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Multi-responsive self-healing metallo-supramolecular gels based on "click" ligand

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Metallo-supramolecular gels were prepared using a ligand macromolecule containing tridentate 2,6bis(1,2,3-trizol-4-yl)pyridine (BTP) ligand unit synthesized via CuAAC "click" chemistry in the main chain together with transition metal ions and/or lanthanide ions. The gelation and gel properties, e.g. swelling, emission, rheological properties, thermo- and chemo-responsive properties, can be tuned by

¹⁰ careful selection of metal ions and their combinations, solvent, concentration, and so on. Most interestingly, the gels exhibited repeatable autonomic healing ability. Moreover, the repeatable selfhealing ability of gels found practical application in repairing of metal coatings.

Introduction

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- ¹⁵ Self-healing polymeric materials are an increasingly active research area of particular scientific and commercial interests.¹ Inspired by biological systems, such materials can undergo either autonomic healing or induced healing triggered by specific mechanisms to repair damage, thereby restoring the strength and
- ²⁰ function. The first mending approach was based on the microencapsulation of reactive species,² which are usually able to polymerize or react with the matrix when released upon crack formation. This reaction at the damage site was irreversible and the supply of healing agents was depleted locally, therefore, the
- ²⁵ repair could not be repeated. Later, specially designed 3D microvascular networks were adopted to attain multiple healing cycles of a single crack.³ However, some limitations still remain. Some other approaches included solvent microencapsulation,⁴ nanoparticle segregation,⁵ coaxial electrospinning,⁶
 ³⁰ thermoset/thermoplastic blending,⁷ magnetic and resistance heating,⁸ UV crosslinking,⁹ and so on. Nevertheless, repetitive

healing was very rare in such systems. Dynamic covalent chemistry and non-covalent interactions,^{10,11}

due to their reversible nature, offer intriguing opportunities of ³⁵ constructing self-healing materials capable of repetitive repairing.

- Self-healing systems based on dynamic covalent chemistry developed so far involved the uses of Diels-Alder (DA) reactions,¹² [2+2] cycloaddition,¹³ acylhydrazone bonds,¹⁴ trithiocarbonate units,¹⁵ disulfide moiety¹⁶ and
- ⁴⁰ diarylbibenzofuranone.¹⁷ Their impressive repetitive healing characteristics were a consequence of the responsiveness of the functional groups to external stimuli such as temperature, chemicals and photo. Non-covalent interactions, including hydrogen bonding,¹⁸ hydrophobic association,¹⁹ π - π stacking,²⁰ ⁴⁵ ionic interactions²¹ and metal-ligand interactions,²² have also

been used to produce both bulk materials and gels with selfhealing properties. Compared to dynamic covalent chemistry, non-covalent interactions are generally more susceptible to external environment. In this sense, supramolecular systems are ⁵⁰ smarter than the dynamic covalent entities. Indeed, self-healing systems based on non-covalent interactions usually exhibited

extraordinary healing and multi-responsive characteristics. Among the various non-covalent interactions, of most interest to us are the metal-ligand interactions that are not only 55 thermodynamically stable but also kinetically labile. There are a vast range of accessible metal-ligand complexes.^{22,23} And their characteristics, e.g., motif structure, thermodynamic stability and dynamics, etc., can be easily tuned depending on the combination of metal ion and ligand used. Furthermore, utilization of metal-60 ligand interactions may afford materials that have attractive functional properties associated with the metal ion. In particular, Weng and coworkers have reported the construction of fast room temperature healable colloidal gels via the self-assembly of ditopic ligand, consisting of а 2,6-bis(1-65 methylbenzimidazolyl)pyridine (BIP) moiety attached to either end of an oligo-PEG core, in the presence of transition metal/lanthanide ions.^{22a-c} More recently, Rowan and coworkers reported an optically healable metallo-supramolecular elastomer based on a macromonomer comprising of a poly(ethylene-co-70 butylene) core with BIP at the two termini.22d

In recent years, copper(I) catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) has attracted considerable attention due to its "click" characteristics and has been widely used as a powerful synthetic strategy in almost all areas of modern ⁷⁵ chemistry ranging from macromolecular engineering to drug discovery.²⁴ Interestingly, the 1,2,3-triazoles produced by CuAAC "click" reaction have been found to be excellent novel ligands and their coordinating properties of have also been well studied.²⁵ Recently, a number of metal chelating systems based

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Scheme 1 Synthesis of ligand macromolecule 5 carrying BTP in the backbone using a polyurethane reaction.

on 1,2,3-triazoles and various 1,2,3-triazole containing ligands synthesized by the "click" chemistry have been reported.²⁵⁻²⁷ Due to their facile synthesis and easy functionalization, 1,2,3-triazoles and 1,2,3-triazole containing ligands have emerged as a novel class of ligands in building new supramolecular architectures. In particular, the tridentate "click" ligands 2,6-bis(1,2,3-triazol-4yl)pyridines (BTP), which are versatile alternatives to BIP and terpyridine (TPY) ligands, have shown great potential for the 20 development of new metallo-supramolecular functional materials. However, so far only one publication by Hecht and coworkers reported the preparation of metallo-supramolecular gels using rigid polymers bearing BTP subunits and their properties

- associated with the dynamic metal-ligand interactions, ²⁵ particularly self-healing behaviors, were not explored.^{26e} Herein, we show that ligand macromolecule bearing built-in tridentate "click" ligand 2,6-bis(1,2,3-triazol-4-yl)pyridine (BTP) moiety produced by "click" chemistry in the polymer backbone could be obtained through a facile synthetic pathway and report for the ³⁰ first time the construction of multi-responsive self-healing bulk
- metallo-supramolecular gels by using the ligand macromolecule together with transition metal ions and/or lanthanide ions.

Results and discussion

"Click" ligand and ligand macromolecule

- ³⁵ The tridentate BTP ligand has been reported to coordinate well to transitional metal ions such as Zn(II), Ni(II), Fe(II), Ru(II) and lanthanide metal ions such as Eu(III).^{25,26} Coordination typically led to stable 1:2 (metal:ligand) complexes in the case of transitional metal ions and 1:3 (metal:ligand) complexes in the
- ⁴⁰ case of lanthanide ions. Our UV-Vis titrations of **4** with $Zn(OTf)_2$ and Eu(OTf)₃ in acetonitrile also confirmed these findings (Figures S8-S11 in Supporting Information). Interestingly, it was possible to adjust the complex stability and complexation dynamics by not only chemicals but also the solvents, which can
- ⁴⁵ be demonstrated by UV-Vis titrations of chemicals and solvents with Zn:4 and Eu:4 complexes in acetonitrile (Figures S12-S39 in Supporting Information). There are many other transition metal and lanthanide ions available. Therefore, it is possible to offer a number of different types of metal:BTP interactions of various memory of the second s
- ⁵⁰ properties. Utilization of the easily accessible BTP ligands thus will create a new avenue to build metallo-supramolecular

functional materials. In particular, the tunable stability and dynamics can be utilized for the construction of multi-responsive supramolecular gels with repeatable self-healing ability.

- ⁵⁵ The BTP containing ligand macromolecule **5** was effectively synthesized via bis-isocyanate functionalized prepolymer formation followed by chain extension using bis-hydroxyl functionalized BTP ligand **4** as chain extender (Scheme 1). The incorporation of BTP moieties was proven by 1H NMR, GPC and
- ⁶⁰ FTIR (Figures S5-S7 in Supporting Information). The number averaged molecular weight, M_n, and polydispersity index, PDI, of the ligand macromolecule were typically about 30,000g/mol and 1.5, respectively, based on GPC measurements using THF as eluant and polystyrene standards. Since the poly(tetrahydrofuran),
- $_{65}$ PTHF (or poly(tetramethylene glycol), PTMG), linker used has a M_n of 2,000, the average number of BTP moieties incorporated in a single polymer backbone is estimated to be about 12.

Supramolecular gelation

⁷⁰ To probe the gelation of **5** in the presence of Zn(II) and/or Eu(III), solutions of Zn(OTf)₂ or Eu(OTf)₃ in various solvents were added into solutions of 5 in chloroform of two different concentrations. It was found that gelation was dependent on the concentration of 5 and the solvent used to dissolve the metal ions (Figure S40 in 75 Supporting Information). The first solution of 5 had a concentration of 100 mg/mL (100 mg 5 dissolved in 1 mL CHCl₃). In the cases of acetonitrile and THF, upon progressive addition of solutions of metal salts, gradual increase in viscosity was firstly observed, then at some points (about 50% and 35% of ⁸⁰ the stoichiometric amounts of required metal ions for Zn(II) and Eu(III), respectively) gels were formed. The difference in the amounts of Zn(II) and Eu(III) required to reach the gel points is consistent with their different binding characteristics, i.e. Zn(II) binds to BTP in a 1:2 ratio and Eu(III) binds in a 1:3 ratio. When 85 methanol was used as the solvent to dissolve the metal salts, however, no gels can be formed, despite that a slight increase in viscosity was observed. This difference in gelation should be due to the chelating ability of methanol which prevented the formation of stable or long-lived metal:BTP complexes. When a 90 second solution of 5 having a concentration of 25 mg/mL was used, however, no gelation was observed whichever solvent was used to prepare the solutions of metal salts. Since the second



Fig. 1 Breakdown (solid symbols, measured with a strain of 500% at 0.15 Hz) and reformation (open symbols, measured with a strain of 1% at 1 Hz) behaviours of a **0/100** gel (45 mg/mL) measured by a time sweep experiment.

solution of **5** had a concentration only 1/4 of the first one, it is assumed that at this dilute condition the tendency to form intrachain loops would be higher than at concentrated conditions. In addition, acetonitrile, THF and methanol are all coordinating

²⁰ by nature, their presence will influence the lifetimes of metalligand complexes. Nevertheless, upon condensation, gels could be eventually obtained for the systems in which acetonitrile and THF were used to prepare metal ion solutions. It is also noteworthy that after solvent evaporation the resulting materials ²⁵ from all the above mentioned different approaches could be reswollen by appropriate solvents to form gels. These observations confirmed the dynamic nature of the Zn:BTP and Eu:BTP complexes, which is critical to the multi-responsive and selfhealing properties.

Swelling properties of metallo-supramolecular gels

- The dynamic properties of the complexes were further investigated by swelling study of the gels. Three systems were studied containing different stoichiometric ratios of Zn(II) to ³⁵ Eu(III) ranging from 100% Zn(II) and no Eu(III) (**100/0**), to 50% Zn(II) and 50% Eu(III) (**50/50**), and to no Zn(II) and 100% Eu(III) (**0/100**). In each case, a piece of dried gel of 50 mg was used. Swelling study was performed by means of stepwise addition of chloroform and checking the stability of the gels by inverting the
- ⁴⁰ vials after equilibration at each step. The equilibration time, defined as the time required for the absorption of solvent and the following homogenization of the gels, was different for different systems. It took about 30 min for the **100/0** system and about 3 min for the **0/100** one, while the time required for the **50/50** one
- ⁴⁵ lied in between 3-30 min. The observation that longer equilibration times were required for the Zn(II) containing systems can be explained by the fact that Zn(II) forms stronger and less dynamic complex with BTP than does Eu(III). It should be pointed out that if different amounts of dried gels were used,
- ⁵⁰ the equilibration times might be different. Based on the inverting vial method, the critical concentrations for the gels to stay stable (no flowing) were about 20 mg/mL (20 mg dried gel swollen by 1)



Fig. 2 Storage modulus G' and loss modulus G" as a function of frequency for 100/0 (triangle symbols) and 0/100 (square symbols) gels 65 (45 mg/mL).

mL solvent), 16.7 mg/mL and 14.3 mg/mL for the three systems, respectively, with the 100/0 one having the highest critical concentration (the lowest swelling ratio) and the 0/100 one 70 having the lowest critical concentration (Figure S41 in Supporting Information). Further addition of chloroform eventually led to complete dissolution of the gels. Similarly, all gels could be recovered by drying and reswelling. It is generally believed that higher crosslinking leads to lower swelling ratio. 75 However, the Eu(III) containing systems, which are supposed to be more crosslinked, exhibited lower critical gel concentrations (higher swelling ratios). A plausible explanation for this observation is that at similar concentrations the systems containing higher ratios of Zn(II) were weaker in mechanical 80 strength and therefore tended to flow at higher critical concentrations, although crosslinked networks still remained at this point.

Rheological properties of metallo-supramolecular gels

85 To provide more insight into the mechanical properties of the gels, rheological characterization was carried out. In this case, toluene instead of chloroform and 1,1,2,2-tetrachloroethane was used to prepare the gels due to its higher boiling point and lower toxicity. After sample loading, a time sweep experiment under oscillatory 90 shear was first conducted to study the breakup and reformation of the gel network. Fig. 1 shows the storage modulus G' and loss modulus G" from the time sweep experiment of a 0/100 sample with a concentration of 45 mg/mL. The results show that when sheared with a strain of 500% at a frequency of 0.15 Hz, the gel is 95 effectively broken into a sol, as revealed by the fact that storage modulus G' is lower than loss modulus G". After the large strain shear is ceased, an almost instantaneous crossover of storage modulus and loss modulus (G' > G'') is observed, indicating the reconstitution of a gel network. Interestingly, the equilibrium 100 storage modulus value characteristic of the fully developed is also almost reached instantaneously. Replacing Eu(III) with Zn(II) or changing gel concentration gave similar recovery behaviors (Figure S42, Figure S44 and Figure S45 in Supporting Information). This recovery (healing) is much more effective than

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Fig. 3 Storage modulus G' and loss modulus G" as a function of strain amplitude for 100/0 (star symbols) and 0/100 (diamond symbols) gels (45 mg/mL).

¹⁵ that of the colloidal metallo-supramolecular gels based on BIP ligands reported by Weng and coworkers.^{22a-c} Such an extraordinary recovery is consistent with the thermodynamically stable but kinetically labile nature of the metal:BTP complexation and is of great importance to applications where a fast response is ²⁰ required.

In addition, measurements of storage modulus G' and loss modulus G" were performed as a function of the oscillatory frequency. The results of the **100/0** and **0/100** samples with a concentration of 45 mg/mL are depicted in Fig. 2. It is seen that ²⁵ G' of the **100/0** sample is dependent on the frequency and is slightly larger than G" at low frequencies, whereas G' of the **0/100** sample is almost constant and about one order of magnitude higher than G" over the entire frequency range.

- Similar behaviors were observed for the two systems at a ³⁰ concentration of 60 mg/mL (Figure S43 and Figure S46 in Supporting Information). These differences in rheological behaviors from frequency sweeps imply that at similar conditions Zn(II) containing gels are less elastic and weaker than the gels containing only Eu(III), consistent with the swelling results.
- ³⁵ Finally, the viscoelasticity of the gels were investigated by strain sweep tests. Fig. 3 shows the moduli as a function of strain amplitude of the **100/0** and **0/100** samples with a concentration of 45 mg/mL. Both samples show large linear viscoelastic regions, where logG' and logG" remain essentially constant up to a strain
- ⁴⁰ of about 30%, beyond which logG' starts to decrease abruptly. The crossovers of G' and G", an indicative of the onset of viscous flow, both occur at a strain of around 100%. These large linear regimes and crossover strains imply that the gels are stretchy and can withstand relatively large deformation. This is very different ⁴⁵ from the behaviors of the colloidal metallo-supramolecular gels
- previously reported by Weng and coworkers.^{22a-c}

Thermo- and chemo-responsive properties of metallosupramolecular gels

50 Having demonstrated that the emission of the gels can be manipulated, the gel-sol transition and optical response upon exposure to heating were studied. In this case, only three systems,



Fig. 4 Picture of gels (20 mg/mL in chloroform) with varying amounts of Zn(II) and Eu(III) (from left to right Zn/Eu: 100/0, 75/25, 50/50, 25/75, 65 0/100) under 365 nm UV light demonstrating the effect of metal combination on the photoluminescence colour.



Fig. 5 Pictures of **100/0** gel (a) at RT and (b) after being heated at 140 °C, ss **25/75** gel (c) at RT and (d) after being heated at 120 °C, **0/100** gel (e) at RT and (f) after being heated at 110 °C under 365 nm UV light. Gels were swollen with chloroform with a concentration of 50 mg/mL.

i.e. 100% Zn(II) (100/0), 25% Zn(II) and 75% Eu(III) (25/75), ⁹⁰ and 100% Eu(III) (0/100), were selected. Upon heating, the 100/0 gel turned into a free flowing sol until at a temperature up to as high as about 140 °C. However, the gel-sol transition temperatures were much lower, *ca.* 120 °C and 110 °C for the gels containing 75% and 100% Eu(III), respectively. This is ⁹⁵ consistent with the weaker complexation of Eu(III) with BTP. While little change in the emission of the gel containing only Zn(II) could be observed when heated, the emissions from



Fig. 6 Photographs of a gel (100 mg/mL in 1,1,2,2-tetra-chloroethane) containing no Zn(II) and 100% Eu(III) (0/100) showing the self-healing behaviour and properties of the healed gel. (a) four blocks of cut gels, two 25 red ones were dyed with rhodamine B; (b) jointed blocks by simply joining together the fresh surfaces; (c) stable self-supporting bar formed after healing for 6 h at RT without any external intervention; (d) squeezing, (e) bending and (f) stretching of the healed gel bar. (g) Simplified schematic illustration of the self-healing mechanism: I, cutting 30 caused the break of the polymer linker between two BTP ligands; II, completely separated blocks after cutting; III, healing as a consequence of exchange of ligand macromolecules between two adjacent blocks.

Eu:BTP in the Eu(III) containing gels were found readily 35 quenched by heating (Fig. 5). As the temperature was returned to ambient, both gels were reformed and the emission from the Eu:BTP could be regained. In addition, the gel-sol transition and emission quenching-recovery could be repeated many times. Therefore, the gels, especially the Eu(III) containing gels, may 40 find potential uses as temperature sensor with reversible characteristics.

To study the response to chemical stimuli, a spectrum of chemicals having different polarity, pH and chelating properties were tested. It was found that most of the chelating chemicals

⁴⁵ selected were able to destroy the gels and at the same time caused changes in photoluminescence (Figures S53-S63 and Table S1 in Supporting Information). Whereas bipyridine readily caused the deconstruction of the gel containing only Zn(II), it had no effecton the gel containing only Eu(III). In addition, both gels



Page 6 of 8

Journal of Materials Chemistry Accepted Manuscript



Fig. 7 Optical microscopic images (magnification 150X) showing a cut (a) and its healing (b) of a coating prepared with a gel containing no Zn(II) and 70% Eu(III) (0/70) on copper surface.

showed sensitive response to the nerve gas agent mimic triethyl phosphate, however, neither of them could be destroyed by triphenylphosphine. It is thus anticipated that careful selection of metal ions, including other metal ions not shown here, and their 65 combinations would allow construction of gel systems with tunable sensory response to chemicals.

Self-healing properties of metallo-supramolecular gels

The observations illustrated above clearly show that the Zn:BTP 70 and Eu:BTP complexes are thermodynamically stable and kinetically labile, suggesting the potential for self-healing of the gels. Thus, to test this hypothesis, we first prepared a gel containing no Zn(II) and 100% Eu(III) (0/100) swollen by 1,1,2,2-tetrachloroethane. 1,1,2,2-tetrachloroethane was selected 75 due to its high boiling point and good ability to form stable gels in this study. Interestingly, the gel exhibited impressive selfhealing properties. As depicted in Fig. 6, four deliberately cut blocks of gels, two of which were dyed with a small amount of rhodamine B, could form a stable self-supporting bar by simply ⁸⁰ joining together the fresh surfaces and keeping contact for about 6 h at room temperature without any external intervention. Although the healed scars were still visible, the joints between the different blocks in the repaired were strong enough to sustain squeezing, bending and stretching. Surprisingly, the repaired gel 85 might not break at the scar location upon stretching (Movie in Supporting Information). When the healed gel was cut at the joints into separated blocks and brought into contact together as before, the self-healing process occurred once again. This cutting and healing cycle can be repeated several times. Moreover, if the 90 blocks were not cut to obtain fresh surfaces, the fusion was also possible and took similar time. When a portion or all of Eu(III) was replaced with Zn(II), the gels healed equally well, except that higher gel concentrations were generally required to obtain mechanically stable blocks and bars (Figure S65 and Figure S66 95 in Supporting Information).

Self-healing properties of bulk coating

Self healing of the metallo-supramolecular gels may find many potential practical uses. One interesting application is the healing 100 of metal coatings made of 5 and various types of metal ions, which can be applied to a number of different metal surfaces. While detailed studies are in progress, preliminary results showed that supramolecular **Eu:5** crosslinking system formed strong and tough solid coating layer on the surface of copper and cuts on the coating could be easily healed by applying a small amount of suitable solvent, e.g. toluene, onto the damage area, followed by

- ⁵ subsequent drying (Fig. 7). Solvent enabled healing has been adopted to the healing of hydrogel thin films^{21b} and solid coatings^{21c} assembled via LBL technique on substrates base on electrostatic interactions. However, to the best of our knowledge, this is the first time self-healing of a metallo-supramolecularly
- ¹⁰ crosslinked coating enabled by solvent treatment is demonstrated. Due to excellent healing properties and the fact that trazole derivative ligands can effectively adhere to metal surfaces,²⁸ we are expecting to develop a series of all new supramolecular crosslinking coatings with self-healing abilities.

Conclusion

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In summary, we have demonstrated that metallo-supramolecular gels were prepared using a ligand macromolecule containing tridentate 2,6-bis(1,2,3-trizol-4-yl)pyridine (BTP) ligand moiety ²⁰ synthesized by CuAAC "click" chemistry in the backbone together with transition metal ions and/or lanthanide ions. Due to the supramolecular and dynamic nature of the metal-BTP complexes, the gels exhibited multi-responsive properties and repeatable autonomic healing ability. The gelation and the

- ²⁵ properties can be tuned by careful selection of metal ions and their combinations, solvent, concentration, and so on. The multiresponsive properties make them attractive for developing sensors and the repeatable self-healing ability may find many practical applications including but are not limited to reshaping
- ³⁰ and regeneration of gels and repairing of metal coatings. To the best of our knowledge, this is the first report showing the preparation of multi-responsive gels using macromolecule with built-in "click" ligand unit in the backbone and their self-healing properties originating from the dynamic nature the metal-ligand
- ³⁵ interactions. The use of macromolecule carrying multiple ligand moieties in the backbone can be advantageous over their counterparts carrying ligand units only at the chain ends. Multiresponsive materials, self-healing polymeric materials and "click" chemistry are increasingly active research areas of particular
- ⁴⁰ scientific and commercial interests. The discovery that tridentate "click" BIP ligand was effective in building multi-responsive and self-healing materials opens up new possibilities of designing new applied functional materials via a combination of "click" chemistry and supramolecular chemistry. Current efforts are
- ⁴⁵ being made to evaluate the influence of polymerization procedure and the design of ligand molecules on the properties of the gels and solid films. In addition, studies are ongoing to develop the applications of the multi-responsive and self-healing properties.

50 Experimental

General methods

All reactions requiring inert gas were performed under N₂ atmosphere. Column chromatography was carried out with 200-400 mesh silica gel using the eluants specified. NMR spectra 55 were recorded on a 400 MHz Brucker Avance II 400 spectrometer at 25 °C using residual protonated solvent signals as internal standard. Gel permeation chromatography (GPC) data were calibrated against polystyrene standards and collected on a Waters 1515 equipped with a Waters 2414 Refractive Index Detector using THF as eluant. FTIR spectra were collected on a Nicolet Avatar 330 (Thermo Electron Corporation, USA). UV-vis spectra were obtained on Thermo Scientific Evolution 300. Photoluminescence spectra were acquired on Hitachi F7000 fluorescence spectrometer. Rheological measurements were

65 conducted on an ARES G2. Optical microscopy was performed using VHX-600 digital microscope (Keyence, UK) in refractive mode.

Gelation study and preparation of gels

 $_{70}$ To study the gelation behaviour, a solution of Zn(OTf)₂ (0.05 mol/L) or Eu(OTf)₃ (0.015 mol/L) in CH₃CN or THF or CH₃OH was added dropwise into a stirred solution of 5 (100 mg or 25 mg) in CHCl3 (1 mL). The total amount of metal added was adjusted to provide for metal:BTP equivalent of 1.0 (accounting for 1:2 75 and 1:3 binding, respectively). During the addition of metal salt, the viscosity change of the solution and gel formation was monitored by visual observation. The resulting gel or sol was allowed to dry under ambient conditions and further dried in vacuo to produce solid supramolecular polymers Zn:5 and Eu:5, 80 which were kept for further uses. For systems containing both Zn(II) and Eu(III), i.e. Zn/Eu:5, prescribed amounts of metal solutions in CH₃CN (usually 0.05 mol/L for Zn(OTf)₂ and 0.015 mol/L Eu(OTf)₃) were added into solutions of 5 in CHCl₃ (usually 100 mg/mL) to form gels first. The gels were then dried 85 under ambient conditions and further dried in vacuo to produce solid supramolecular polymers, which were kept for further uses. In subsequent studies, metallo-supramolecular gels were produced by reswelling dry supramoluecular polymers with prescribed amounts of specific solvent.

Rheological tests

Rheological measurements were performed using parallel plate geometry. The plate used has a diameter of 25 mm and the gap is set at 500 µm for all measurements. All measurements were 95 conducted at a temperature of 25±0.5 °C, and the samples were covered with a thin layer of ethylene glycol to prevent evaporation of the solvent or absorption of atmospheric water. Gels used for theological measurements were swollen with toluene instead of chloroform, due to the higher boiling point of 100 toluene. And the gels were made in two concentrations, 45 mg/mL and 60 mg/mL. After sample loading and gap setting, the sample was first presheared with a large strain amplitude of 500% at 0.15 Hz, then allowed to equilibrate for 20 min to complete the gelation process, during which the sample was monitored by 105 oscillatory shear of small strain amplitude (1 %, in the linear viscoelastic regime) at 1 Hz, in time steps of 30 s. After equilibration, a frequency sweep was carried out to measure G' and G" as a function of deformation frequency from 0.01 Hz to 100 Hz at a strain amplitude of 1%. This frequency sweep was then followed by a strain sweep in a strain range from 0.1-1000% at 1 Hz.

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Self-healing of gels

To study the self-healing of the gels, gels swollen by 1,1,2,2tetrachloroethane were used. In this case, the gels had a ⁵ concentration of 100 mg/mL. In a typical experiment, a piece of gel was cut into four blocks, two of which were then dyed with a small amount of rhodamine B. The four blocks then were joined together by placing the fresh surfaces into close contact and kept them in place without any external intervention at RT for 6 h

¹⁰ under a saturated 1,1,2,2-tetrachloroethane atmosphere. The healed sample was then subjected to bending, squeezing and stretching to check the stability of the healed joints.

Self-healing of coatings

¹⁵ Typically, a coating on copper surface was damaged by cutting the coating to a depth of about 30-50% using a razor blade. The cut was imaged with an optical microscope. Then 50 μ L toluene was applied to the damaged area every 1 h for continuous 5 h, and finally allowed to dry completely and visualized using optical ²⁰ microscopy.

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