

Tough Double Metal-ion Cross-linked Elastomers with Temperature-adaptable Self-healing and Luminescence Properties

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Electronic Supplementary Information

Abstract Smart materials with a combination of tough solid-like properties, fast self-healing and optical responsiveness are of interests for the development of new soft machines and wearable electronics. In this work, tough physically cross-linked elastomers that show high mechanical strength, intriguing temperature-adaptable self-healing and fluorochromic response properties are designed using aluminum (Al) and fluorescent europium (Eu) ions as cross-linkers. The ionic Al-COOH binding is incorporated to construct the strong polymer network which mainly contributes to the mechanical robustness of the elastomer consisting of two interpenetrated networks. The Eu-iminodiacetate (IDA) coordination is mainly used to build the weaker but more dynamic network which dominates the elasticity, self-healing and luminescence of the elastomer. Moderate Eu³⁺ and Al³⁺ contents give these supramolecular elastomers high toughness. The temperature-sensitive Eu-IDA coordination enables tunable self-healing rate and efficiency along with fast Eu-centered “ON/OFF” switchable red emission. The mechanical, self-healing and luminescence properties of these elastomers can be adjusted by tuning the ratio of the two types of metal ions. This elastomer is potentially applicable for biosensors, wearable optoelectronics and anticounterfeiting materials.

Keywords Elastomer; Tough; Self-healing; Luminescence; Temperature-sensitive

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INTRODUCTION

Due to the dynamic nature of metal-ligand coordination^[1–6] and metal-anion ionic interaction,^[7–11] self-healable and stimuli-responsive polymeric elastomers cross-linked by metal ions are of profound interests for the development of new soft machines^[12–15] and wearable electronics.^[16–19] In recent years, many metal-ion cross-linked polymeric elastomers with good self-healing or optical responsiveness have been developed, yet most of these elastomers had relatively low mechanical strength. To improve the mechanical robustness, one approach is increasing the amount of metal ions or using stronger metal-ligand coordination/ionic interaction.^[1,9,20–27] One example is the using of Fe³⁺-2,6-pyridinedicarboxamide coordination for the fabrication of a self-healable and highly stretchable elastomer.^[9] Increasing amount of Fe³⁺ ions in the elastomer dramatically enhanced mechanical strength, yet high Fe³⁺ ion concentration led to the deterioration of elasticity, self-healing and stimuli-responsiveness.

An alternative strategy is to introduce different types of metal ions of varied interaction strength with the ligand or anion, which results in multiple kinetically distinct metal-ion crosslinks in the elastomer. As to these kinetic effects dominated elastomers, slow-relaxation cross-links (strong cross-links) mainly determine the mechanical strength, while fast-relaxation cross-links (weak cross-links) mainly impart energy dissipation to the elastomer. To the authors' knowledge, most metal-ion cross-linked elastomers were cross-linked by only one type of metal ion,^[1,9,19–21,28–34] and only a few of them incorporated two or more types of metal ions, yet, mostly in gels to improve the stimuli-response properties^[35–42] or to control the viscoelastic properties of these materials by tuning the ratio between different types of metal-ligand cross-links from rheological analysis.^[3,43,44] Reports on well-balanced mechanical robustness, self-healing and stimuli-responsiveness investigations in one multiple metal-ion cross-linked elastomer are rare.^[45]

In this contribution, we report a new design of tough double metal-ion interpenetrating polymer network (IPN) supramolecular elastomers with high mechanical strength (comparable to covalently cross-linked elastomers), intriguing temperature-adaptable self-healing and thermo-

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fluorochromic response properties. Our design strategy is, on the one hand, to utilize Al-COOH ionic bindings in one type of polymer chains as the strong physical cross-links, which mainly contribute to the mechanical strength of the IPN elastomer; on the other hand, to use iminodiacetate (IDA) as binding motifs in another type of polymer chains to mainly coordinate with Eu^{3+} ions. These Eu-IDA complexes act as more dynamic cross-links, which dominate the elasticity, temperature-adaptable self-healing and luminescence of the IPN elastomer. The Eu^{3+} and Al^{3+} contents both affect the toughness remarkably. It is found that moderate Eu^{3+} and Al^{3+} contents give these supramolecular elastomers high toughness. The mechanical, self-healing and luminescence properties of this IPN elastomer can be easily adjusted by tuning the relative concentration of the two types of metal ions. This thermofluorochromic feature of IPN elastomer is expected to be able to control the multicolor manipulation of smart polymeric elastomers when combining the use of other luminescent lanthanide metals.^[37,46,47] This elastomer will be of interests for biosensors,^[48,49] wearable optoelectronics^[50,51] and anti-counterfeiting materials.^[52,53]

EXPERIMENTAL

Materials

All solvents and chemicals were purchased from commercial sources and used as received unless otherwise noted. Diethylene glycol monomethyl ether methacrylate (MEO_2MA) and 2,2'-azobis(isobutyronitrile) (AIBN) were supplied by TCI. Glycidyl methacrylate (GMA), 2-hydroxy-2-methylpropiophenone (photo initiator) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Macklin. Acrylic acid (AA) and iminodiacetic acid disodium salt hydrate (Na_2IDA) was purchased from Alfa Aesar. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was purchased from Adamas Reagent. MEO_2MA and GMA were passed through a basic aluminum oxide column prior to use. AIBN was recrystallized from ethanol. Deionized water (High-Q, Inc. 103S Stills) with a resistivity of $>10.0 \text{ M}\Omega$ was used throughout the preparation of elastomers.

Synthesis of P($\text{MEO}_2\text{MA-co-GMA}$)

The copolymer of MEO_2MA and GMA was prepared by free radical polymerization. MEO_2MA (5 g, 26.5 mmol), GMA (0.75 g, 5.3 mmol) and AIBN (7 mg, 0.043 mmol) were dissolved in 10 mL of anisole in a 50 mL flask. The reaction mixture was degassed under vacuum and filled with nitrogen for 10 min. The flask was then sealed and placed in a pre-heated oil bath at 65°C for 5 h. After reaction, the mixture was cooled down to room temperature. The polymer was collected after precipitation in hexane and dried under vacuum for 24 h.

Preparation of IDA-modified Copolymer

The grafting of IDA to the copolymer P($\text{MEO}_2\text{MA-co-GMA}$) was carried out via the ring-opening reaction of epoxide moieties.^[54] The Na_2IDA was used to react with epoxy groups. In a typical synthesis, P($\text{MEO}_2\text{MA-co-GMA}$) (3 g, 2.8 mmol in terms of GMA units) was firstly dissolved in the mixed solvents of methanol (23.7 g, 30 mL) and dioxane (3.1 g, 3 mL). The Na_2IDA aqueous solution (10 wt%, 10 mL and 5.6 mmol of IDA) was then added into the P($\text{MEO}_2\text{MA-co-GMA}$) solution dropwise and refluxed at 65°C for 9 h to yield poly(di(ethylene glycol) methyl ether methacrylate-co-3-iminodiacetate-2-hydroxypropylmethacry-

late) P($\text{MEO}_2\text{MA-co-IDHPMA}$). The IDA-modified copolymer was precipitated in cold ethanol for three times and dried under vacuum for 24 h.

Preparation of the Double Metal-ion Cross-linked Elastomers

Typically, to prepare the IPN elastomer with a Eu-to-IDA ratio of 0.2:1 and an Al-to-COOH ratio of 0.01:1, 1.5 mL of P($\text{MEO}_2\text{MA-co-IDHPMA}$) methanol solution (10 wt%), 475 μL of AA (0.498 g, 6.9 mmol), 250 μL of MEO_2MA (0.255 g, 1.35 mmol) and 15 μL of photo initiator (0.1 mmol) were first mixed together. To this solution, 130 μL of 20 wt% $\text{Al}(\text{NO}_3)_3$ methanol solution (0.069 mmol Al^{3+}) and 106 μL of 10 wt% $\text{Eu}(\text{NO}_3)_3$ (0.024 mmol Eu^{3+}) aqueous solution were further added where the gelation occurred immediately. After incubation for 2 h at room temperature, the gel was transferred to a Petri dish and further exposed to UV light (1 mW/cm^2 , 365 nm) for 30 min to polymerize MEO_2MA and AA into P($\text{MEO}_2\text{MA-co-AA}$). After subsequent drying of the as-prepared organogel, a transparent double metal-ion cross-linked IPN elastomer film with two penetrated networks was obtained. Using similar procedures, elastomers with different Eu-to-IDA and Al-to-COOH ratios were prepared.

Characterization

UV irradiation was carried out using a 365 nm UV lamp (UV-20A, Shanghai-Yaozhuang) with a light intensity of 1 mW/cm^2 . Fluorescence emission of all samples was visualized under a 365 nm UV lamp (ZF-7A, Shanghai-Gucun). The SEC instrument package was supplied by Shimadzu and comprised the following setup: a Shimadzu LC-20AD pump, two series of connected columns (Shodex, K-803 and K-804) in a Shimadzu CTO-20 oven at 35°C and a Shimadzu RID-10A refractive index detector. THF was used as the mobile phase at a flow rate of 1 mL/min at 40°C and the molecular weight was calibrated against polystyrene standards. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker Ascend 400 MHz spectrometer using CDCl_3 and D_2O as the solvent for P($\text{MEO}_2\text{MA-co-GMA}$) and P($\text{MEO}_2\text{MA-co-IDHPMA}$), respectively. The Al and Eu distribution in the elastomer was investigated by a scanning electron microscopy (SEM) instrument (Su-70, Hitachi, Japan) operated at 15 kV coupled with an energy-dispersive X-ray (EDX) spectrometer (EDAX, AMETEK Materials Analysis Division, USA). The rheological frequency-sweep (strain=1%) spectra of different samples were recorded using a Haake Mars III rheometer. Measurements were performed on a 35 mm parallel plate with the frequency ranging from 0.01 Hz to 10 Hz. All measurements were conducted at 25°C . A solvent trap was used to minimize the evaporation of solvent. The fluorescence spectra were recorded by a fluorescence spectrometer (Hitachi, F-4600, Japan). All samples were transferred into quartz cuvettes for measurements. The emission spectra were recorded using a 10 nm (excitation)/10 nm (emission) slit widths with a scanning rate of 1200 nm/min. Uniaxial tensile tests were performed on a standard tensile MTS Criterion Model 43 material testing machine with a loading cell of 1 kN. Tensile tests were conducted at a stretching rate of 50 mm/min with a temperature of 25°C and a relative humidity of 55%. Samples for tensile tests were dumbbell shaped thin strips with a dimension of 1 mm $\times$ 6 mm $\times$ 25 mm. All fluorescence emission and mechanical tests of the elastomer films were conducted at

an ambient relative humidity (RH) of 60% to avoid the influence of moisture.

Self-healing Test

Self-healing experiments were carried out by splicing two pieces of the elastomers together at room temperature. To visualize the self-healing of the elastomer, we first cut one fluorescein-doped elastomer (green emissive) film and one red emissive elastomer film. The two fresh-cut double metal-ion IPN elastomer films were then spliced together. The green emissive elastomer film (fluorescein-to-Eu molar ratio of 1:5.5) was prepared using the same procedure mentioned in the preparation of the red emissive double metal-ion cross-linked elastomer. Healing experiments under high temperatures (60, 70 and 80 °C) were carried out in an oven for 10 min. All self-healing tests were conducted at an ambient RH of 60%.

Thermo-fluorochromism Measurement

A double metal-ion cross-linked elastomer film (0.4 mm × 10 mm × 14 mm) was used to verify the thermo-fluorochromism. The PRT-8A (Cossim, China) hot plate was first heated to 100 °C. As the sample was heated on the hot plate for about 10 s, it was immediately transferred out onto the cold surface (~25 °C) by the side. The sample was transferred back and forth for three cycles between the hot plate (100 °C) and the cold surface by the side. The change in emission (luma versus time) was visualized in real time using a Canon 600D camera and jpg files were extracted by Apple QuickTime from the video. NIH Image J was used to analyze the RGB components from the images to calculate the luma using the formula $Y = 0.299R + 0.587G + 0.114B$, where R , G and B denote the red, green and blue color values, respectively. The red fraction was calculated by R/Y and plotted versus time.

RESULTS AND DISCUSSION

The poly(di(ethylene glycol) methyl ether methacrylate-co-3-iminodiacetate-2-hydroxypropylmethacrylate (denoted as P(MEO₂MA-co-IDHPMA)) (see ¹H-NMR spectra in Fig. S1 in the electronic supplementary information, ESI) was prepared according to our previous work.^[55] The copolymer poly(di(ethylene glycol) methyl ether methacrylate-co-glycidyl methacrylate) (denoted as P(MEO₂MA-co-GMA) ($M_n = 15.8$ kg/mol, $\bar{D} = 3.33$ and the molar ratio of MEO₂MA-to-GMA is 5:1) was first prepared by free radical polymerization (Fig. 1a and Fig. S2 in ESI). A postpolymerization modification was carried out *via* the ring-opening reaction of epoxides with excess sodium iminodiacetate to yield P(MEO₂MA-co-IDHPMA).^[54] To prepare the IPN elastomer, MEO₂MA, acrylic acid (AA), Al(NO₃)₃ and photoinitiator were first mixed with the P(MEO₂MA-co-IDHPMA) methanol solution (10 wt%). To this solution, a predetermined amount of Eu(NO₃)₃ (the molar ratio of Eu-to-IDA of 0.2:1 was used as an example and the same ratio was used throughout the paper unless otherwise stated) was further added where the gelation occurred immediately. After incubation for 2 h at room temperature, the organogel was further exposed to UV light (1 mW/cm², 365 nm) for 30 min to polymerize MEO₂MA and AA into P(MEO₂MA-co-AA) (Fig. 1a). Through subsequent drying of the IPN organogel, a transparent double metal-ion cross-linked IPN elastomer was formed (see the photo image in Fig. 1b) with a P(MEO₂MA-co-IDHPMA)-to-P(MEO₂MA-co-AA) mass ratio of 1:5. Scheme for the network structure of this IPN elastomer is shown in Fig. 1(b). This IPN elastomer had an Eu-to-IDA ratio of 0.2:1, Al-to-COOH ratio of 0.01:1 and Eu-to-Al ratio of 0.35:1, (molar ratio). The IPN elastomer is red-emissive and stretchable (Fig. 1c).

To clarify the roles of the multiple cross-links in this IPN

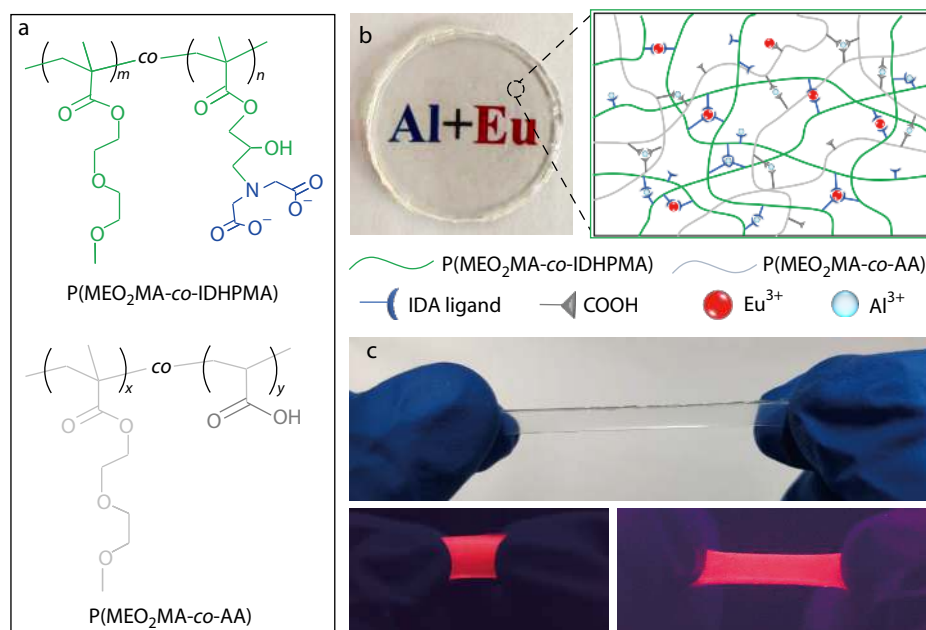


Fig. 1 (a) Molecular structures of P(MEO₂MA-co-IDHPMA) and P(MEO₂MA-co-AA). (b) Illustration of the double metal-ion cross-linked IPN elastomer. The photo image shows the transparency of IPN elastomer. (c) Optical images to show the stretchability of the IPN elastomer and its luminescence under UV light (365 nm). The IPN elastomer given in this figure has an Eu-to-IDA ratio of 0.2:1, Al-to-COOH ratio of 0.01:1 and Eu-to-Al ratio of 0.35:1 (molar ratio).

elastomer, we first simply mixed Eu^{3+} or Al^{3+} ions with the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ and $\text{P}(\text{MEO}_2\text{MA-co-AA})$ methanol solutions (Fig. 2), respectively. To mix metal ions with $\text{P}(\text{MEO}_2\text{MA-co-AA})$ solution, metal ions were first mixed with photoinitiator and monomers of MEO_2MA and AA in methanol. After photopolymerization, $\text{P}(\text{MEO}_2\text{MA-co-AA})$ solutions with different metal ions were obtained. On the one hand, both Eu^{3+} and Al^{3+} ions were able to cross-link $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ through Eu-IDA coordination and Al-IDA ionic binding (Fig. 2a). On the other hand, Al^{3+} ions cross-linked $\text{P}(\text{MEO}_2\text{MA-co-AA})$ by the ionic interaction between Al^{3+} and COOH groups, while Eu^{3+} ions hardly cross-linked $\text{P}(\text{MEO}_2\text{MA-co-AA})$ (Fig. 2b). It indicates that the Al-COOH cross-linking contributes to the mechanical strength of the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ network.

To further understand the competition between Eu^{3+} and Al^{3+} ions, rheological measurements were conducted on the double metal-ion cross-linked IPN gels (Fig. 3). The Eu^{3+} and Al^{3+} ions were simultaneously mixed with each polymer methanol solution. Keeping the amount of one type of metal-ion in the polymer solution constant, we investigated the influence of another type of metal-ion on the rheological properties of the IPN gels. Evidently, Eu^{3+} ions competed with Al^{3+} ions to break the Al-COOH cross-linking, and Al^{3+} ions also disrupted the Eu-IDA cross-linking.^[56] Therefore, the two metal ions reached a final competitive equilibrium state^[3,35] to form multiple cross-linking in the IPN organogel. Since Eu^{3+} ions did not cross-link the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ and increasing amount of Eu^{3+} ion weakened the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ gel (Fig. 3a), it is deduced that the COOH accommodated one

Eu^{3+} ion to dissociate Al^{3+} ion from COOH groups, resulting in the disruption of the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ network (see schematic drawing in Fig. 1b). Because the IDA is a much stronger ligand than COOH ,^[37,57] we deduce that the Eu^{3+} ions mainly coordinate with IDA in the IPN organogel.

It is known that both Eu^{3+} and Al^{3+} ions could cross-link the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ and increasing amount of Al^{3+} ion also weakened the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ gel (Fig. 3b). It demonstrates that the Al-IDA cross-linking is much weaker than the Eu-IDA cross-linking at the same metal-to-ligand ratio. This can also be proved by the rheological tests in Fig. S3(a) (in ESI). Although there were more Al^{3+} ions in the IPN organogel (Eu-to-IDA ratio of 0.2:1 and Al-to-IDA ratio of 0.57:1), the result in Fig. S3(b) (in ESI) proves that the Eu-IDA cross-linked $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ gel was still much stronger than the Al-IDA cross-linked $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ gel. Moreover, only a small fraction of Al^{3+} ions cross-linked the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ since the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ was cross-linked by Al^{3+} ions. Therefore, it is concluded that the Eu-IDA cross-linking mainly contributes to the mechanical robustness of the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ network. The reason can be understood by the comparison of the binding constants of Eu-IDA and Al-IDA complexes. The Eu^{3+} ions coordinate up to three IDA ligands. The binding constants for M-L, M-L₂ and M-L₃ are *ca.* $10^{6.7}$, $10^{12.1}$, and $10^{15.5}$,^[58] respectively. When forming hydrogel networks, the average coordination of Eu^{3+} ions for Eu-IDA complexes is >2 . The average binding constant of the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ to Eu^{3+} ions will be $>10^{12.1}$. Alternatively, Al^{3+} ions coordinate up to two IDA ligands. The binding constants for M-L and M-L₂ are *ca.* $10^{8.2}$ and

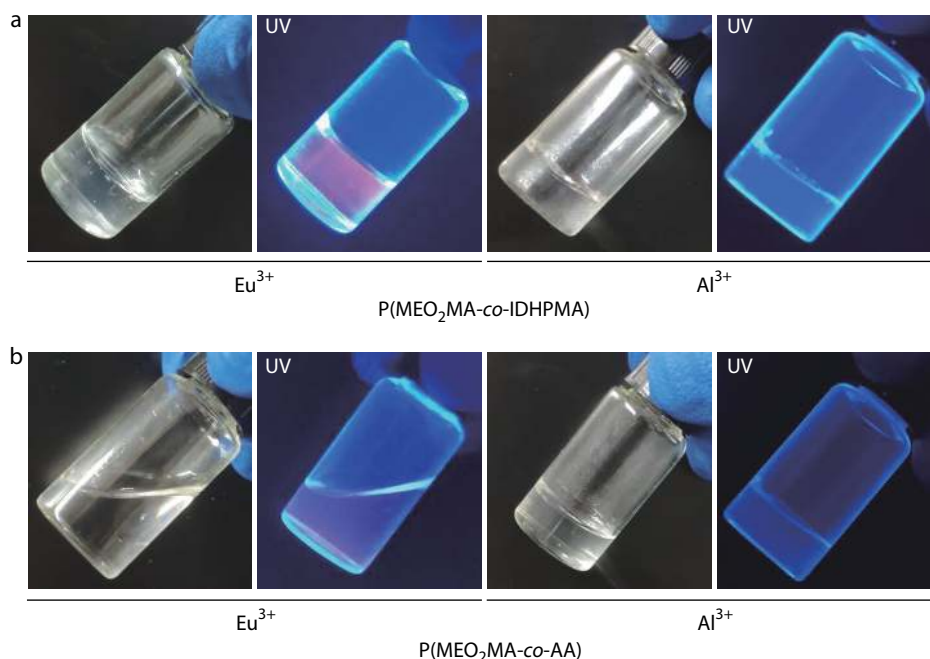


Fig. 2 Photo images to show the mixing of Eu^{3+} and Al^{3+} ions with (a) $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ and (b) $\text{P}(\text{MEO}_2\text{MA-co-AA})$ methanol solutions (10 wt%). The mass concentration of $\text{Eu}(\text{NO}_3)_3$ in each polymer solution is 0.5 wt% and the Eu-to-IDA molar ratio in the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ solution is 0.2:1, while the mass concentration of $\text{Al}(\text{NO}_3)_3$ in each polymer solution is 0.9 wt% and the Al-to-COOH molar ratio in the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ solution is 0.01:1.

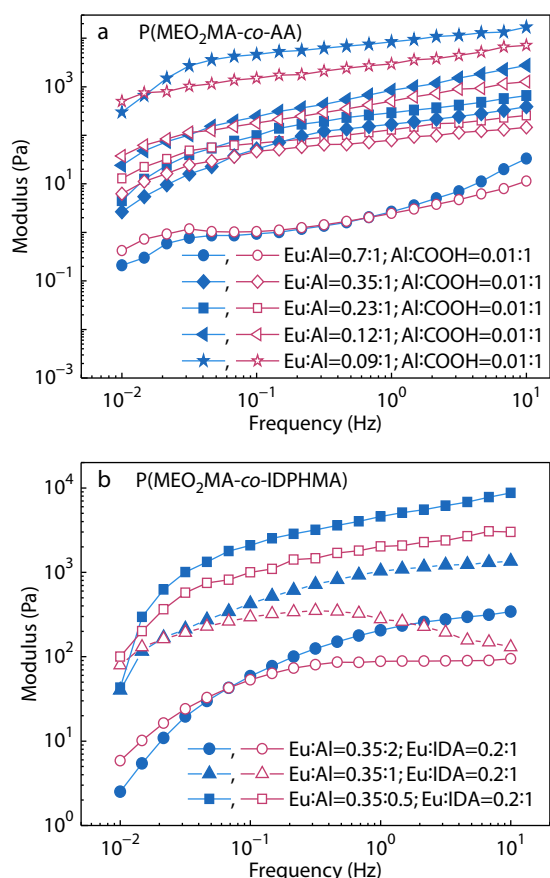


Fig. 3 Rheological measurements showing the competition between Eu^{3+} and Al^{3+} ions with (a) $\text{P}(\text{MEO}_2\text{MA-co-AA})$ and (b) $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$. Each organogel has a polymer mass concentration of 10 wt%. The solid blue symbols denote the storage modulus G' , while the hollow symbols indicate the loss modulus G'' . The Eu-to-Al, Al-to-COOH and Eu-to-IDA molar ratios are shown in the inset.

$10^{7.4}$,^[59] respectively. Then, the average coordination of Al^{3+} ions for Al-IDA complexes is 1–2, and the average binding constant of the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ to Al^{3+} ions will be $10^{7.4}$ – $10^{8.2}$. Evidently, Eu-IDA cross-linking is much stronger than the Al-IDA cross-linking in the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ network, indicating the mechanical robustness of the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ network is dominated by Eu-IDA cross-linking.

The coexistence of the two types of metal ions also affected the fluorescence emission from Eu^{3+} ions (Fig. 4). By increasing the amount of Eu^{3+} ions and keeping the Al^{3+} concentration constant, the emission intensity increased obviously in the Eu- and Al-containing $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ solution, while the emission intensity did not give a significant increase in the Eu- and Al-containing $\text{P}(\text{MEO}_2\text{MA-co-AA})$ solution (Figs. 4a and 4b). After extracting the fluorescence intensity at the emission peak of 617 nm, the fluorescence intensity was plotted versus Eu/Al ratio in Fig. 4(c). It can be seen more clearly in Fig. 4(c) that Eu^{3+} ions in the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ solution gave much stronger fluorescence emission especially when the Eu/Al ratio was larger than 0.23:1. This phenomenon can be attributed to the “antenna effect” from the sensitizing ligand, IDA, which enables intense metal-

center luminescence.^[36,60,61] As shown in Fig. 4(d), the emission intensity decreased by increasing the amount of Al^{3+} and keeping Eu^{3+} concentration constant (Eu-to-IDA ratio of 0.2:1). This is because Al^{3+} ions disrupted the Eu-IDA coordination and weakened the “antenna effect”. Therefore, we can easily understand that the coexistence of Eu^{3+} and Al^{3+} ions in the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})/\text{P}(\text{MEO}_2\text{MA-co-AA})$ solution gave weaker emission intensity than the Eu-containing $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})/\text{P}(\text{MEO}_2\text{MA-co-AA})$ solution in the absence of Al^{3+} ions in Fig. 4(e).

After the removal of solvent in the organogels, solid IPN elastomers were obtained. To know the Al and Eu distributions in the elastomer matrix, typical SEM imaging and elements mapping were carried out for the elastomer with an Al-to-COOH ratio of 0.01:1 and an Eu-to-IDA ratio of 0.2:1. The SEM image is shown in Fig. 5(a), where no inhomogeneity is seen. Figs. 5(b) and 5(c) give the Al and Eu distributions analyzed from Fig. 5(a). It is obviously seen that both Al^{3+} and Eu^{3+} were homogeneously distributed in the matrix. Compared with the Eu^{3+} ions, the Al^{3+} ions were more densely distributed in the matrix, indicating higher Al-COOH cross-linking. This is because the content of Al^{3+} ions was higher than that of Eu^{3+} ions (Eu-to-Al mole ratio of 0.35:1).

Knowing the cross-linking and luminescence features of the two polymers in the presence of Al^{3+} and Eu^{3+} ions, we further investigated the mechanical properties of the double metal-ion IPN elastomers. In the absence of Eu^{3+} ion (Figs. 6a and 6b), the IPN elastomer was plastic with a low fracture strain of ~50%, a high yield strength of ~20 MPa, fracture strength of 16.8 MPa and toughness of 8.9 J/cm³. As the content of Eu^{3+} ions increased (i.e., the increase of Eu-to-IDA ratio), the elastomer was softened and more stretchable due to the competition between the two metal ions discussed above. When the Eu-to-IDA ratio increased to 0.07:1, the yield strength decreased obviously to ~12.3 MPa, fracture strength was down to 11.3 MPa, and the fracture strain and toughness increased to ~135% and 14.6 J/cm³, respectively. With a further increase of the Eu-to-IDA ratio (>0.07:1), a transition from plastic to elastic was noted, since the stress increased gradually after yielding and fracture strain increased further. When the Eu-to-IDA ratio increased to 0.2:1, fracture strength was ~6.1 MPa and fracture strain increased to ~210%. Meanwhile, the toughness decreased to 10.3 J/cm³, which was quite close to the toughness (10.4 J/cm³) of the elastomer when Eu-to-IDA ratio was 0.13:1. Although the elastomer became more elastic at the Eu-to-IDA ratio of 0.4:1 (fracture strain of ~280%), the fracture strength (2.7 MPa) and toughness (4.8 J/cm³) were quite low.

Obviously, the double metal-ion cross-linked elastomer prepared in this work had quite high toughness values.^[6,55] The mechanical strength was also comparable to those covalently cross-linked elastomers.^[62] Particularly, the toughness of the elastomer increased with the Eu-to-IDA ratio when the elastomer was in plastic state (relatively low Eu-to-IDA ratios), whereas it decreased with the Eu-to-IDA ratio when the elastomer was in elastic state (relatively high Eu-to-IDA ratios). It indicates that elastomers with moderate stiffness and stretchability (i.e., moderate Eu^{3+} content) had the highest energy dissipation. Moreover, it is also deduced that the mechanical

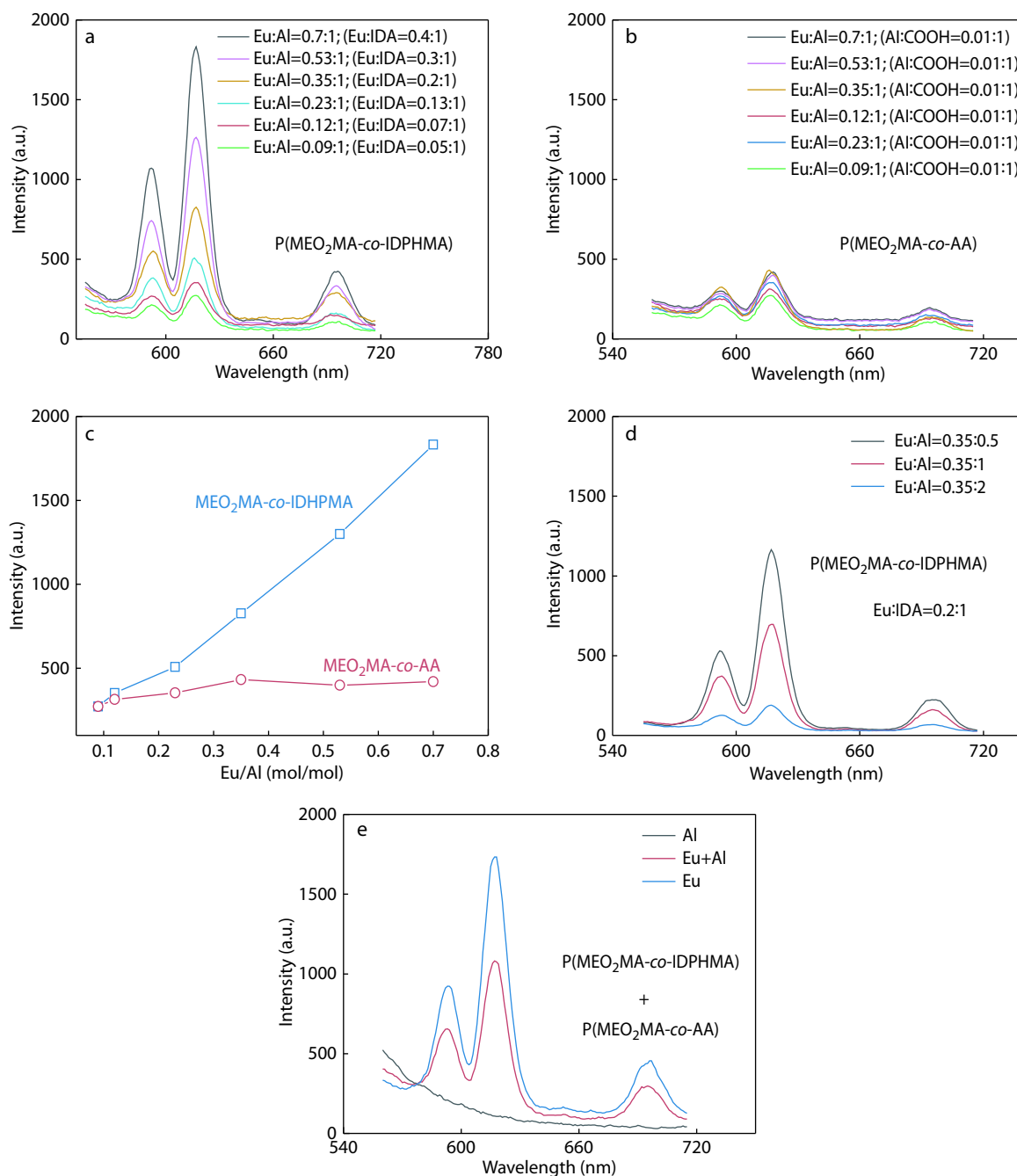


Fig. 4 Fluorescence spectra changing by a continuous increase of Eu-to-Al molar ratio in the (a) P(MEO₂MA-co-IDHPMA) and (b) P(MEO₂MA-co-AA) methanol solutions. The amount of Al³⁺ ions was kept constant in both polymer solutions. (c) The variation of the fluorescence intensity at an emission peak of 617 nm with an increase of the Eu/Al ratio (extracted from a and b). (d) The changing of fluorescence intensity of the P(MEO₂MA-co-IDHPMA) solution in the presence of both types of metal ions by varying the Al³⁺ concentration. The Eu-to-IDA molar ratio was kept constantly to be 0.2:1. (e) The emission spectra of the P(MEO₂MA-co-IDHPMA)/P(MEO₂MA-co-AA) methanol solution mixed with Al³⁺, Eu³⁺ and both types of metal ions.

state of the IPN elastomer can be readily switched in a wide range between the plastic and elastic states by changing the content of Eu³⁺ ions.

Based on the results in Figs. 4(a) and 6(a), when the Eu-to-IDA ratio was 0.2:1, the elastomer had a strong enough fluorescence emission, good enough mechanical properties and typical elastic deformation. Therefore, an Eu-to-IDA ratio of

0.2:1 was chosen for further analysis. We also investigated the mechanical properties of the IPN elastomer influenced by the content of Al³⁺ ions (Fig. 6c). When there was no Al³⁺ ion (Eu-to-IDA ratio of 0.2:1), the IPN elastomer had a fracture strength of only ~1.9 MPa and a fracture strain of ~220%. When Al³⁺ ions were added to an Al-to-COOH ratio of 0.005:1, the fracture strength increased obviously to ~4.9 MPa and the



Fig. 5 (a) SEM image of the elastomer with an Al-to-COOH ratio of 0.01:1 and an Eu-to-IDA ratio of 0.2:1 (Eu-to-Al molar ratio of 0.35:1). The (b) Al and (c) Eu element-distributions analyzed by an EDX from the region in (a).

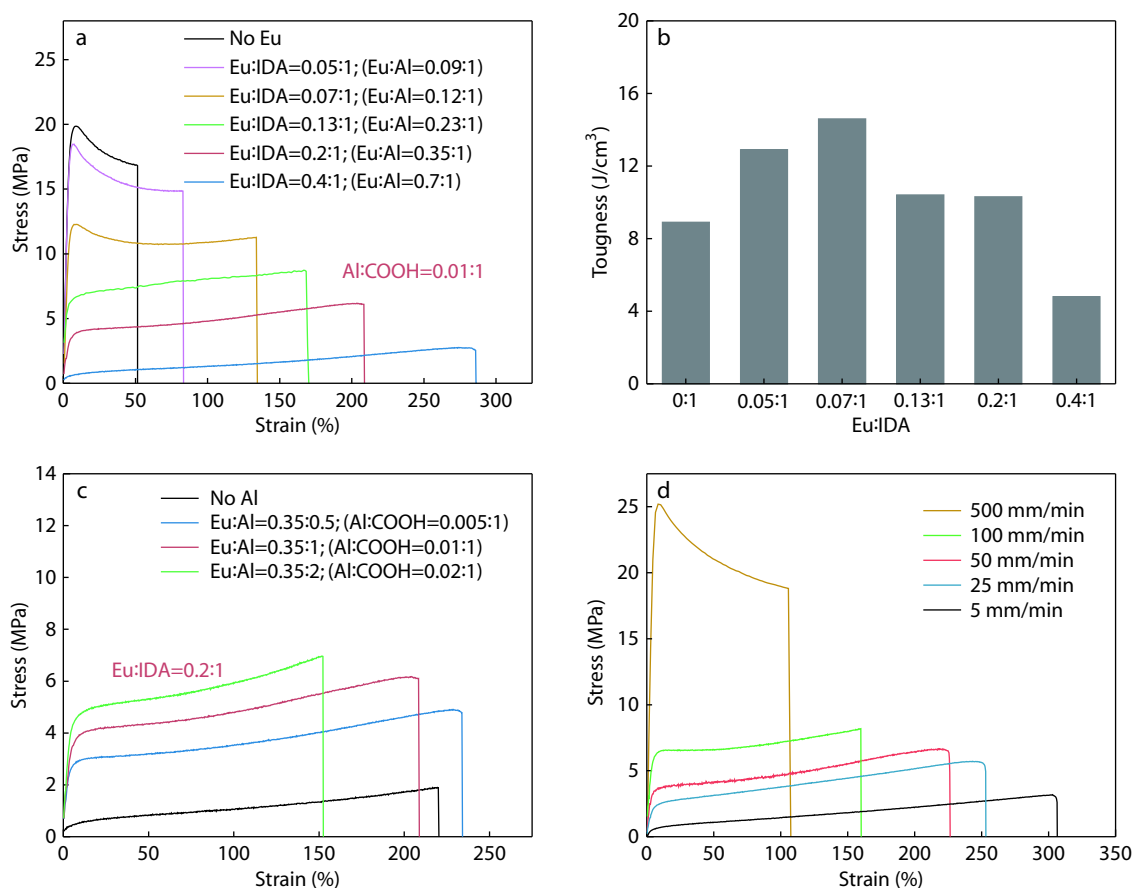


Fig. 6 (a) The stress-strain curves of the elastomers with different Eu^{3+} concentrations (different Eu-to-IDA ratios) in the presence of constant Al-to-COOH molar ratio of 0.01:1. The COOH denotes the carboxylic group from P(MEO₂MA-co-AA). (b) Toughness values calculated from (a) as a function of Eu-to-IDA ratio. (c) The stress-strain curves of the elastomers with different Al^{3+} concentrations (different Al-to-COOH ratios) in the presence of constant Eu-to-IDA molar ratio of 0.2:1. (d) Stretching rate dependence of the double metal-ion IPN elastomers with an Al-to-COOH ratio of 0.01:1 and an Eu-to-IDA ratio of 0.2:1.

fracture strain slightly increased to ~230%, indicating the larger cross-linking density from Al-COOH ionic interaction. With the increase of the Al-to-COOH ratio from 0.005:1 to 0.02:1, the mechanical strength increased gradually from ~4.9 MPa to ~7 MPa while the fracture strain dropped to ~150%. Similarly, IPN elastomers with moderate stiffness and stretchability (*i.e.*, moderate Al^{3+} content) had the highest toughness (10.3 J/cm³ when Al-to-COOH ratio was 0.01:1). Taking a combined consideration of the results in Figs. 6(a) and 6(c), the Al^{3+} content was higher than Eu^{3+} content in the elastomer.

Meanwhile, the mechanical strength and fracture strain changed more significantly when varying the Eu^{3+} content. Therefore, it is deduced that the mechanical properties of the IPN elastomer were more sensitive to the Eu^{3+} content.

According to the results from Figs. 6(a) and 6(c), it is known that more Eu^{3+} ions weaken the mechanical strength and enhance the elasticity of the IPN elastomer while more Al^{3+} ions stiffen the IPN elastomer. Meanwhile, considering that the IPN elastomer in the absence of Eu^{3+} ions had a much higher fracture strength of ~20 MPa (Fig. 6a) than the IPN

elastomer in the absence of Al^{3+} ions (fracture strength of ~ 1.9 MPa) (Fig. 6c), it is deduced that the Al^{3+} cross-linking of the $\text{P}(\text{MEO}_2\text{MA-co-AA})$ mainly contributes to the mechanical strength of the IPN elastomer, while the Eu-IDA coordination is mainly responsible for the elasticity of the IPN elastomer. Because the Al-COOH ionic interaction forms stronger and less dynamic cross-links with a higher Al-COOH cross-linking density (see Figs. 5b and 5c), the mechanical strength is dominated by Al-COOH cross-linking. Since Eu-IDA coordination generates more dynamic and relatively weak cross-links, the association/dissociation process during deformation made the elastomer bear more strain energy. Then, higher elastic deformation was seen when more Eu^{3+} ions were added (see Fig. 6a). Therefore, the Eu-IDA coordination mainly contributes to the elasticity. Now, we can also easily understand why more Eu^{3+} ions weaken the mechanical strength of the IPN elastomer. Although more Eu^{3+} ions strengthen the $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ network, the mechanical strength of the IPN elastomer is much more sensitive to the disruption of Al-COOH cross-links due to the increasing amount of Eu^{3+} ions. Thus, the mechanical strength of the IPN elastomer is weakened. Since high Eu^{3+} or Al^{3+} content weakens toughness, the toughness achieves high values only when the Eu-to-Al ratio is well-balanced, i.e., moderate Eu^{3+} and Al^{3+} contents.

Additionally, it is shown in Fig. 6(d) that the mechanical properties including yield strength and fracture strength were highly dependent on the stretching rate. As the stretching rate increased from 5 mm/min to 500 mm/min, the elastomer stiffened gradually. At a high stretching rate of

500 mm/min, the elastomer even changed into plastic state with remarkable enhancement on the mechanical strength. This is typical for metal-ligand or ionic dynamic cross-linking of polymers that the mechanical properties including yield strength and fracture strength increase with increasing stretching rate.^[6,20]

Owing to the physical cross-linking by Eu^{3+} and Al^{3+} ions, the IPN elastomer is expected to be self-healable. The self-healing results are shown in Fig. 7. To visualize the self-healing of the elastomer, we first cut one fluorescein-doped elastomer (green emissive) film and one red emissive elastomer film. The two fresh-cut double metal-ion IPN elastomer films were then spliced together. Similar to other supramolecular elastomers,^[1,63] the two pieces of elastomer films were reassembled without any external stimuli. It is clear that optical images show the remerging of surfaces under UV light. The healed elastomer film was mechanically robust, and it could sustain a large strain without fracture after a healing duration of 5 days (Fig. 7a). As shown in Fig. 7(b), a longer healing time results in the higher recovered fracture strain. After a healing time of 1 day at room temperature, the rejoined elastomer had a recovered fracture strain of $\sim 120\%$ and a healing efficiency of $\sim 52\%$ (defined as the ratio between the fracture strain restored relative to the original fracture strain). Healing at room temperature for 5 days led to a recovered fracture strain of $\sim 210\%$ and a healing efficiency of $\sim 90\%$.

Since metal-ion mediated coordination or ionic cross-linking is temperature sensitive, it is desired that higher healing temperature also results in a higher healing efficiency.^[64] As given in Fig. 7(c), after the elastomer films were healed at

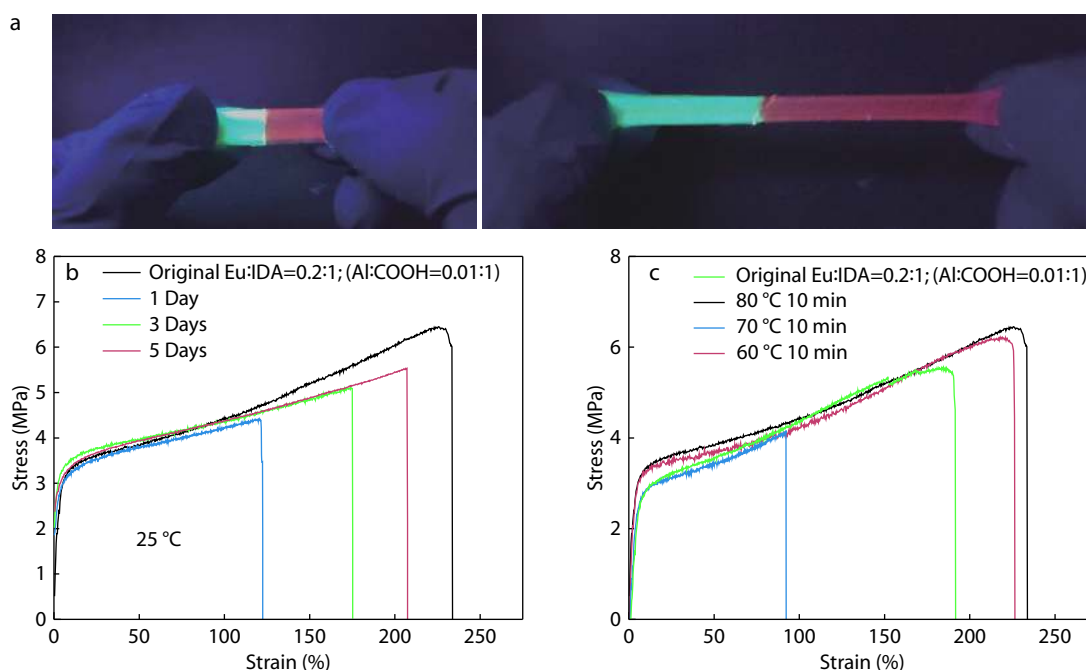


Fig. 7 (a) Images to show the self-healing of two pieces of the elastomer. To make the cut region more distinguishable, the left piece of elastomer was doped with fluorescein to give green luminescence. The photos were taken under 365 nm UV light. The elastomer was healed under room temperature for 5 days. (b) Stress-strain curves of an elastomer film healed at room temperature for different time scales. (c) Stress-strain curves of an elastomer film healed at different temperatures for the same time scale of 10 min. All elastomer films had an Al-to-COOH ratio of 0.01:1 and a Eu-to-IDA ratio of 0.2:1.

60 °C for only 10 min, the rejoined elastomer film reached a healing efficiency of ~40%. By increasing the healing temperature to 80 °C, a rather high healing efficiency of ~96% was

reached after a healing time of 10 min. This is indicative of highly dynamic nature of the cross-links under high temperature.

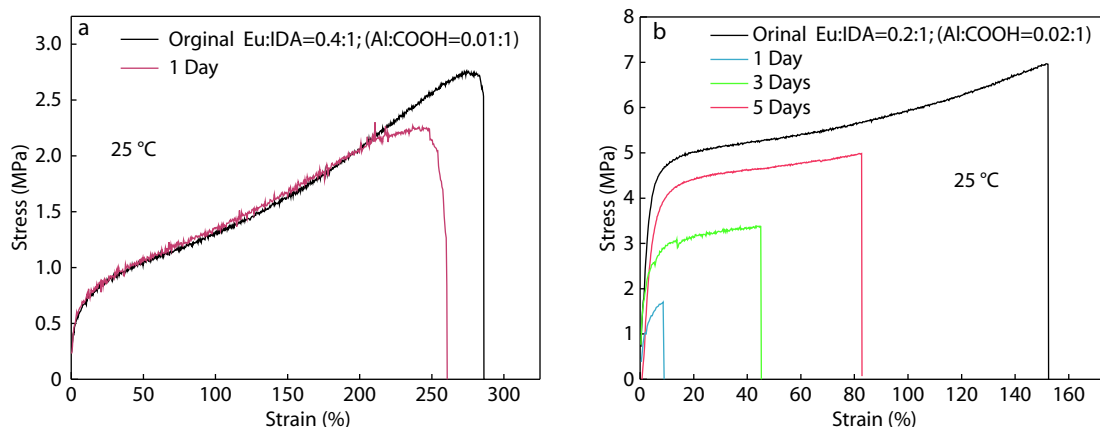


Fig. 8 Stress-strain curves showing the self-healing behavior of the IPN elastomer with (a) more Eu^{3+} ($\text{Eu:IDA} = 0.4:1$) and (b) more Al^{3+} ($\text{Al:COOH} = 0.02:1$) at 25 °C.

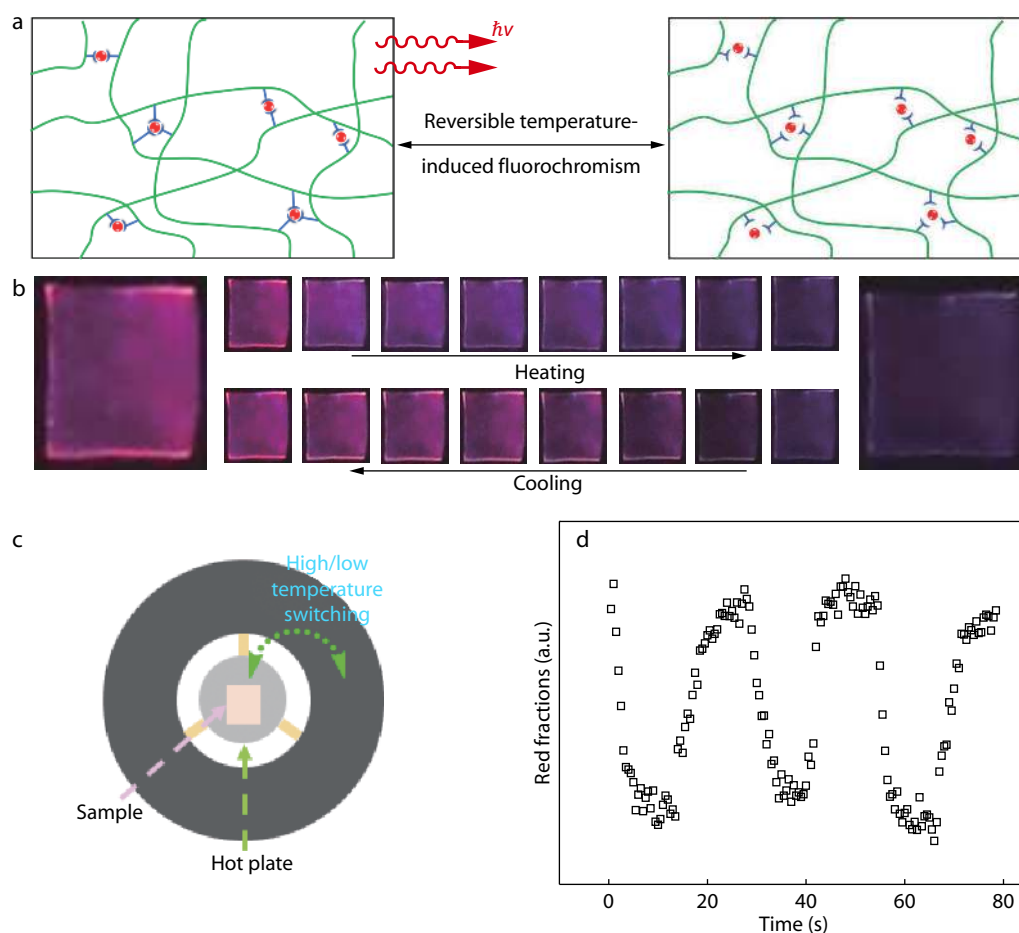


Fig. 9 (a) Scheme to show the reversible disruption/reformation of the Eu-IDA coordination in the polymer network under heating/cooling cycles. To give a more distinguishable illustration, only Eu-IDA cross-linking points in $\text{P}(\text{MEO}_2\text{MA-co-IDHPMA})$ network are shown. (b) Heating/cooling induced fluorescence quenching/recovery. The elastomer film had an Al -to- COOH ratio of 0.01:1 and an Eu -to- IDA ratio of 0.2:1. The fluorescence of elastomer film was quenched under 100 °C and recovered under room temperature. (c) Scheme illustrating the temperature induced fluorescence quenching on the hot plate (100 °C). As the fluorescence was quenched about 10 s, the sample was immediately transferred onto the cold surface by the side (room temperature, the dark region). (d) The red emission analysis of the IPN elastomer film during three heating/cooling cycles.

With the increasing content of Eu^{3+} ions (Eu-to-IDA ratio of 0.4:1), it is seen that the elastomer shown in Fig. 8(a) had a much higher healing efficiency of ~90 % than the result (~52 %) shown in Fig. 7(b), after the same healing time of 1 day at room temperature. However, incorporation of more Al^{3+} ions made the healing efficiency even decrease (Fig. 8b). After a healing time of 1 day, the healing efficiency was only ~6%. Increasing the healing time to 5 days only obtained a healing efficiency of ~54%. According to the above analysis, as the Al^{3+} content increased, ionic competition from Al^{3+} ions broke more Eu-IDA complexes and generated more Al-COOH cross-links, resulting in a stiffer elastomer. Then, the polymer chain and metal ion diffusion rates became slower, leading to worse self-healing efficiency. Since more Al-COOH cross-links led to worse self-healing efficiency, it is deduced that Eu-IDA complexes are more dynamic and dominate the self-healing of the elastomer.

The dynamic property of the Eu-IDA coordination is sensitive to temperature since high temperature can promote the random thermal diffusion of Eu^{3+} ions,^[56] which breaks the Eu-IDA coordination (see Fig. 9a). The breakage of Eu-IDA coordination at high temperature deactivates the “antenna effect”, thus we can see the double metal-ion IPN elastomer film emitted very weak luminance at 100 °C (Fig. 9b). As the elastomer film was cooled under room temperature, the fluorescence was almost fully recovered due to the reformation of Eu-IDA complexation. The heating/cooling cycle was repeated three times by using a hot plate (Fig. 9c). It is clear that the fluorescence quenching or recovery finished only in about 10 s and the fluorescence was almost fully recovered during each cycle (Fig. 9d and Video S1 in ESI).

CONCLUSIONS

To summarize, we demonstrated tough double metal-ion cross-linked IPN elastomers with high mechanical strength (comparable to covalently cross-linked elastomers), temperature-adaptable self-healing property and thermo-fluorochromic response. In the IPN elastomer, the Al^{3+} ion cross-linking of the P(MEO₂-MA-co-AA) mainly contributed to the mechanical strength of the IPN elastomer, while Eu-IDA coordination was mainly responsible for the elasticity of the IPN elastomer. Well-balanced Eu^{3+} and Al^{3+} contents (moderate Eu^{3+} and Al^{3+} contents) gave these supramolecular elastomers high toughness. The competition between Eu^{3+} and Al^{3+} ions made the mechanical behavior (including strength, stretchability and toughness) of the elastomer readily tunable by changing the content of metal ions.

Dynamic nature of the double metal-ion cross-linking of the IPN elastomer allowed the temperature-adaptable reversible formation and disruption of the polymer networks which made the elastomer self-healable. Healing at room temperature for 5 days led to a healing efficiency of ~90%. By increasing the healing temperature to 80 °C, a rather high healing efficiency of ~96% was reached after a healing time of only 10 min. The Eu-IDA coordination was more dynamic and dominated the self-healing of the elastomer. The disruption and reformation of Eu-IDA coordination under heating/cooling cycles led to reversible deactivation and activation of the IDA enabled intense Eu-center luminescence, which made the IPN elastomer show fast “ON/OFF” switchable red emis-

sion under heating/cooling cycles with fast response rate. We expect this IPN elastomer will pave a new way for preparing elastomers with high mechanical performance, particularly for the applications in wearable optoelectronics where self-healing and temperature response are required.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2517-z>.

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