the strain ratio (Fig. 4e). This indicates that the control Rh molecule could not be mechanically activated when they were cross-linked in the hydrogel. It demonstrates that regardless of the material properties, whether the rhodamine moieties can exhibit mechanoresponsiveness or not

mainly depends on the linking positions of their cross-linking junctions, which has been proved in a previous report.<sup>[29]</sup> Additionally, because the Rh mechanophore bears three cross-linker groups, and it is unlikely that all three groups are linked, linking of only two groups in the gel is possible (Fig. 5). If two lower groups are linked, the corresponding Rh moiety is the same as the control Rh molecule cross-linked in the gel, and it will make no contribution to the mechanoresponsiveness of the hydrogel. As for the other case, we synthesized the corresponding cross-linker, namely control mechanophore (Fig. 6b), and using it, we fabricated another control DN hydrogel, C3 DN-1.5-0.5. The gel showed a weak color change after stretching, and the fluorescent band at 558 nm increased with increases in the strain ratio (Figs. S12b and S13a in ESI); however, its mechano responsiveness was worse than that of DN-1.5-0.5 (Figs. S12 and S13b in ESI). Thus, the Rh moiety corresponding to the other case would contribute less to the mechanoresponsiveness of the hydrogel. These results indicate that among the three Rh moieties, our main target, the Rh mechanophore, is the most sensitive to stress.

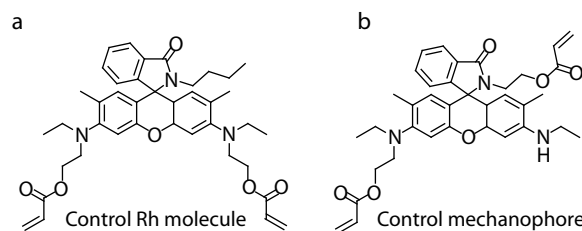


**Fig. 6** Chemical structures of (a) control Rh molecule and (b) control mechanophore.

We also studied the mechanoresponsive behavior of the swollen DN hydrogel upon stretching. When the gel swelled to its equilibrium state in pure water, the swelling ratio was 4.4, and its mechanical property was very poor (Fig. S14 in ESI). However, this swollen gel still showed mechanochromic or mechanofluorescent behavior (Fig. 4f). Furthermore, the mechanoresponsive behavior of the DN hydrogel after swelling in saline solutions (PB) was also investigated. When the DN hydrogels reached their swelling equilibrium states in 200 and 80 mmol/L PB solutions, their swelling ratios were 1.83 and 2.75, respectively, lower than that of the gel swelled in pure water. Nonetheless, their mechanical properties were better; specifically, their corresponding fracture stress and strain were higher (Fig. S14 in ESI). This was because the ions in solutions can weaken the repulsive interactions between network chains, resulting in a decrease in the swelling ratio of the DN gels;<sup>[10,37]</sup> consequently, the toughness and mechanical strength were enhanced. As expected, these two swollen hydrogels also exhibited mechanochromic and mechanofluorescent properties (Figs. S15 and S16 in ESI). These results demonstrate although the mechanical properties of swollen DN hydrogels are poor, they are enough to guarantee the mechanoactivation of Rh mechanophore. Therefore, there should be no concern that the mechanoresponse might disappear during swelling. The DN hydrogel fabricated here is promising to be used in sensors for the detection of changes

related to damage or stress in biological systems.

### Freezing-induced Mechanochromism of the DN Hydrogel

The Rh mechanophore-functionalized DN hydrogel also showed freezing-induced mechanochromism and mechano-fluorescence. When the gel sealed in a plastic tube was immersed in liquid nitrogen and frozen for 1 h, it showed a visible color change from colorless to pink and emitted red fluorescence under UV irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ). After thawing for about 30 min, the gel recovered to colorless (Fig. 7a). By contrast, the control Rh molecule-functionalized DN hydrogel did not exhibit similar color changes after freezing (Fig. S17 in ESI). These results suggest that activation of Rh mechanophore is induced by force. In fact, freezing of water can generate mechanical stress, and the stress can affect the polymer chains, triggering activation of the Rh mechanophore.<sup>[26,39,40]</sup>

Furthermore, we investigated the temperature-dependent mechanoactivation of Rh mechanophore in the DN hydrogel using photographs taken at different temperatures (all samples sealed in plastic tubes were cooled for 12 h) and the peak intensities in the fluorescence spectra (Fig. 7b). After cooling at different temperatures, which were all below  $0^\circ\text{C}$ , the gel was red and emitted yellow or red fluorescence. In parallel, the peak intensities in the fluorescence spectra increased remarkably after cooling, suggesting a large amount of Rh was activated during the cooling process. Additionally, as the cooling temperature decreased, the fluorescence intensity increased monotonically (Fig. 7b), and the fluorescence emission spectra were red-shifted. These results demonstrate that the temperature can affect mechanoactivation of the Rh mechanophore in the cooling process. To explain this, we supposed that as the cooling temperature decreased, internal

mechanical stress induced by freezing of water increased and stress relaxation weakened. As a result, mechanoactivation of Rh was enhanced, and conformational change of the stretched planarized Rh to its bent geometry was suppressed.<sup>[29]</sup>

To gain further insight into the freezing-induced mechanochromism or mechanofluorescence of the DN hydrogel, we investigated the reversibility of the mechano-activation of Rh mechanophore. The mechanoactivation degree of Rh mechanophore ( $I_{\text{max}}/I_{440}$ ) was measured with cycling of the temperature repeatedly between  $25$ ,  $-15$ , and  $-196^\circ\text{C}$  (Fig. 8). Notably, over six cycles, the degree of activation of the Rh mechanophore changed little, and the visible and fluorescent color changes appeared as expected. These results suggest that the freezing-induced mechanochromism of the hydrogel is highly reversible. This implies that the mechanical stress induced by water freezing is large enough to trigger mechanochromism of the hydrogel. However, it is still too low to induce catastrophic fracture of the network chains, which would adversely affect the reversibility of mechanochromism. Therefore, it is also demonstrated that the Rh mechanophore-functionalized DN hydrogel possessed high stress sensitivity. To the best of our knowledge, this is the first example of a freezing-induced mechanochromic hydrogel.

### pH-regulated Mechanochromic Behavior of the DN Hydrogel

Interestingly, we accidentally found that mechanochromic behavior of the DN hydrogel could be regulated by pH of the solution inside the gel. This finding was beyond our expectations, and we decided to investigate this phenomenon further. First, we prepared a series of hydrogels with different pH values ( $6.0$ ,  $7.0$ ,  $7.4$ ,  $8.0$ , etc.) and examined their mechanochromic behaviors.

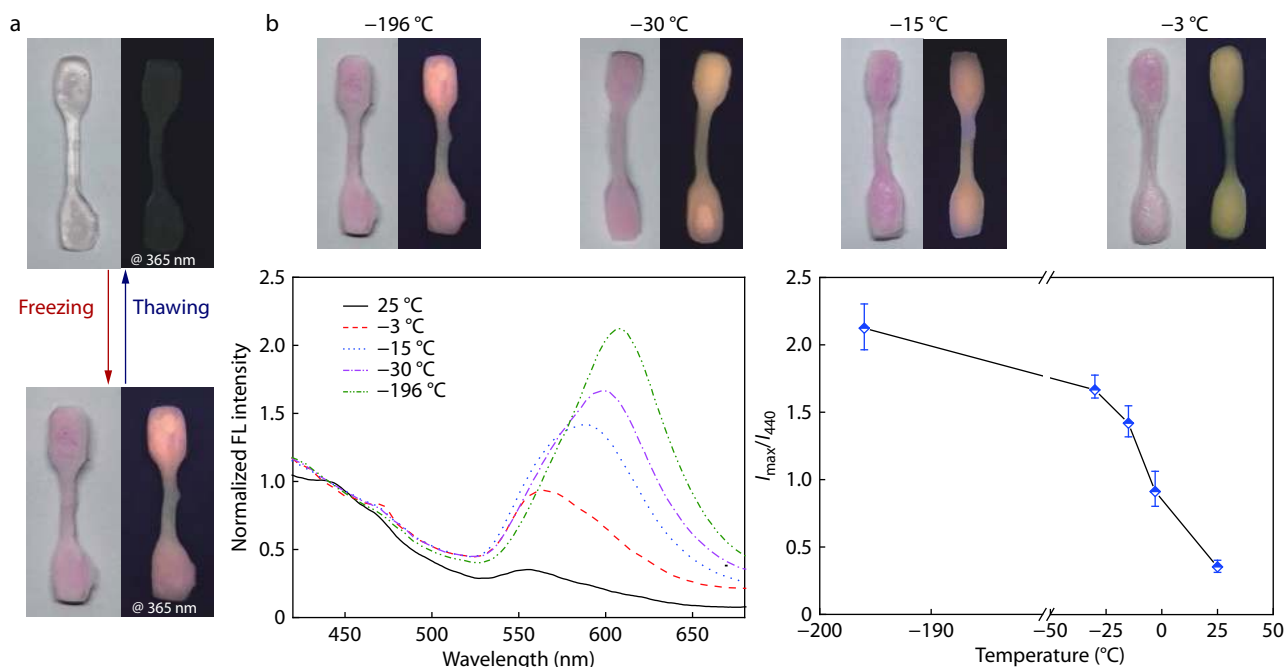


**Fig. 7** (a) Freezing-induced mechanochromism and mechanofluorescence of the DN hydrogels ( $-196^\circ\text{C}$ ) under ambient conditions and under UV irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ); (b) The fluorescence emission spectra and the peak intensities of fluorescence spectra at different temperatures ( $-196^\circ\text{C}$  to  $25^\circ\text{C}$ ) during the cooling process together with photographs taken at each temperature.

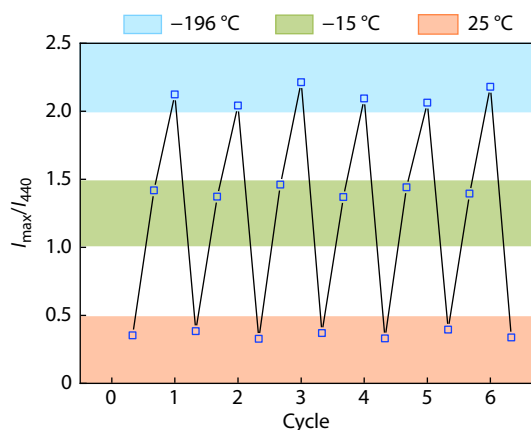


**Fig. 8** Mechanoresponsiveness of the Rh mechanophore in the DN hydrogel in response to reversible temperature change cycles (−196, −15, and 25 °C).

We recorded images of DN hydrogels upon and after stretching or compressing (Fig. 9a, Figs. S18 and S19 in ESI). Hydrogels with different pH values showed various color intensities. As the pH value increased, the intensity of the red color induced by stretching or compressing gradually decreased. Specifically, when the solution in the gel was weakly acidic (pH 6.0 or 6.5), the red coloration was dark. By contrast, when the solution inside the gel was alkaline, the coloration was light. These results indicate that pH of the solution inside the DN hydrogel can affect the mechanochromic behavior of the gels.

To procure further insight into the degree of pH influence on the mechanochromic behavior of the DN hydrogel, we examined the mechanofluorescence of DN hydrogels with different pH values. Mechanofluorescence is easy to quantify and is often consistent with the change in mechanochromism. We recorded fluorescence spectra of the DN hydrogels with different pH values at different strain ratios (Fig. S20 in ESI). The corresponding fluorescence intensities as a function of strain ratio are shown in Fig. 9(b). From these results we saw that when the DN hydrogels with different pH values were stretched to the same strain level, their fluorescence intensities were different. As the pH increased from 6.0 to 8.0, the fluorescence intensity decreased linearly. However, since notable differences existed among the fluorescence results of unstretched DN hydrogels with different pH values, the directly measured fluorescence corresponding to different strain ratios could not be used to represent the level of mechanofluorescence or mechanochromism. To better reflect the real fluorescence intensity induced by force, we focused on the changes in the fluorescence intensity ratio,  $I_{558}/I_{440}$ , of the stretched gel relative to the unstretched gel, and plotted the changes against the strain ratio (Fig. 9c). When DN hydrogels with different pH values were stretched to the same strain level, the changes in the fluorescence intensity ratios of these gels were also different (Fig. 9c). Overall, with increases in the pH values from 6.0 to 8.0, the changes in the fluorescence intensity ratios decreased linearly. Thus, the degree of pH influence on the mechanochromic behavior can be analyzed quantitatively.

To investigate possible reasons behind the pH-regulated

mechanochromic properties, we first examined the gels' mechanical properties because mechanical properties greatly affect mechanochromism.<sup>[41]</sup> When we measured stress-strain curves of hydrogels with the same solid content but different pH values, there were few differences among the mechanical properties (Fig. S21 in ESI). So, the mechanical properties of the DN hydrogels were not the main contributor to the pH-regulated mechanochromism.

Considering that the Rh mechanophore cross-linked in the DN gel was sensitive to both force and acid/alkali (Fig. 2), we suspected that the pH-regulated mechanochromism might be associated with the pH responsiveness of Rh mechanophore. In fact, under acidic conditions, a certain amount of Rh derivatives exist in the ring-opened form and the ring-closing reaction is suppressed. Under alkaline conditions, the ring-opened Rh derivatives can rapidly undergo a ring-closing reaction.<sup>[34,35]</sup> Therefore, we presumed that, for the present Rh mechanophore-functionalized DN hydrogel, after the mechanophore was activated by force,  $H^+$  probably stabilized the activated ring-opened Rh under acidic conditions, and ring-closing would be suppressed. By contrast, in alkaline solutions,  $OH^-$  would catalyze and promote cyclization of the activated ring-opened Rh to decrease stability, and as a result, ring-closing might be accelerated. Furthermore, a short time after the mechanoactivation of Rh mechanophore, we speculated that the amount of activated and ring-opened Rh under acidic conditions would be more than that under neutral conditions, and much more than that under alkaline conditions. Correspondingly, the color induced by force under acidic conditions would be deeper than that under neutral conditions, and much deeper than that under alkaline conditions. This seems to be in accordance with the pH-regulated mechanochromic phenomenon we observed.

Finally, we inferred that the differences in the mechanochromic behaviors of the gels might mainly depend on the difference in stability of the activated mechanophore, which could probably be regulated by pH. In this case, the mechanochromic behaviors we observed were “apparent” rather than true. Moreover, pH might also affect mechanoactivation of the Rh mechanophore, and the mechanochromic behaviors might be affected as well. However, effect of pH on mechanoactivation of the Rh mechanophore is not well understood, and we will explore it further in our future work.

To verify our hypothesis and confirm the influence of pH on the stability of ring-opened Rh, we first studied coloration decay courses of the gels upon stretching or compressing and the corresponding courses after relaxation. Our results showed that the decay rates for gels with neutral or alkaline pH values were higher than those with acidic pH values (Figs. S18 and S19 in ESI). Furthermore, we investigated the fluorescence intensity decay of gels with different pH values after stretching (Fig. S22 in ESI). The decay rates for the gels increased linearly with increasing pH. To gain further insight into the decay kinetics, the fluorescence intensity ratio,  $I_{558}/I_{440}$ , was plotted against time and fitted to a single-exponential decay equation  $N(t) = N_0 + N_1e^{-t/\tau}$  with different time constants (Fig. 9d and Fig. S23 in ESI). The fluorescence decay time constants as a function of pH are shown in Fig. 9(e). When pH was increased from 6.0 to 8.0, the decay time constant,  $\tau$ , decreased from 33.8 min to 1.8 min (Fig. 9e). This

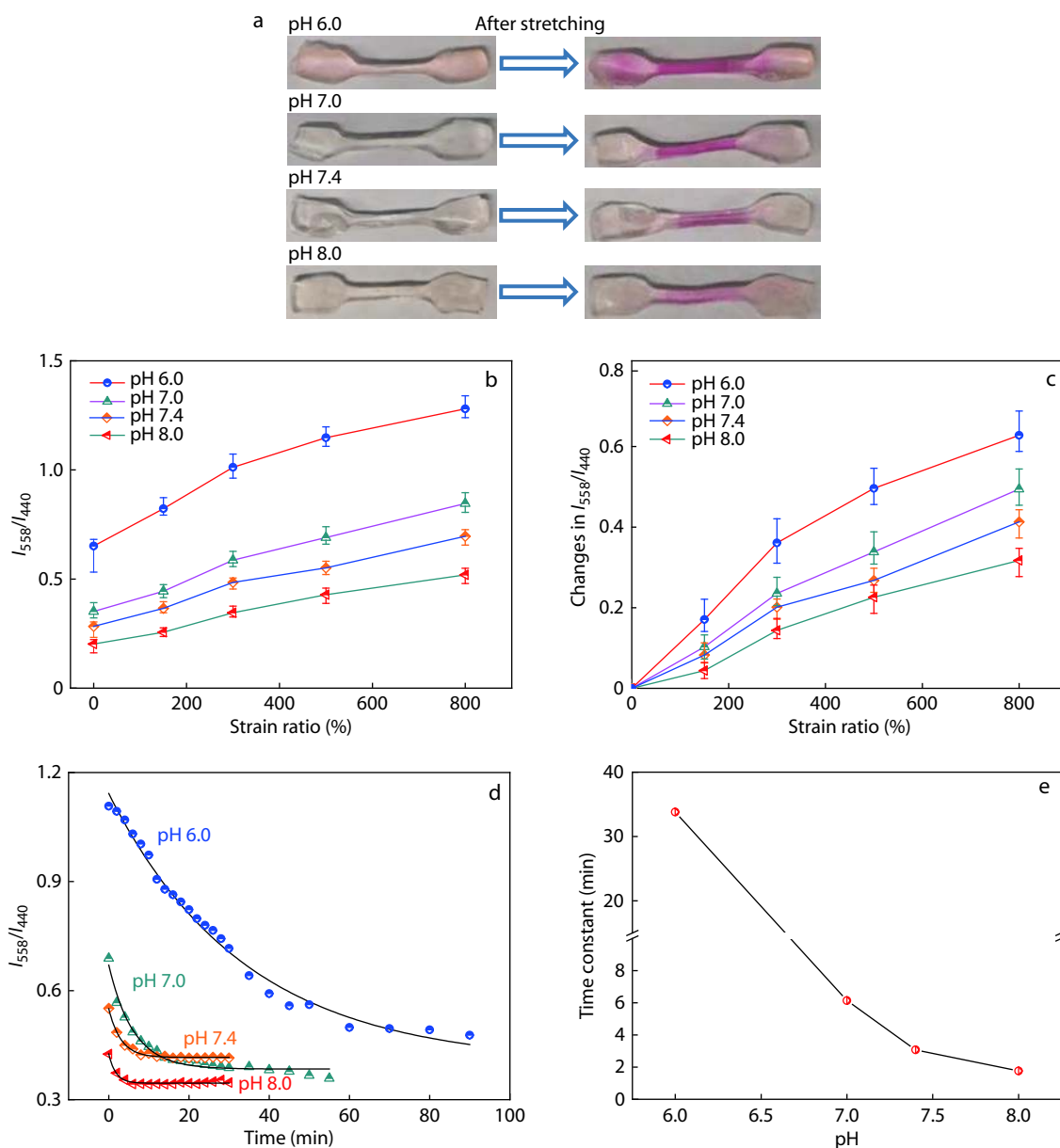


**Fig. 9** (a) Mechanochromic optical images of DN hydrogels with different pH values (the strain ratio was ~500%); (b) The peak intensities of fluorescence spectra and (c) changes in the fluorescence intensity ratio of  $I_{558}/I_{440}$  as a function of the strain ratio for DN hydrogels with different pH values; (d) Fluorescence intensity decay of the DN hydrogels with different pH values; (e) Plots of decay time constants of conversion of the ring-opened Rh to its ring-closed form in the DN hydrogels versus pH values.

quantitatively indicated that the decay rates for the gels increased linearly with increasing pH. In fact, rapid coloration or a high fluorescence decay rate means the activated Rh mechanophore has a fast ring-closing reaction rate and the activated Rh has poor stability. We can conclude that as pH inside the gel increases, the stability of the activated Rh gradually worsens. Shortly after mechanoactivation, the less stable activated Rh would make the gel the less stable contain fewer activated Rh and the color of the gel would be light. Therefore, we also concluded that the color intensities of the gels would decrease with increasing pH soon after mechanoactivation. This is consistent with the pH-regulated “apparent” mechanochromic behaviors we observed.

Above result shows that pH could affect the stability of the activated Rh mechanophore and further affect the “apparent” mechanochromic behavior of the DN hydrogel. To the best of our knowledge, our Rh mechanophore-functionalized DN hydrogel is the first gel showing pH-regulated mechanochromism. We believe our work will provide important guidance for enhancing the stress detection capability of the Rh mechanophore in aqueous systems.

## CONCLUSIONS

We successfully synthesized a mechanochromic and mechanofluorescent DN hydrogel with high stress sensitivity for the first

time. Because of high pre-stretching of the first network, together with the positive effect of water on the mechano-activation of Rh mechanophore, the hydrogel had a very sensitive response to stress. In fact, the stress threshold to activate the mechanochromism of the hydrogel was less than 200 kPa. The mechanochromism was even observed with the hydrogel in its equilibrium swollen state. Moreover, due to the improved sensitivity of the hydrogel to stress, the DN hydrogel exhibited reversible freezing-induced mechanochromism. To the best of our knowledge, this is the first example of a freezing-induced mechanochromic hydrogel. Specifically, the DN hydrogel showed pH-regulated mechanochromic behavior that benefits from the sensitivity of Rh mechanophore to both pH and force. This hydrogel preparation strategy introduces sensitive mechanochromism and preserves the advantageous mechanical properties of DN hydrogels simultaneously. Our efforts will be beneficial to the design and preparation of mechanochromic hydrogels with high stress sensitivity. We hope the mechanochromic DN hydrogels can function as sensors to detect stress activation in biological systems or as effective probes for fundamental studies on polymer solutions, especially at low temperatures.

### Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2293-1>.

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