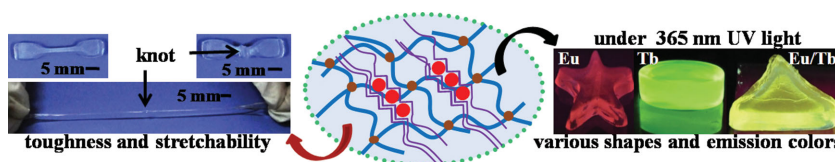


# Tough Photoluminescent Hydrogels Doped with Lanthanide

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Photoluminescent hydrogels have emerged as novel soft materials with potential applications in many fields. Although many photoluminescent hydrogels have been fabricated, their scope of usage has been severely limited by their poor mechanical performance. Here, a facile strategy is reported for preparing lanthanide (Ln)-alginate/polyacrylamide (PAAm) hydrogels with both high toughness and photoluminescence, which has been achieved by doping Ln<sup>3+</sup> ions (Ln = Eu, Tb, Eu/Tb) into alginate/PAAm hydrogel networks, where Ln<sup>3+</sup> ions serve as both photoluminescent emitters and physical cross-linkers. The resulting hydrogels exhibit versatile advantages including excellent mechanical properties (~MPa strength, ≈20 tensile strains, ≈10<sup>4</sup> kJ m<sup>-3</sup> energy dissipation), good photoluminescent performance, tunable emission color, excellent processability, and cytocompatibility. The developed tough photoluminescent hydrogels hold great promises for expanding the usage scope of hydrogels.



## 1. Introduction

Hydrogels are soft materials constituted by chemically or physically cross-linked water swollen 3D polymer networks.<sup>[1–6]</sup> In order to meet different requirements, scientists have doped various functional compounds (e.g., photoluminescent, magnetic, thermoresponsive and electroconductive substances) into hydrogel matrix,<sup>[7–12]</sup>

endowing them with designed functionality. Among them, doping various photoluminescent substances, including nanomaterials (e.g., quantum dots, carbon nanotubes, carbon dots),<sup>[13–20]</sup> metal complex<sup>[21–25]</sup> and lanthanide (Ln) ions,<sup>[26–28]</sup> into hydrogel matrix results in photoluminescent hydrogels. In particular, Ln-doped hydrogels have attracted increasing interests due to the unique features of Ln<sup>3+</sup> ions, such as high

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photochemical stability, narrow bands of emission and low toxicity.<sup>[26,27,29]</sup>

So far, photoluminescent hydrogels have found widespread applications in biomedicine (e.g., bioimaging,<sup>[30–32]</sup> drug delivery,<sup>[33,34]</sup> biosensors<sup>[35,36]</sup> and engineering (e.g., optical switches,<sup>[33]</sup> pH sensors<sup>[23,37,38]</sup> and thermosensors.<sup>[39,40]</sup> In some applications, such as tissue engineering and soft devices, photoluminescent hydrogels with good mechanical properties are preferred. Although several methods have been proposed for fabricating tough hydrogels, such as double-network hydrogels,<sup>[41–43]</sup> nano-composite hydrogels,<sup>[44,45]</sup> nanostructured hydrogels,<sup>[46]</sup> hybrid cross-linked hydrogels,<sup>[47,48]</sup> and tetra-armed polymer hydrogels,<sup>[49,50]</sup> none of those has been implemented for photoluminescent hydrogels. There is still an unmet need for a promising strategy to prepare photoluminescent hydrogels with enhanced mechanical toughness.

Inspired by our previous study on tough alginate/polyacrylamide (PAAm) hydrogels prepared by using various multivalent cations,<sup>[48]</sup> we rationally designed a facile approach to synthesize tough photoluminescent hydrogels in this contribution. Ln-alginate/PAAm hydrogels (Ln = Eu, Tb, Eu/Tb), which simultaneously obtain characteristics of high toughness and good photoluminescence, can be synthesized by combining chemically cross-linked PAAm and physically cross-linked sodium alginate (Na-alginate). Ln<sup>3+</sup> ions serve as both cross-linkers of alginate polymers and photoluminescent emitters. The hydrogels showed high strength ( $\approx$ MPa), strain ( $\approx$ 20), high energy dissipation ( $\approx 10^4$  kJ m<sup>-3</sup>), and good photoluminescent performance. These excellent features of Ln-alginate/PAAm hydrogels are attributed to physically cross-linked alginate networks by Ln<sup>3+</sup> ions and loosely covalently cross-linked PAAm networks. In addition, the emission colors and shapes of hydrogels can be tuned using our approach. Cell viability and proliferation assays confirmed the cytocompatibility of the hydrogels. To the best of our knowledge, the present work is the first effort of preparing hydrogels with high toughness and good photoluminescence characteristics simultaneously. These tough photoluminescent hydrogels hold great potential for applications in biomedical and engineering fields.

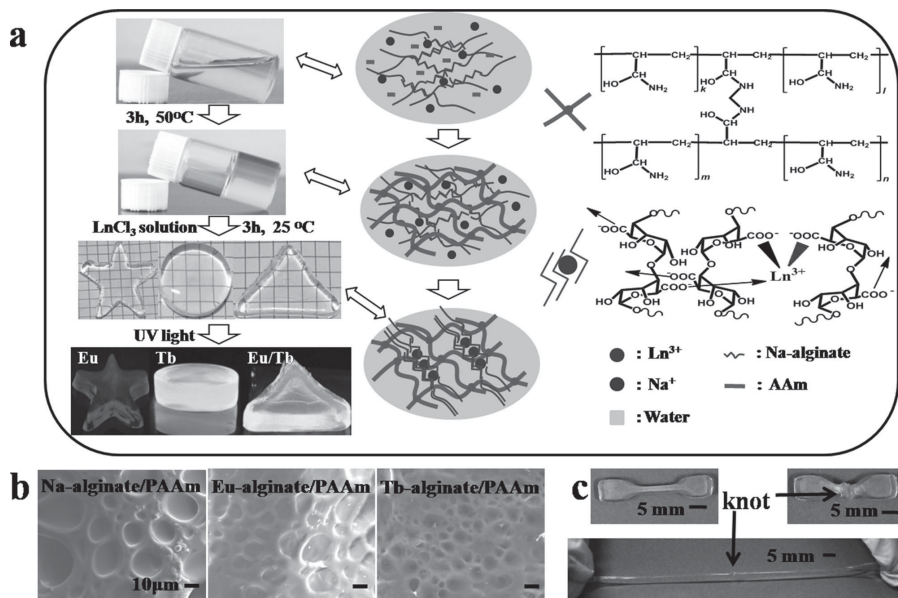
## 2. Experimental Section

Materials, methods, analysis and additional experimental data are supplied in the Supporting Information.

## 3. Results and Discussion

### 3.1. Preparation of Tough Photoluminescent Hydrogels

The tough photoluminescent Ln-alginate/PAAm hydrogels mainly consist of four components: water, Na-alginate, PAAm, and Ln<sup>3+</sup> ions. Alginate is a kind of abundant natural polysaccharide extracted from brown algae containing  $\alpha$ -L-guluronic acid (G unit) and  $\beta$ -D-mannuronic acid (M unit), while PAAm is a popular hydrophilic polymer with good biocompatibility,<sup>[35,36,51]</sup> both of which are cheap to purchase. Here, Ln<sup>3+</sup> ions play the roles of both cross-linkers of alginate polymers and photoluminescent emitters. They are doped into the hydrogel matrix to fabricate tough photoluminescent hydrogels by a straightforward ion-exchange approach. The preparation procedures of Ln-alginate/PAAm hydrogels include two steps (Figure 1a). First, Na-alginate/PAAm hydrogel was synthesized by radical polymerization of AAm



**Figure 1.** Preparation scheme, SEM images, and photographs of Ln-alginate/PAAm hydrogels. a) Two-step approach to prepare tough photoluminescent hydrogels. Na-alginate, AAm, APS, MBAA, and TEMED were dissolved in deionized water. Then AAm monomers were polymerized to obtain Na-alginate/PAAm hydrogel. Finally Na-alginate/PAAm hydrogel was soaked in LnCl<sub>3</sub> (EuCl<sub>3</sub>, TbCl<sub>3</sub> or mixture of EuCl<sub>3</sub> and TbCl<sub>3</sub>) aqueous solutions at room temperature for obtaining Ln-alginate/PAAm hydrogels. The hydrogels with various shapes and colors were harvested by using different molds and doping or co-doping different Ln ions. b) SEM images of Na-alginate/PAAm hydrogel, Eu-alginate/PAAm hydrogel, and Tb-alginate/PAAm hydrogel (Scale bar: 10 μm). c) The photographs of unknotted, knotted and stretched knotted Eu-alginate/PAAm hydrogels. A color version is available in the Figure S7 (Supporting Information).

monomers in the solution containing Na-alginate polymers, cross-linker *N,N'*-methylenebisacrylamide (MBAA), initiator ammonium peroxydisulphate (APS), and accelerator *N,N,N',N'*-tetramethylethylenediamine (TEMED). In this step, only AAm monomers were polymerized and cross-linked, non-cross-linked Na-alginate polymer chains interweaved into covalently cross-linked PAAm hydrogel networks. Subsequently, Na-alginate/PAAm hydrogel was immersed into  $\text{LnCl}_3$  ( $\text{Ln} = \text{Eu}, \text{Tb}, \text{Eu/Tb}$ ) aqueous solution, and  $\text{Ln}^{3+}$  ions cross-linked alginate polymer chains via interaction with carboxylate ( $\text{COO}^-$ ) groups of mannuronate (MM blocks) and guluronate residues (GG blocks).<sup>[52]</sup> Finally, the tough photoluminescent Ln-alginate/PAAm hydrogels with interpenetrating networks were obtained.

To prove the dynamic cross-linking of Na-alginate polymers, the rheological property of Na-alginate/PAAm hydrogel soaked in  $\text{EuCl}_3$  aqueous solution ( $C_{\text{Eu}} = 0.025 \text{ mol L}^{-1}$ ) was measured as an example. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of the hydrogel gradually increased and became a constant with prolonging soaking time, which may be due to the gradual cross-linking of  $\text{COO}^-$  groups of alginate polymers by  $\text{Eu}^{3+}$  ions (Figure S1, Supporting Information). The tough photoluminescent hydrogels with various shapes (star, cylinder, and triangle) were prepared via this facile synthesis approach using molds with designed shapes for gelation, demonstrating excellent processability (Figure 1a). Moreover, the emission colors were tunable by doping  $\text{Eu}^{3+}$  ions (red luminescence),  $\text{Tb}^{3+}$  ions (green luminescence) or mixture of  $\text{Eu}^{3+}/\text{Tb}^{3+}$  ions (mole rate:  $\text{Eu/Tb} = 3:2$ , yellow luminescence). The color could be clearly identified under UV light irradiation (365 nm) at room temperature (Figure 1a). The surface texture of freeze-dried Na-, Ln-alginate/PAAm hydrogels was observed by SEM images (Figure 1b). Compared with Na-alginate/PAAm hydrogel, the porous structures of Eu-alginate/PAAm and Tb-alginate/PAAm hydrogels were obviously denser and more uniform, which is possibly due to the stronger interaction

between trivalent cations ( $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions) and alginate polymers, than that of the  $\text{Na}^+$  ions. As a result, when Na-alginate polymers were cross-linked by  $\text{Ln}^{3+}$  ions, the mechanical properties of the hydrogels can be greatly enhanced. For example, Eu-alginate/PAAm hydrogel can be knotted and stretched without damage (Figure 1c).

### 3.2. Photoluminescent Properties

Eu-alginate/PAAm hydrogels soaked in  $\text{EuCl}_3$  solution with different concentration ( $C_{\text{Eu}} = 0.025, 0.1 \text{ mol L}^{-1}$ ) were excited at 394 nm and the emission spectra displayed a series of typical peaks corresponding to the intra $4f^6$   $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$  transitions. The characteristics of emission spectra for Eu-alginate/PAAm hydrogels were similar to that of  $\text{EuCl}_3$  aqueous solution (Figure 2a), demonstrating that Eu-alginate/PAAm hydrogels could retain photoluminescent characteristics of  $\text{Eu}^{3+}$  ions. In addition, compared with  $\text{EuCl}_3$  aqueous solution, a reverse of relative PL intensities at 592 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$ , orange emission) and 615 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ , red emission) was observed for Eu-alginate/PAAm hydrogel ( $C_{\text{Eu}} = 0.025 \text{ mol L}^{-1}$ ). The PL intensity ratios of peaks  $I_{615}/I_{592}$  (IRP) were used to show the reverse according to if the IRP was greater or less than 1, and a greater IRP indicated better red color purity.<sup>[26,53]</sup> The IRP was less than 1 ( $\approx 0.30$ ) for  $\text{EuCl}_3$  aqueous solutions with various concentrations (Table S1, Supporting Information), but it increased to 1.67 for Eu-alginate/PAAm hydrogel ( $C_{\text{Eu}} = 0.025 \text{ mol L}^{-1}$ ). This reverse phenomenon was attributed to the binding of  $\text{Eu}^{3+}$  ions ( $\text{Eu}^{3+}$  ions coordinated with  $\text{COO}^-$  groups of alginate polymer chains) in the hydrogels, and they mainly enhanced the PL intensity at 615 nm.<sup>[53]</sup> While in aqueous solution, free  $\text{Eu}^{3+}$  ions ( $\text{Eu}^{3+}$  ions coordinated with water molecules),<sup>[54]</sup> mainly improved the PL intensity at 592 nm.<sup>[53]</sup> However, the IRP of the hydrogels decreased to 0.86, when the soaking concentration increased to  $0.1 \text{ mol L}^{-1}$ . Thus, we considered that the quantity of free  $\text{Eu}^{3+}$  ions containing in the hydrogels increased

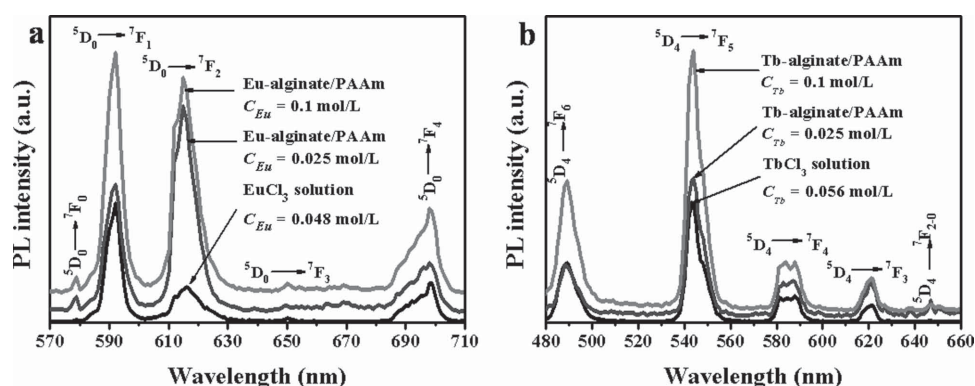


Figure 2. Emission spectra of a) Eu-alginate/PAAm hydrogels soaked in 0.025 and 0.1  $\text{mol L}^{-1}$   $\text{EuCl}_3$  aqueous solution and 0.048  $\text{mol L}^{-1}$   $\text{EuCl}_3$  aqueous solutions. b) Tb-alginate/PAAm hydrogel soaked in 0.025 and 0.1  $\text{mol L}^{-1}$   $\text{TbCl}_3$  aqueous solution and 0.056  $\text{mol L}^{-1}$   $\text{TbCl}_3$  aqueous solutions. A color version is available in the Figure S8 (Supporting Information).

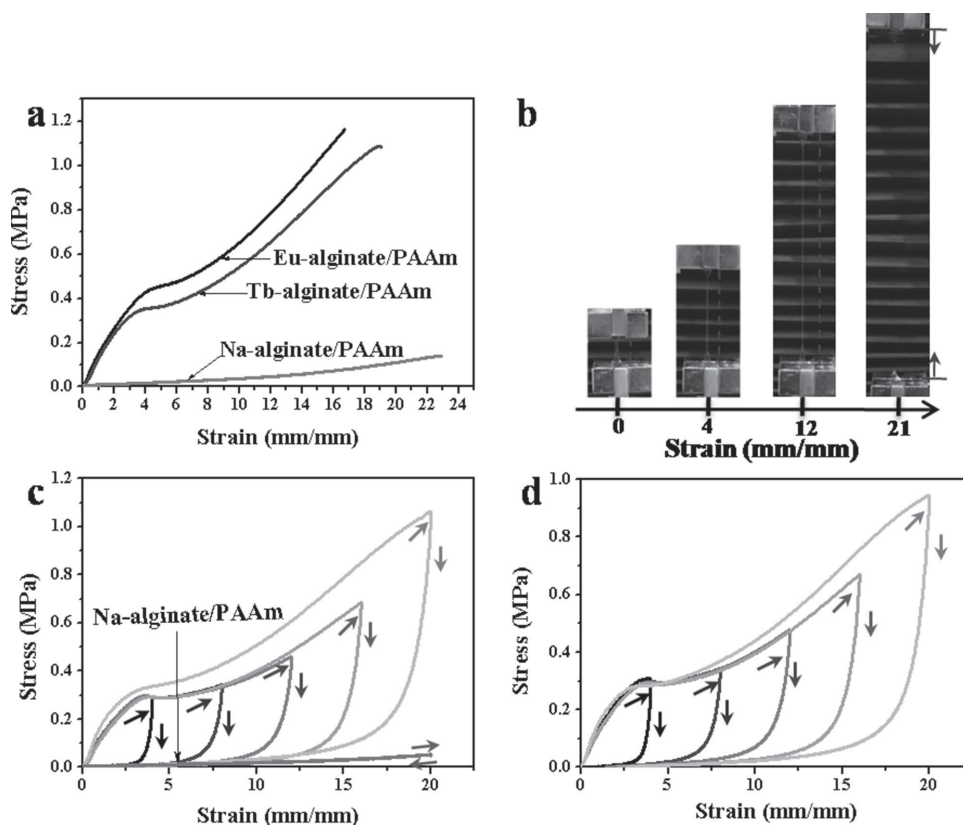
with increasing soaking concentration, which affected the IRP. The quantities of free and binding  $\text{Eu}^{3+}$  ions in Eu-alginate/PAAm hydrogels were measured by inductively coupled plasma atomic emission spectrometer analysis (ICP-AES). The ratio of free  $\text{Eu}^{3+}$  ions to binding  $\text{Eu}^{3+}$  ions was 0.89 and 16.19 when the soaking concentration was 0.025 and 0.1 mol L<sup>-1</sup>, respectively (Table S2, Supporting Information). These results agree with our prediction. ICP-AES analysis revealed that the  $\text{Eu}^{3+}$  ions concentration in Eu-alginate/PAAm hydrogels soaked in 0.025 mol L<sup>-1</sup>  $\text{EuCl}_3$  aqueous solutions was 0.048 mol L<sup>-1</sup> (Supporting Information). Compared with  $\text{EuCl}_3$  solution under the same concentration, the PL intensities at 592 nm and 615 nm of the hydrogels were evidently enhanced. In the hydrogel,  $\text{Eu}^{3+}$  ions coordinated with  $\text{COO}^-$  groups of alginate polymer and some water molecules were expelled from their coordination shell, whereas hydroxyl groups (OH) of water could effectively quench  $\text{Eu}^{3+}$  ions luminescence.<sup>[27,55]</sup>

The emission spectra of Tb-alginate/PAAm hydrogels ( $C_{\text{Tb}} = 0.025, 0.1$  mol L<sup>-1</sup>) exhibited a series of narrow bands ascribing to the intra $4f^8$   $^5\text{D}_4 \rightarrow ^7\text{F}_{6-0}$  transitions under 369 nm, which had a maximal emission wavelength ( $\lambda_{\text{em}}$ ) at 544 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ) (Figure 2b). The emission

spectra were similar to that of  $\text{TbCl}_3$  aqueous solution, demonstrating that  $\text{Tb}^{3+}$  ions could maintain their photoluminescent performance in the hydrogels.  $\text{Tb}^{3+}$  ions concentration in Tb-alginate/PAAm hydrogels soaked in 0.025 mol L<sup>-1</sup>  $\text{TbCl}_3$  aqueous solutions was 0.056 mol L<sup>-1</sup>, as calculated from ICP-AES results (Supporting Information). Same as Eu-alginate/PAAm hydrogels, the PL intensities of Tb-alginate/PAAm hydrogels were much stronger than that of  $\text{TbCl}_3$  aqueous solution. The results reveal that the PL intensities of hydrogel can be enhanced by  $\text{Tb}^{3+}$  ions coordinated with  $\text{COO}^-$  groups.

### 3.3. Mechanical Properties

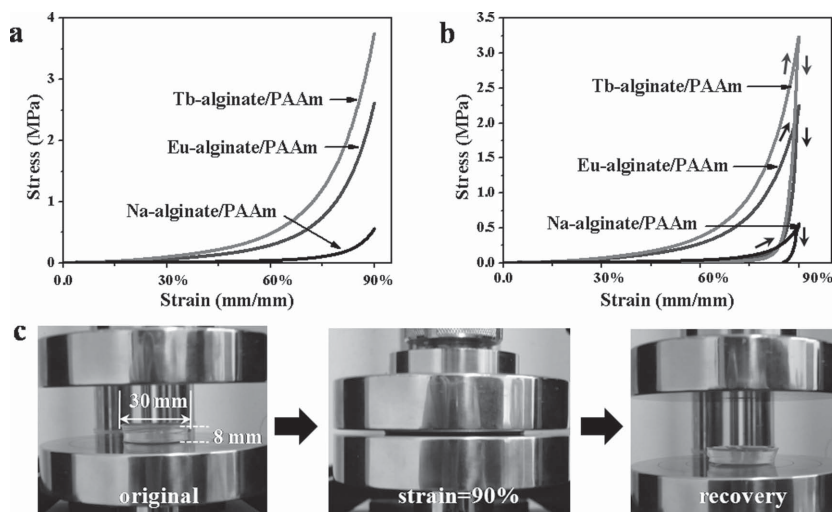
We tested the tensile and compressive performances of the photoluminescent Ln-alginate/PAAm hydrogels ( $C_{\text{Ln}} = 0.025$  mol L<sup>-1</sup>), and compared these with Na-alginate/PAAm hydrogel (Table S3, Supporting Information). The  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions doped photoluminescent hydrogels exhibited excellent mechanical toughness. In Figure 3a the tensile stress–strain curves of Eu-alginate/PAAm and Tb-alginate/PAAm hydrogels are plotted, and that of Na-alginate/PAAm hydrogel was also included for comparison.



**Figure 3.** Tensile mechanical properties of various hydrogels. a) Tensile stress–strain curves of Eu-alginate/PAAm hydrogel, Tb-alginate/PAAm hydrogel and Na-alginate/PAAm hydrogel. b) Photographs of tensile process of Eu-alginate/PAAm hydrogel. c) Tensile hysteresis curves of Eu-alginate/PAAm hydrogel at different strains and Na-alginate/PAAm hydrogel with a maximum strain of 20. d) Tensile hysteresis curves of Tb-alginate/PAAm hydrogel with different maximum strains. a–d)  $C_{\text{Ln}} = 0.025$  mol L<sup>-1</sup>. A color version is available in the Figure S9 (Supporting Information).

The tensile strength was  $1.13 \pm 0.03$  MPa and  $1.02 \pm 0.07$  MPa, and the Young's modulus was  $71.33 \pm 16.60$  kPa and  $63.33 \pm 7.40$  kPa for Eu-alginate/PAAm hydrogel and Tb-alginate/PAAm hydrogel, respectively (Figure 3a). Noteworthy, Ln-alginate/PAAm hydrogels were highly stretchable, reaching maximum uniaxial tensile strain  $\approx 20$ , which was demonstrated in Figure 3b for Eu-alginate/PAAm hydrogel. In contrast, hydrogels with single network, such as Na-alginate/PAAm, Eu-alginate, and Tb-alginate, have low tensile strengths ( $143.16 \pm 6.90$ ,  $157.10 \pm 6.00$ , and  $63.00 \pm 11.30$  kPa, respectively). It should be pointed out that both Eu-alginate/PAAm hydrogel and Tb-alginate/PAAm hydrogel would undergo a yielding point at  $\approx 4$  strain, a characteristic plastic deformation behavior observed for most of tough hydrogels,<sup>[48]</sup> which was devoid for Na-alginate/PAAm hydrogel.

Besides their high strength and stretchability, Ln-alginate/PAAm hydrogels also exhibited superior toughness, which was expressed in terms of energy dissipation. Energy dissipation obtained from hysteresis tests is a more adequate parameter to characterize the mechanical properties of hydrogels. The area under the loading–unloading curves gives the energy dissipation.<sup>[48]</sup> Eu-alginate/PAAm and Tb-alginate/PAAm hydrogels exhibited pronounced hysteresis and retained significant permanent deformation after unloading (Figure 3c,d). In contrast, Na-alginate/PAAm hydrogel showed negligible hysteresis and almost fully recovered its original length after unloading. For instance, for a cycle with a maximum strain of 20, the energy dissipation was  $9389.66 \pm 80.82$  kJ m<sup>-3</sup> for Eu-alginate/PAAm hydrogel and  $8477.98 \pm 60.36$  kJ m<sup>-3</sup> for Tb-alginate/PAAm hydrogel, demonstrating their high toughness. Whereas the energy dissipation was only  $50.17 \pm 1.70$  kJ m<sup>-3</sup> for Na-alginate/PAAm hydrogel. In addition, the energy dissipation of Eu-alginate/PAAm and Tb-alginate/PAAm hydrogels had the same order of magnitude, indicating that Eu<sup>3+</sup> and Tb<sup>3+</sup> ions had similar ability to improve the hydrogel toughness via cross-linking alginate polymer chains. The extremely high toughness of Ln-alginate/PAAm hydrogel is probably attributed to the energy dissipation induced by unzipping the physical cross-linking of alginate networks.<sup>[48]</sup> We also performed systematic experiment to study the effects of Eu<sup>3+</sup> ions concentration ( $C_{Eu} = 0.01, 0.025, 0.1, 0.3, 0.5, 0.8, 1.0$  mol L<sup>-1</sup>) on the mechanical properties of Eu-alginate/PAAm hydrogels. But we did not observe obvious dependence of mechanical prop-



**Figure 4.** Compressive mechanical properties of various hydrogels. a) Compressive stress–strain curves of Eu-alginate/PAAm hydrogel, Tb-alginate/PAAm hydrogel, and Na-alginate/PAAm hydrogel. b) Compressive hysteresis curves of Eu-alginate/PAAm hydrogel, Tb-alginate/PAAm hydrogel, and Na-alginate/PAAm hydrogel with a maximum strain of 90%. c) Photographs of compressive process of Eu-alginate/PAAm hydrogel. a–c)  $C_{Ln} = 0.025$  mol L<sup>-1</sup>. A color version is available in the Figure S10 (Supporting Information).

erties on Eu<sup>3+</sup> ions concentrations (Figure S4 and S5, Supporting Information).

The excellent mechanical properties were further confirmed by compression tests (Figure 4a). Compressive strength at strain of 90% was  $2.43 \pm 0.17$  MPa for Eu-alginate/PAAm hydrogels and  $3.37 \pm 0.33$  MPa for Tb-alginate/PAAm hydrogels and calculation of Young's modulus was  $100.20 \pm 8.78$  and  $102.17 \pm 22.74$  kPa, respectively. As expected, these values were much greater than that of Na-alginate/PAAm hydrogel, which gave low compressive strength ( $0.55 \pm 0.03$  MPa) and Young's modulus ( $23.13 \pm 3.98$  kPa) (Table S3, Supporting Information). For a loading–unloading cycle with a maximum strain of 90%, the energy dissipation was  $314.28 \pm 12.71$  kJ m<sup>-3</sup> for Eu-alginate/PAAm hydrogel and  $385.18 \pm 15.06$  kJ m<sup>-3</sup> for Tb-alginate/PAAm hydrogel (Figure 4b). However, Na-alginate/PAAm hydrogel had insignificant hysteresis ( $45.14 \pm 1.25$  kJ m<sup>-3</sup>). The snapshots of compression experiment demonstrated that the hydrogels could recover even for large compression strain up to 90% (Figure 4c).

### 3.4. Cytotoxicity

In order to evaluate the cytocompatibility of Ln-alginate/PAAm hydrogels, we quantified the viability and proliferation of NIH/3T3 fibroblasts incubated with hydrogel extracts.<sup>[51]</sup> Cells were incubated with the hydrogel extracts for 72 h and then live/dead assay was conducted to check cell viability. Cell culture medium was used as control. Live cells were stained green, whereas dead cells were stained red (Figure S6a,b, Supporting Information). The viability of

cells cultured in both Eu-alginate/PAAm hydrogel and Tb-alginate/PAAm hydrogel extracts was higher than 95%, indicating their good cytocompatibility (Figure S6c, Supporting Information). In addition, cell proliferation assay demonstrated that the cell number increased with incubation time (Figure S6d, Supporting Information). Compared with control, we did not observe significant difference for cell viability and proliferation, when cells were incubated with the extracts of Eu-alginate/PAAm hydrogel and Tb-alginate/PAAm hydrogel. The results indicate good cytocompatibility of the tough photoluminescent Ln-alginate/PAAm hydrogels.

#### 4. Conclusion

In this work, tough photoluminescent Ln-alginate/PAAm (Ln = Eu, Tb, Eu/Tb) hydrogels have been synthesized by combining physical and chemical cross-linkers. The effects of Ln<sup>3+</sup> ions in the hydrogels are twofold: its emissive properties yield good photoluminescence characteristics, while interpenetrating networks of alginate polymers with PAAm toughens the hydrogels. The tough hydrogel exhibits ≈1 MPa tensile strength, ≈20 uniaxial tensile strains, ≈3.4 MPa compressive strength, as well as, ≈10<sup>4</sup> kJ m<sup>-3</sup> energy dissipation. The emission colors of Ln-alginate/PAAm hydrogels can be tuned by doping different Ln<sup>3+</sup> ions. Owing to the tough mechanical properties and excellent processability of Ln-alginate/PAAm hydrogels, hydrogels with various shapes were obtained in a straightforward manner. Cell viability and proliferation assays confirmed the cytocompatibility of the hydrogels. With these superior properties, we expect that the tough photoluminescent hydrogels would expand and open up new applications of soft materials.

#### Supporting Information

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

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