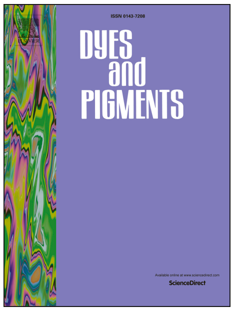

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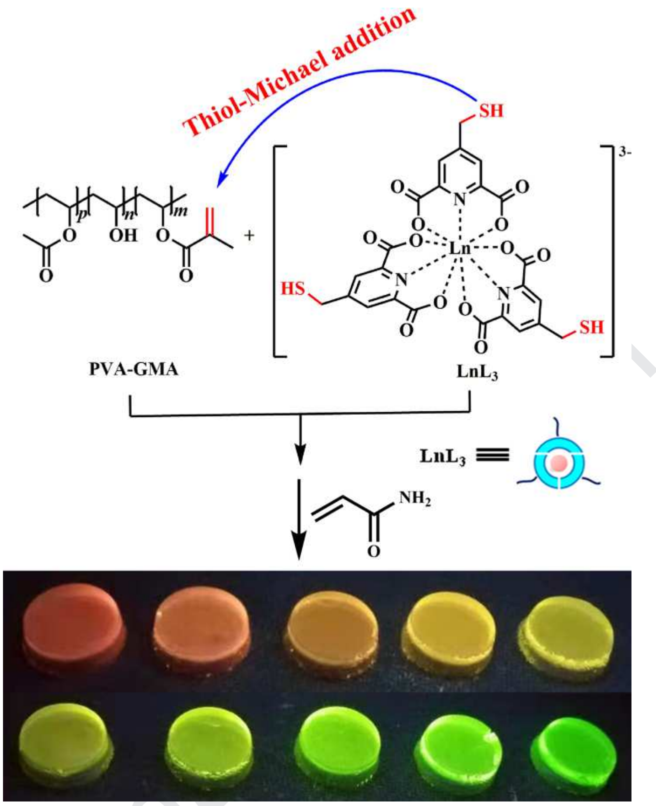
Graphical Abstract

Double-network lanthanide-based hydrogels with adjustable luminescent properties synthesized by thiol-Michael addition



Lanthanide-based hydrogels with adjustable luminescent properties synthesized by thiol-Michael addition

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Abstract

Luminescent hydrogels have been widely used in many fields because of their excellent optical properties. Although there are many mature preparation methodologies, the development of new luminescent hydrogels with adjustable fluorescence properties and good mechanical properties is still an urgent need to explore. In this paper, we describe a simple and effective way to synthesize highly luminescent PVA/AM-Ln(DPA)$_3$ double network hydrogels by thiol-Michael addition reaction and *in situ* polymerization. We firstly synthesized a bifunctional chelating ligand named as 4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid, which can react with electron-deficient carbon-carbon double bonds and effectively sensitize the luminescence of Tb^{3+} and Eu^{3+} ions. And then, the luminescent lanthanide complexes were grafted onto the methacrylated polyvinyl alcohol via thiol-Michael addition reaction. Finally, the modified polymers were polymerized with acrylamide monomer to form the luminescent double network hydrogels. The obtained hydrogels possess bright luminescence, long luminescence lifetimes and good mechanical properties. Moreover, the emission colors of the hydrogels are adjustable by varying the molar ratio of $Eu^{3+}$and Tb^{3+}.

Keywords: luminescence; lanthanide complexes; Michael addition reaction; hydrogels

1. Introduction

Luminescent hydrogels have gained considerable interest due to their excellent optical properties and inventive applications in controlled drug release, sensing, 3D printing and tissue engineering [1-4]. Various luminophores, including organic dyes, luminescent quantum dots, metal complexes are frequently used as emitting sources to fabricate luminescent hydrogels [5-9]. Recently, much effort has been directed towards hybridizating hydrogels with lanthanide complexes through non-covalent interaction or covalent connection. This is related to some feature of lanthanide complexes [10,11]: (1) Strong designability. Lanthanide complexes with different functional groups can be prepared by organic synthesis and coordination assemble technology, which is beneficial to realize the hybridization of lanthanide complexes with hydrogels; (2) Outstanding emission properties. including wide range of emission from ultraviolet to near-infrared regions, high color purity, long luminescence lifetime; (3) Small size. Thus, hybridization of lanthanide complexes with hydrogels at the molecular level is easy to achieve, which is helpful to obtain a luminescent hydrogel with uniform structure and stable performance; (4) Unique paramagnetic properties, which make them potentially useful in magnetic resonance imaging and paramagnetic labeling of proteins.

Over the years, several different approaches, including click chemistry, photo-initiated/free radical polymerization and Michael-like addition reaction, have been explored for preparation of chemical crosslinking hydrogels [12-15]. Michael-like addition reaction, by contrast, are especially appealing due to its high atom economy (no by-products), environmental friendliness, and mild reaction conditions (no need for heating or ultraviolet light). For instance, Lensen and coworkers developed a PEG-based hydrogel with tunable stiffness and post gelation chemical functionality via amine-Michael addition reaction [16]. Misra et al reported a pH and reduction dual-stimuli-responsive hydrogel synthesized by thiol-Michael addition reaction for anticancer drug delivery [17]. Recently, we have synthesized a bifunctional chelating ligand named as 4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid (L) which contains: a free thiol group that can react with electron-deficient carbon-carbon double bonds via a Michael-like addition reaction [18, 19] and a 2,6-pyridinedicarboxylic acid moiety that can effectively sensitize the luminescence of Tb^{3+} and Eu^{3+} ions [20]. Moreover, three such ligands can bind to one lanthanide ion so as to form a trithiol complex ($Ln{\cdot}L_3$). This work has aroused our interest to explore its potential applications in the synthesis of novel luminescent hydrogels.

Herein, we developed a novel method for synthesis of luminescent lanthanide double network hydrogels *via* thiol-Michael addition reaction and *in situ* polymerization (Scheme 1). Firstly, methacrylated polyvinyl alcohol (PAV-GMA) was crosslinked by the trithiol complexes ($Ln{\cdot}L_3$) *via* thiol-Michael addition reaction to obtain a network polymer which was used to polymerize with acrylamide monomer to form the luminescent double network hydrogels. It should be noted that $Ln{\cdot}L_3$ has a good water solubility which enables its homogeneous distribution in the hydrogels. In addition, we used weak base (catalyst) instead of photoinitiator to accelerate the thiol-Michael addition reaction because the competition absorption of excited light energy between photoinitiator and $Ln\cdot L_3$ has strong adverse effects on the luminescence quality of $Ln\cdot L_3$.Thus, the prepared hydrogels exhibited excellent luminescent properties. We expect that this work will provide a simple way for fabricating luminescent lanthanide hydrogels by means of thiol-Michael addition reaction.

2. Material and methods

2.1. Preparation of 4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid (L)

4-(bromomethyl)pyridine-2,6-dimethyl dicarboxylate (0.56 g, 2.0 mmol) and thiourea (0.20 g, 2.6mmol) were added to 20 mL methanol. The resulting solution was refluxed under an atmosphere of N_2 for 8 h, and then cooled down to room temperature. The solvent was removed by vacuum distillation. The remaining residue was redispersed in acetone (20 mL), filtered and dried under vacuum. The obtained solid together with NaOH (0.62 g) was added in 20 mL H_2O. The mixture was heated at 80 ℃ for 2 h under N_2 atmosphere. The pH of the above mixture was adjusted to 2 by H^+ ion exchange resin. After filtering out the resin, the filtrate was evaporated to dryness. Finally, 4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid was obtained as a pale yellow solid in a 63% yield.^{1}H-NMR (300 MHz, D_2O, pD>14) δ ppm: 7.73 (s, 2H), 3.53 (s, 2H). ^{13}C-NMR (300/4 MHz, D_2O, pD>14) δ ppm: 173.6, 159.6, 152.8, 124.4, 28.0 (Fig. S1). ESI-MS: M/Z calcd for $C_8H_7NO_4S$: 213.0096; $[M-1]^-$, found: 212.0036 (Fig. S2).

2.2. Preparation of lanthanide complexes ($Ln\cdot L_3$)

4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid (0.0478 mmol) and $LnCl_3\cdot 6H_2O$ (0.0159 mmol Ln = Tb or Eu) were firstly dissolved in distilled water. And then the pH of the mixture was adjusted to about 7.0 (total volume: 2.0 mL). Finally, the prepared sample was stored in a refrigerator at -20 ℃ for use later.

2.3. Synthesis of methacrylated polyvinyl alcohol (PVA-GMA)

Polyvinyl alcohol (PVA, 5.0 g) was dissolved in dimethyl sulfoxide (DMSO, 100 mL) to form a clear solution. Glycidyl methacrylate (0.32 g) and 4-dimethylaminopyridine (DMAP) were added into the PVA solution. The mixture was stirred at 60 ℃ for 6 h, and then diluted to 600 mL with acetone. After centrifugation, the obtained sample was washed three times with acetone, dried under vacuum and stored at -5 ℃ in the dark.

2.4. Synthesis of luminescent double network (DN) hydrogels

PVA-GMA (0.05 g) was dissolved in H_2O (1.0 mL) to form a clear solution. Then, aqueous ammonia (2.5 μL, 3wt%) and $Eu \cdot L_3$ (37.5 μL) were mixed with the above solution under stirring. After standing under N_2 atmosphere for one day, acrylamide monomer was added. The reaction system was cooled in an ice bath and bubbled with N_2 for 20 min. Finally, N,N,N',N'-tetramethyl ethylene diamine (5.0μL) and ammonium persulfate (2.0 mg) were added to the reaction solution. The Eu^{3+}-containing DN hydrogel (PVA/AM-$Eu(DPA)_3$) was formed after the mixture was kept at room temperature for 5 min. The Tb^{3+}-containing DN hydrogel (PVA/AM-$Tb(DPA)_3$) was prepared according to a similar procedure except that $Eu \cdot L_3$ was replaced by $Tb \cdot L_3$. Hydrogels with adjustable luminescent color were prepared by varying the molar ratio of $Eu \cdot L_3$ and $Tb \cdot L_3$ during the synthesis (the total volume of $Eu \cdot L_3$ and $Tb \cdot L_3$ is 37.5 μL). PVA/AM was synthesized through the same process without adding lanthanide complexes for comparison.

2.5. Synthesis of PVA-$Eu(DPA)_3$ hydrogels

PVA-GMA (0.05 g) was firstly dissolved in H_2O (1.0 mL) to form a clear solution. Then, aqueous ammonia (2.5 μL, 3wt%) and $Eu \cdot L_3$ (37.5 μL) were added under stirring. After standing under N_2

atmosphere for one day, the reaction system was cooled in an ice bath and bubbled with N_2 for 20 min. Finally, N,N,N',N'-tetramethyl ethylene diamine (5.0μL) and ammonium persulfate (2.0 mg) were added to the above solution. The hydrogel (PVA-Eu(DPA)$_3$) was formed after the mixture was kept at room temperature for 10 min.

2.6. Swelling measurements

The swelling properties of the as-prepared hydrogels were determined by gravimetric analysis. The dried hydrogels were weighed accurately and immersed in an excess amount of deionized water at 37 ℃. At specific intervals, the swollen hydrogels were removed from water and weighted after carefully wiping off excess surface water. The swelling ratio (SR) of the as-fabricated was calculated by using the following equation (1):

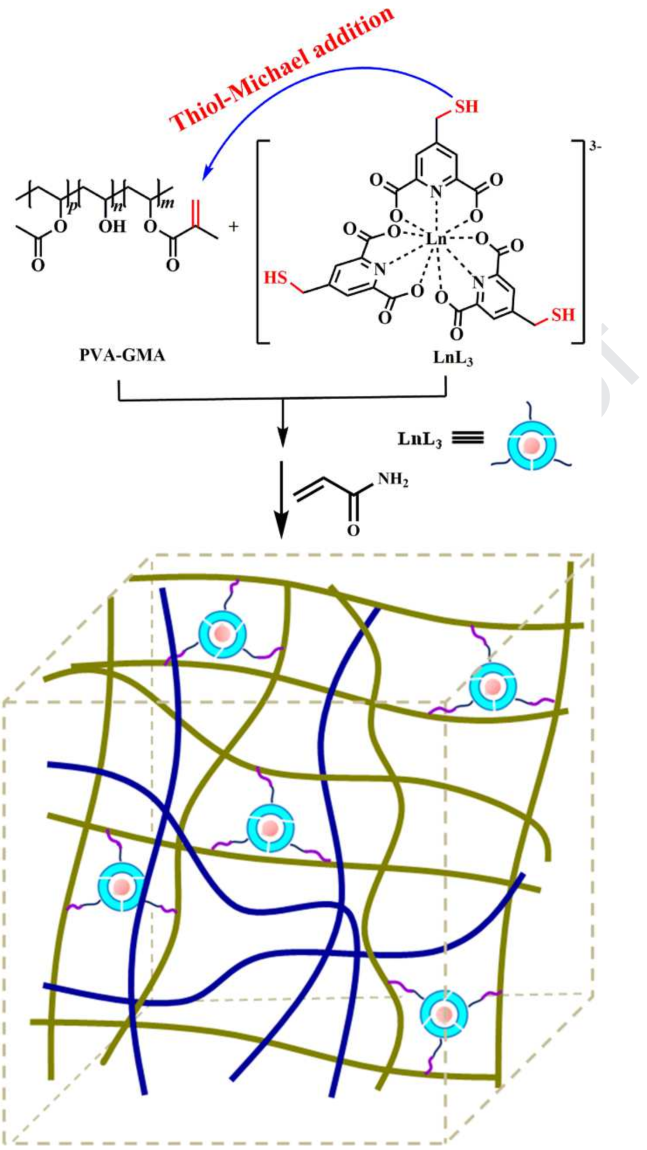
$$SR = (W_s - W_d)/W_d \times 100\% \qquad (1)$$

where W_s and W_d are the weight of the swollen and dried hydrogels, respectively.

2.7. Characterization

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AV-300 or AV-400 spectrometer. Mass spectrum was acquired on an Agilent 6520 Q-TOF mass spectrometer. The photoluminescence and lifetime measurements were measured on an Edinburgh instruments FLS920 spectrofluorometer. Quantum efficiency was measured by using an integrating sphere whose inner face was coated with Benflect. FT-IR spectrum was carried out using a Thermo Nicolet 5700 spectrophotometer. The compression test of the prepared hydrogels (cylinder-shape, diameter × height = 16.0 mm × 5 mm) were performed at a constant velocity of 1.0 mm/min on a Shimadzu universal testing machine (AGS-X500N) with a 500 N load cell. Rheological tests were carried out by an Anton Paar MCR302 rheometer. Scanning electron microscopy (SEM) measurements were performed on a FEI Quanta200 electron microscope.

3. Results and discussion



Scheme 1 Proposed structures and synthetic route of the lanthanide double network hydrogels. The yellow curve represents PVA and the blue one represents polyacryamide.

PVA-GMA was synthesized from polyvinyl alcohol and glycidyl acrylate and characterized by ^{1}H-NMR. As shown in Fig. 1, the signals at δ = 5.98 and 5.62 ppm were assigned to the olefinic protons on C9. The signal at δ = 1.86 ppm corresponds to the methyl protons on C8 (Fig. 1a) [21]. These results confirm that methacryloyl group has been successfully grafted onto the polyvinyl alcohol by using glycidyl acrylate. Moreover, the degree of substitution of -OH groups by methacryloyl groups was determined from ^{1}H-NMR. Before that, the alcoholysis degree of polyvinyl alcohol was firstly measured from the integral area ratio of the protons on C11 (δ = 4.68ppm) and C13 (δ = 3.81 ppm) (Fig. 1b). And an alcoholysis degree of 84% was obtained according to the ^{1}H-NMR analysis. The presence of ester groups in PVA was also confirmed by FT-IR spectrum. The absorption peak at 1714 cm^{-1} (Fig. S3) can be ascribed to C=O stretching vibration of aliphatic eater [22]. And then the degree of substitution was calculated from the relative integral area of olefinic protons on C9 (δ = 5.98 ppm) and the methyl protons on C3 (δ = 1.86 ppm). By calculation, the degree of substitution was determined to be 1 %.

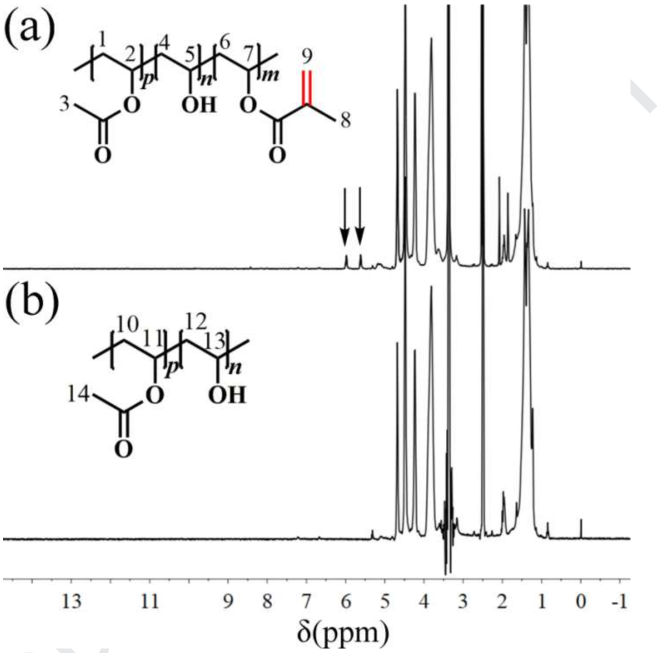


Fig.1^{1}H-NMR spectra of PVA-GMA (a) and PVA (b) in DMSO-d_6.

4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid was prepared using 4-bromomethylpyridine-2,6-dimethyl dicarboxylate and thiourea as the raw materials. The coordination stoichiometry between 4-(mercaptomethyl)pyridine-2,6-dicarboxylic acid and lanthanide ions was determined by fluorescence titration [23]. As shown in Fig. 2, upon addition of Eu^{3+} to ligand solution, the characteristic emission bands of Eu^{3+}with sharp peaks at 589, 594, 615, 649 and 694 nm appeared and increased gradually until a Eu^{3+} to ligand molar ration of 1:3 was reached. However, further increasing of Eu^{3+} concentration leaded to a decrease in fluorescence intensity. The inflection point occurred at a molar ration of 0.33, corresponding to a

1:3 complexation stoichiometry between Eu^{3+} and L. Previous studies have shown that 1:3, 1:2 or 1:1 Eu^{3+}/DPA coordination complexes can be formed by addition of Eu^{3+}to DPA solution with different molar ratio. As for 1:2 or 1:1 Eu^{3+}/DPA coordination complexes, its luminescence would be quenched to a certain level by energy transfer from excited state of Eu^{3+} to the higher O-H vibration overtones of coordination H_2O. Therefore, an inflection point was observed on the fluorescence induction curve.

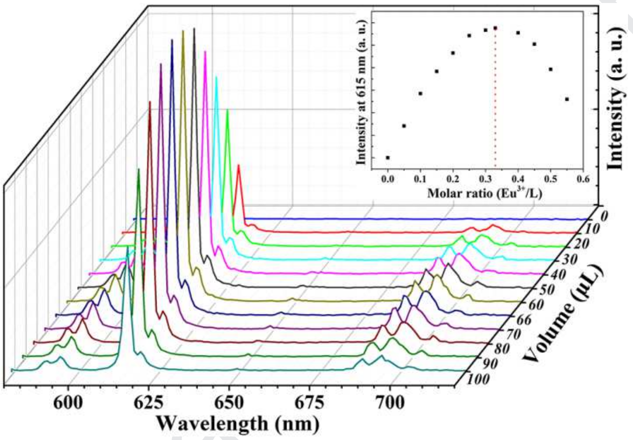


Fig. 2 Fluorescence spectra of L (0.02 mM, 3mL) upon the addition of different amounts of Eu^{3+} (0.3 mM). Inset: the fluorescence intensity changes at 615 nm *vs* Eu^{3+}/L molar ratio. (λ_{ex}=280 nm).

As shown in Fig. 3, simple mixing of PVA-GMA and Eu·L_3 under base condition only gave a clear solution (Fig. 3a) which could be further polymerized to form a hydrogel with ammonium persulfate as the initiator (Fig. 3b). Whereas *in situ* polymerization of acrylamide in the presence of PVA-GMA or Eu·L_3/PVA-GMA led to the formation of transparent double network hydrogels, which could easily be molded into free-standing object with a certain shape (Fig. 3c to e). The Eu^{3+}-containing hydrogel exhibited the characteristic red emission under a 254 nm UV lamp (Fig. 3f). During this process, the thiol-Michael addition reaction between PVA-GMA and Eu·L_3 can be monitored by Ellman's reagent (DTNB, 5,5'-dithiobis-(2-nitrobenzoic acid)) [24]. The reaction of free thiol groups with DTNB produces a yellow 5-mercapto-2-nitrobenzoic acid anion with strong absorption at 412 nm (Fig. S4). Therefore, a naked color change from colorless to bright yellow was observed upon the addition of DTNB to the solution of $Eu\cdot L_3$. However, when DTNB were added into the mixture of PVA-GMA and $Eu\cdot L_3$, no obvious color changes were observed, indicating that the thiol groups were consumed by the Michael addition reaction. Meanwhile, the above inference was also confirmed by UV-vis absorption spectra. As shown in Fig. S5, an obvious absorption peak at 412 nm belonging to 5-mercapto-2-nitrobenzoic acid was observed (Fig. S5a), showing that $Eu\cdot L_3$was reacted with DTNB by thiol-disulfide exchange reaction. However, similar absorption peak did not appear in Fig. S5b, suggesting the absence of free thiol groups in the reaction solution of PVA-GMA and $Eu\cdot L_3$. In fact, according to the alcoholysis degree and degree of substitution of PVA, the minimum molar ratio of Michael receptor (electron-deficient double bonds) and donor (thiol groups) in this thiol-Michael addition reaction was found to be 10:1, which ensured that thiol groups were completely consumed in this reaction.

Fig. 3g showed the swelling behaviors of PVA-Eu(DPA)$_3$, PVA/AM and PVA/AM-Eu(DPA)$_3$. Obviously, PVA/AM and PVA/AM-Eu(DPA)$_3$ exhibited a smaller swelling ratio than PVA-Eu(DPA)$_3$, indicating that PVA/AM and PVA/AM-Eu(DPA)$_3$ have a more compact network structure [25]. In addition, the mechanical properties of PVA-Eu(DPA)$_3$, PVA/AM and PVA/AM-Eu(DPA)$_3$ were studied by compression tests (Fig. 3h). The compressive strength at strain of 80% was 0.489 MPa for PVA/AM and 0.464 MPa for PVA/AM-Eu(DPA)$_3$, respectively. However, PVA-Eu(DPA)$_3$ was apt to fracture under the relatively low compress load (Strain: 68%, Stress: 0.08 MPa). Compared to PVA-Eu(DPA)$_3$, the prepared double network hydrogels (PVA/AM and PVA/AM-Eu(DPA)$_3$) showed improved mechanical performance.

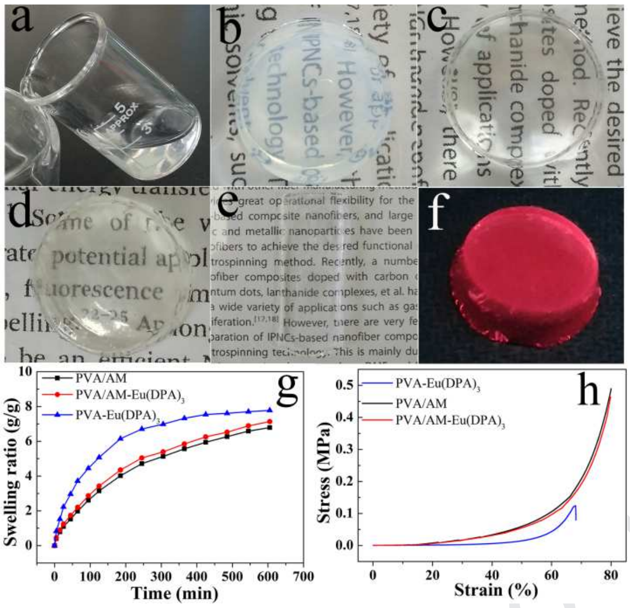


Fig. 3 The digital photos of the mixture of PVA and Eu·L_3 (a), PVA-Eu$(DPA)_3$ (b), PVA/AM (c), PVA/AM-Eu$(DPA)_3$ under sunlight (d and e) or a 254 nm UV lamp (f). The swelling kinetics (g) and compressive properties (h) of the prepared hydrogels.

To gain insight into the dynamic mechanical behavior of the as-prepared hydrogels, we performed some rheological tests on two representative samples at different frequencies and strains. As seen from Fig. 4a and 4b, the storage modulus (G') value was larger than the loss modulus (G'') value over the whole investigated frequency range, indicating that the as-prepared double network hydrogels has strong gel-like behavior [23]. Moreover, the value of $G''/G'(\tan\delta)$ was not frequency-independent, showing that both of the hydrogel systems were kept stable over a broad frequency range. The corresponding strain sweep of the Eu^{3+}-containing hydrogel was also carried out (Fig. 4c). Interestingly, the storage modulus remained steady when the strain increased from 1% to 20%, indicating a satisfactory damage resistance capacity of the Eu^{3+}-containing hydrogel. However, the loss modulus exceeded the storage modulus when the strain increased to more than 200%, implying that gel-sol transition behavior appeared. Therefore, the strain was fixed at γ=1% in the rheology measurements. Furthermore, the continuous step tests at γ=100% and at γ=0.1%

with ω=10 rad/s were used to evaluate the recovery property of the prepared hydrogel (Fig. 4d). It is clearly seen that the Eu^{3+}-containing hydrogel possessed similar storage modulus and loss modulus when exposed to higher strain (100%), resulting in the formation of a metastable fluid state. However, a sudden increase in storage modulus and decrease in loss modulus were observed when the strain decreased to 0.1%, indicating that the hydrogel was reformed. The storage modulus and loss modulus immediately returned to their initial values when the strain was increased from 0.1% to 100%. This rheology behavior confirmed excellent self-recovery property of the Eu^{3+}-containing hydrogel [26].

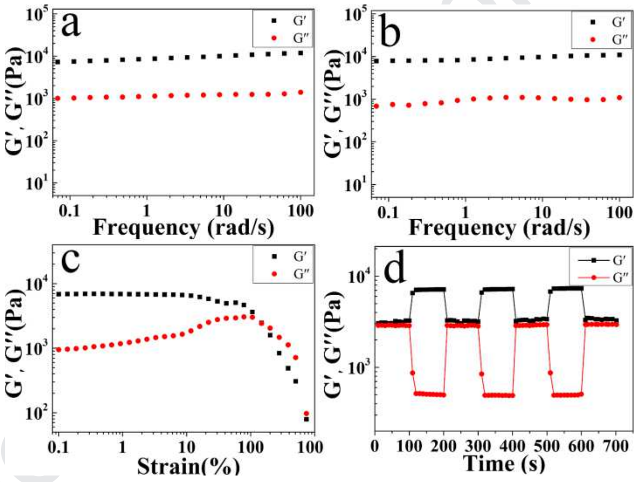


Fig. 4 Rheological properties. Frequency (ω) sweep tests at ω=0.05-100 rad/s and strain (γ)=1% of PVA/AM (a), PVA/AM-$Eu(DPA)_3$ (b). Strain sweep tests of PVA/AM-$Eu(DPA)_3$ at ω=10 rad/s, γ=0.1-1000% (c). Continuous step strain tests of PVA/AM-$Eu(DPA)_3$ at γ=100% (black) and 0.1 % (red) with ω=10 rad/s.

The surface morphology of the prepared hydrogels was investigated by SEM. It should be noted that the samples were first frozen in liquid nitrogen, and then dehydrated by freeze drying process before investigation. Fig. 5 showed that both of the hydrogels have a rough surface morphology with a number of irregular pores. However, the pore diameter of the double network hydrogel was increased slightly with the incorporation of lanthanide complexes. And many smaller pores with diameter below 1μm were observed in PVA/AM, which indicated that PVA/AM-Eu(DPA)$_3$ has a lower crosslinking density than PVA/AM [27-29]. This result was also consistent with the analysis from the swelling and compression measurements.

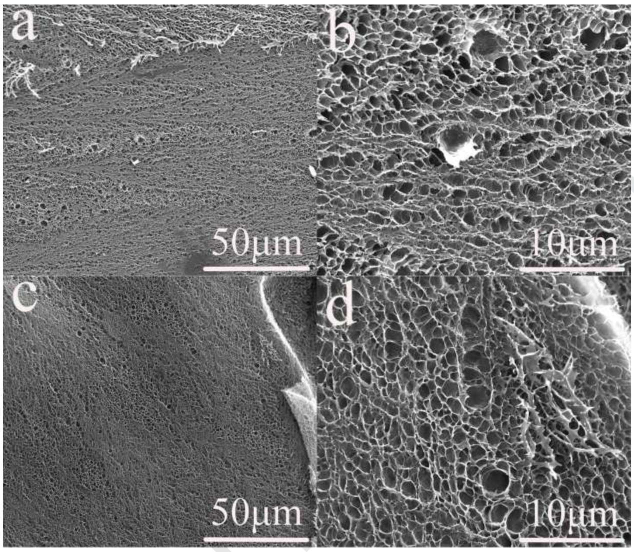


Fig. 5 SEM images of PVA/AM-Eu(DPA)$_3$ (a, b) and PVA/AM (c, d) with low and high magnifications.

Benefitting from the high color purity and high luminescence efficiency of Ln·L$_3$, the subsequently obtained lanthanide-containing hydrogels exhibited excellent optical properties under UV lamp illumination. Fig. S6 showed that Tb^{3+}and Eu^{3+}-containing hydrogels displayed a broad excitation band ranging from 240 to 310 nm with a maximum at 280 nm [30-32], which indicated that these two kinds of hydrogels can be excited by the UV light of the same wavelength. The emission spectrum of Tb^{3+}-containing hydrogel exhibited four characteristic emission lines at 490, 542, 581 and 620 nm, which can be assigned to the $^5D_4\rightarrow{}^7F_J$ (J=6, 5, 4, 3) transitions of Tb^{3+}, in which the emission line corresponding to $^5D_4\rightarrow{}^7F_2$ is the strongest and responsible for the green emission (Fig. 6a) [33-37]. The emission spectrum of Eu^{3+}-containing hydrogel showed four sharp emission lines at 593, 615, 650 and 694 nm, assigned to $^5D_0\rightarrow^7F_J$ (J=1, 2, 3, 4) transitions of Eu^{3+}. Among these emissions, the emission line corresponding to $^5D_0\rightarrow^7F_2$ is prominent, resulting in a red luminescence (Fig. 6a) [38-41]. The addition of DPA ligands to Tb^{3+} solution brings about noticeable alterations in spectral shape. And the appearance of splitting peaks at 490, 542 and 582 nm indicates the formation of 1:3 Tb^{3+}/Ligand coordination complexes [42]. Moreover, the emission colors of the hydrogels can be tuned by altering the molar ratio of the two types of lanthanide luminophores in hydrogels. The intensity ratio of red to green emission (I_{615nm}/I_{542nm}) decreased with the increasing Tb^{3+} concentrations. Thus, a color change from red to green though yellow was observed (Fig. 6b and Fig. S7). To further investigate the optical performance of these luminescent hydrogels, the corresponding decay curves were measured. It is clear that the decay curves were well fitted into a single-exponential function described as $I= I_0\exp(-t/\tau)$ (Fig. S8), implying that the coordination environment of Tb^{3+} or Eu^{3+} in hydrogel is uniform [43]. According to the fitting results of Fig. S8, the lifetime values of Tb^{3+} in PVA/AM-Tb(DPA)$_3$ and Eu^{3+} in PVA/AM-Eu(DPA)$_3$ were determined to be 1.41 ms and 1.46 ms, respectively. The quantum yield of PVA/AM-Tb(DPA)$_3$ and PVA/AM-Eu(DPA)$_3$ are 3.02% and 7.85%, respectively. Furthermore, the excitation/emission wavelength (Fig. S9), lifetimes (Fig. S10) and quantum efficiency of $Ln\cdot L_3$ also measured and listed in Table S1. It can be clearly seen that the polymer matrixes used in PVA/AM-Ln(DPA)$_3$ have a little effect on the luminescent properties of the lanthanide complexes. Moreover, in order to determine the stability of the hydrogel, a simple experiment was carried out. The prepared PVA/AM-Eu(DPA)$_3$ was first immersed into deionized water (10 mL) for two days, and then removed from the deionized water. However, when the soaking solution was excited by a UV lamp (280 nm), no obviously emission peak was found, showing that the luminophore did not escape from the hydrogel. (Fig. S9). These result also shows that it is feasible to synthesize lanthanide complexes-based hydrogels using our strategy.

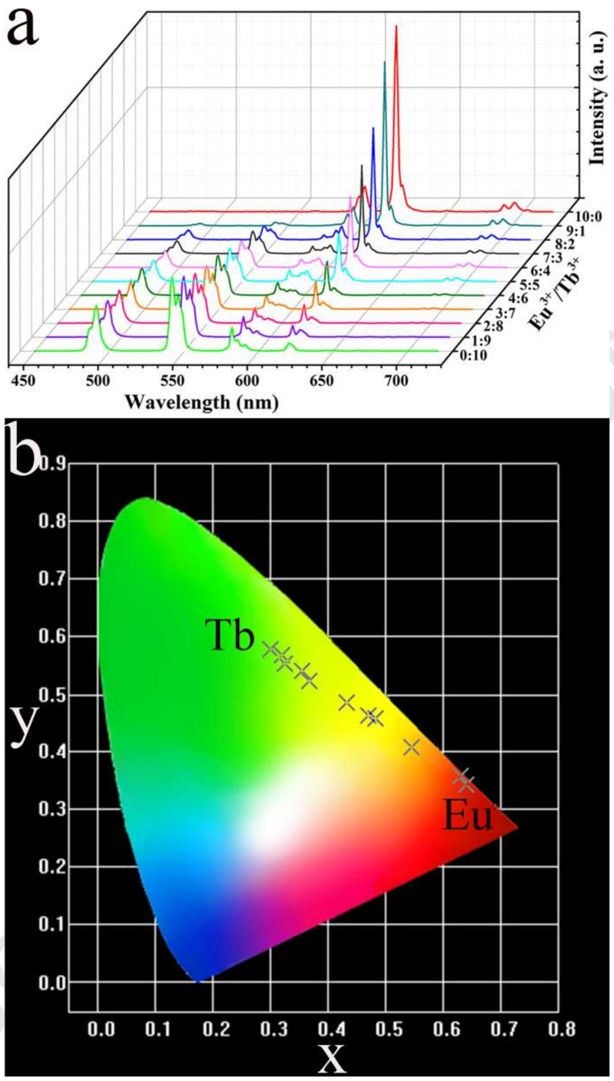


Fig. 6 Emission spectra of the lanthanide-containing double network hydrogels (a), the corresponding CIE 1931 chromaticity diagram, (Eu^{3+}/Tb^{3+} = 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10) (b).

4. Conclusions

In summary, we developed a novel and simple strategy to prepare luminescent hydrogels by a combination of thiol-Michael addition reaction and free radical polymerization. Luminophore was successfully fixed into the hydrogel by employing a bifunctional organic ligand. Lanthanide complexes and double network structures were used to improve the luminescence properties and mechanical strength of hydrogels, respectively. The obtained PVA/AM-Tb(DPA)$_3$ and PVA/AM-Eu(DPA)$_3$ double network hydrogels exhibit the characteristic emission of Tb^{3+} (green) and Eu^{3+} (red), long luminescence lifetimes and high quantum efficiency. Moreover, emission color-tunable luminescent hydrogels were obtained by adjusting the molar ratio of Eu^{3+} and Tb^{3+}.

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Research Highlights

- A trithiol luminescent lanthanide complex was developed.
- The trithiol luminescent lanthanide complex was grafted onto the methacrylated polyvinyl alcohol via Michael-like addition reaction.
- The obtained hydrogels displayed multi-color luminescence and good mechanical properties..

Qing-Feng Li: Conceptualization, Investigation, Writing-Original Draft. **Shaowen Chu**: Investigation. **Erqing Li**: Formal analysis. **Meng Li**: Resources. **Jin-Tao Wang**: Writing-Review and Editing. **Zhenling Wang**: Supervision.

Declaration of interests

☑The authors declare that they have no known competing financial interestsor personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: