# Self-healing hydrogels by metal complexation of 2,6-bis(1,2,3-triazol-4yl)pyridine functionalized tetra-arm star poly(ethylene glycol)

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## Abstract

The fabrication of btp-based gels has been mainly focusing on organogels. Only recently, we reported the synthesis and metallo-supramolecular hydrogel formation of linear poly(ethylene glycol) with multiple btp units in the main chain. In this manuscript, we report metallo-supramolecular hydrogels that were constructed using 4-arm star PEG modified with btp end-groups upon complexation with transition metal ions. This btp-functionalized star-PEG precursor is more easily accessible and more defined than the previously reported linear system while also yielding stronger hydrogels. The gelation was selectively induced by $Ni^{2+}$ ions and strongly depended on the metal-ligand ratio and polymer concentration. The successful formation of organogels could be induced selectively by $Ni^{2+}$ or $Fe^{2+}$ ion complexation in acetonitrile, which lead to the strongest complexes. The inability to from hydrogels with $Fe^{2+}$ ions was ascribed to the partial oxidation of $Fe^{2+}$ to $Fe^{3+}$ ions in aqueous solution. Furthermore, the optimal conditions for achieving self-healing capabilities were also determined (i.e., 4 wt% polymer concentration and

btp:$Ni^{2+}$ molar ratio of 2:1) using rheology. The high strain resistance and fast self-healing characteristics make these specific $Ni^{2+}$ metallo-supramolecular hydrogels a promising platform for materials design with the potential application in supramolecular chemistry, coordination chemistry, and catalysis.

## Introduction

Self-healing materials have received significant attention due to their ability to heal mechanical damage such as cracks and scratches.[1-3] When the healing mechanism is related to the molecular dynamics of the polymer itself instead of external manipulation, autonomous self-healing materials can be prepared.[4] Autonomous self-healing polymers can be constructed using dynamic interactions, which can be reversible covalent bonds (e.g., disulfide bonds,[5, 6] Diels-Alder reactions,[7] imine,[8] and acylhydrazone[9]) or physical interactions such as ionic interaction,[10] host-guest interaction,[11-13] hydrogen bonding[14], and metal-ligand coordination.[15, 16] Metal coordination is an appealing synthetic method for intrinsic self-healing materials as the reformation of such bonds do not require external stimuli such as heating, pressure or harsh reaction conditions.[17] In general, the coordination of metal ions to a molecule possessing suitable coordinating sites could trigger supramolecular self-assembly and lead to physical gelation.[18] Moreover, the combination of relatively high thermodynamic stability and kinetic lability offered by the metal coordination bonds represents a promising choice for the utilization in polymeric gels.[19] Metallo-supramolecular hydrogels are particularly attractive since their properties can be easily tailored by exploiting the cooperative effects of metal-ligand and solute-solvent interactions.[20] and have been successfully used in different areas such as materials chemistry, catalysis, and molecular recognition.[21]

As a ligand unit, 1,2,3-triazole and its derivatives are well known to coordinate transition metal ions effectively.[22] Especially, considerable progress has been made in the synthesis of 2,6-bis(1,2,3-triazol-4yl)pyridine (btp) derivatives on account of its versatile synthesis and modification with different functionalities via copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC).[23-26] The stability of transition metal complexes with btp units is influenced by several factors including the choice of metal ions, temperature, solvent and pH.[27]

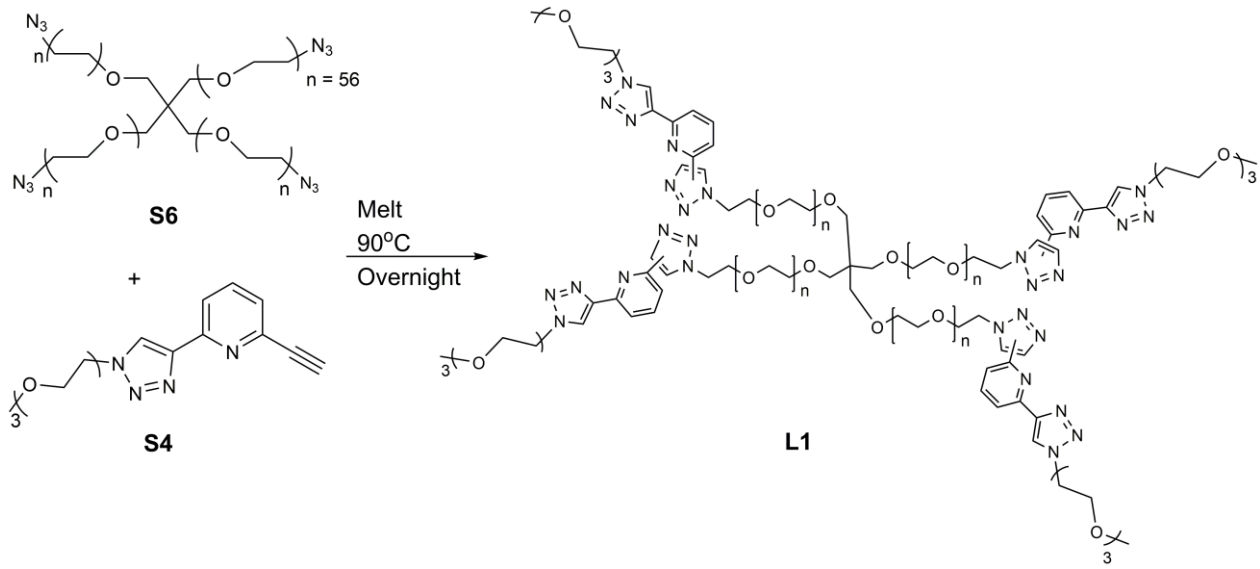
Several articles and reviews concerning the btp chemistry and its complexes with a range of transition metal ions have been reported in the past decade.[28-31] However, the synthesis of btp based gels has been mainly focusing on organogels, and only few examples have been devoted to hydrogels. Reports on btp-based hydrogels were mainly focused on small molecules. For example, Gunnlaugsson reported a lanthanide luminescent supramolecular hydrogel from tri-carboxylic acid substituted btp ligand. The tri-carboxylic acid substituted btp ligand first formed a hydrogel via the H-bonding between the carboxylic acid groups, while the addition of $Eu^{3+}$ ions solution in methanol conferred healable and luminescent properties.[29] Moreover, the analogous terpyridyl ligand has been successfully used in the construction of metallo-hydrogels, starting from macromolecular ligands,[32-35] while the only report dealing with btp-based polymer hydrogels was recently reported by us based on rather ill-defined linear poly(ethylene glycol) (PEG) with multiple btp-units in the main chain, obtained through CuAAC polyaddition.[23]

In the present study, we report the synthesis of a tetra-arm star-PEG functionalized with btp moieties at each chain-end, using the azide-alkyne Huisgen cycloaddition reaction and its subsequent use in the construction of metallo-supramolecular hydrogels. The gelation was specifically induced by $Ni^{2+}$, while the addition of other divalent metal ions (e.g., $Cu^{2+}$, $Zn^{2+}$, and $Fe^{2+}$) resulted only in an increased viscosity of the solution. Moreover, the influence of polymer concentration and $Ni^{2+}$: btp ratio on the mechanical properties of the metallo-hydrogel was also

investigated. To further verify the gelation mechanism, organogels were also prepared with various divalent metal ions in acetonitrile and their mechanical properties were studied as well. The self-healing properties of both the hydrogels and organogels were evaluated by cyclic strain time sweep rheology evidencing a very fast self-healing time and good stability during multiple damage cycles.

**Results and discussion**

Our studies focused on preparing supramolecular polymeric hydrogels exhibiting close to regular network topologies using metal-ligand coordination. To achieve this goal, a tetra-arm PEG functionalized with btp ligand at each end (**L1**) was synthesized following the concept of Seiffert et al, who reported a metallo-hydrogel based on terpyridine end-group functionalized tetra-arm PEG with transition metal ions.[32] Rather than using CuAAC, the btp moieties were attached to the chain ends using a thermally induced azide–alkyne Huisgen cycloaddition method, i.e. without copper(I) catalyst, which is both simple as well as quantitative. More specifically, we first synthesized the tetra-arm PEG tetraazide (**S6**) and 2-ethynyl-6-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2H-1,2,3-triazol-4-yl)pyridine (**S4**). The tetra-arm PEG tetraazide was obtained starting from commercially available tetra-arm PEG-OH ($M_n$ = 10 kDa, Đ = 1.1) via mesylation and subsequent substitution with sodium azide, as depicted in Scheme S1. The compound **S4** was synthesized using the procedure reported in our previous work[26] and also shown in Scheme S1. Subsequent attachment of the compound **S4** to the tetra-arm PEG tetraazide was achieved via the Huisgen cycloaddition reaction performed at 90$^{o}$C in the melt without solvents, as shown in Scheme 1.




Scheme 1. Schematic representation of the synthesis route of L1 via thermal azide-alkyne Huisgen cycloaddition reaction between S6 and S4.

The unimodal distribution in SEC of **L1** cleanly shifted to a higher molar mass ($M_n$ = 21.0 kDa, Đ = 1.14) (Figure S1) compared to that of tetra-arm PEG tetraazide (**S6**) ($M_n$ = 18.0 kDa, Đ = 1.09), indicating that no chain cross-linking or extension has occurred. The $^1$H NMR spectrum of **L1** (Figure 1a), showed the characteristic signals corresponding to the protons of the pyridyl rings in the aromatic region of 7.94-8.01 ppm, while the peak at 8.60 ppm can be attributed to the protons of the triazole rings. Additionally, the two triplet signals at 3.89 and 4.63 ppm can be assigned to the methylene protons (triazole-*CH*$_2$-CH$_2$-O-PEG and triazole-CH$_2$-*CH*$_2$-O-TEG) between the triazole ring and the PEG, as well as the triazole and the triethylene glycol (TEG) confirming the proposed structure. Moreover, using the $^1$H NMR spectroscopy, we could also calculate the number-average molecular weight of **L1**. The integral region of the protons at ca. 3.41-3.59 ppm corresponding to the PEG backbone offered an estimate of the number of repeating units when compared with the integral of the aromatic protons at 8.60 ppm ascribed to the triazole ring. The

number-average molecular weight of **L1** was calculated to be around 12 kDa using the following equation:

$$M_n = \frac{\int(3.58-3.72)}{4} \times 44.05 + 1432 \qquad (1)$$

The $M_n$ obtained by $^1$H NMR spectroscopy corresponds quite well to the theoretical Mn (ca. 11.5 kDa based on the commercially available tetra arm PEG-10 kDa), while the Mn obtained from the SEC deviates owing to the relative calculation against PMMA standards. The successful reaction was evidence also by the disappearance of the peak at 2100 cm$^{-1}$ corresponding to the azide units in the FT-IR spectrum (Figure 1b).

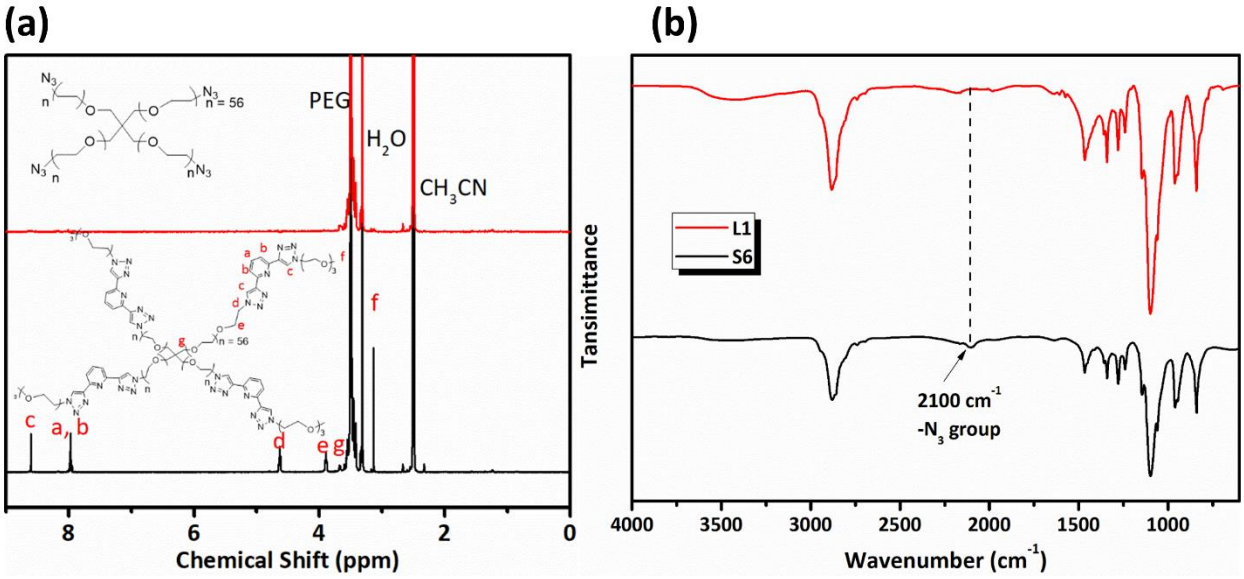



Figure 1. (a) $^1$H NMR spectrum of **L1** macroligand in $CD_3CN$; (b) FT-IR spectra of **L1** macroligand and **S6**.

Previous reports have shown that the tridentate btp ligand can coordinate well with transition metal ions such as $Fe^{2+}$, $Ni^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ ions.[36] Coordination typically results in stable 1:2 (metal:

ligand) complexes. Based on these previous observations, several metal ions were initially tested for hydrogel formation using a polymer solution having a concentration of 10 wt%. The hydrogelation was found to be selectively triggered by the addition of $Ni^{2+}$, as was previously also observed for the macroligand containing the btp units in the polymer backbone,[25] while addition of $Zn^{2+}$, $Fe^{2+}$, and $Cu^{2+}$ ions only resulted in an increase in the viscosity of the solution. Moreover, the color of the solution changed to green and brown upon addition of $Cu^{2+}$ and $Fe^{2+}$ ions, respectively, indicating the formation of (intramolecular) complexes (Figure 2a). Although the mechanism of this specific $Ni^{2+}$ ion triggered gelation is not perfected understood, it is assumed that the $Ni^{2+}$ ions may afford more stable bis-complexes in combination with the btp ligand than the other divalent metal ions, thereby offering efficient junctions towards the formation of supramolecular networks.

Nevertheless, it has been well reported that $Fe^{2+}$ ions should also form a very stable bis-complex with btp because of the high binding constants. Thus, it is hypothesized that the $Fe^{2+}$ ions might be easily oxidized to $Fe^{3+}$ ions in aqueous solution, resulting in insufficient crosslinking points and subsequent failure of gelation. If this hypothesis was correct, switching the aqueous solution to an organic solvent (e.g., acetonitrile) at the same polymer concentration and metal to ligand ratio would lead to formation of an organogel. To verify this aspect, L1 was dissolved in acetonitrile with a polymer concentration of 10 wt% followed by addition of various transition metal ions ($Cu^{2+}$, $Zn^{2+}$, $Fe^{2+}$ and $Ni^{2+}$ ions) and a metal to btp ratio of 1:2. The results are shown in Figure 2b. Addition of $Cu^{2+}$ or $Zn^{2+}$ ions only induced the change of the color while no hydrogel was observed due to the formation of kinetically labile btp complexes, which is in accordance with the previous result using aqueous solution. On contrast, organogels were successfully obtained with $Fe^{2+}$ or $Ni^{2+}$ ions, as expected based on the high association constants of their btp complexes. The successful

organogelation formation with $Fe^{2+}$-btp complexes in acetonitrile further indicated that oxidation of $Fe^{2+}$ to $Fe^{3+}$ ions in water could indeed suppress hydrogel formation.

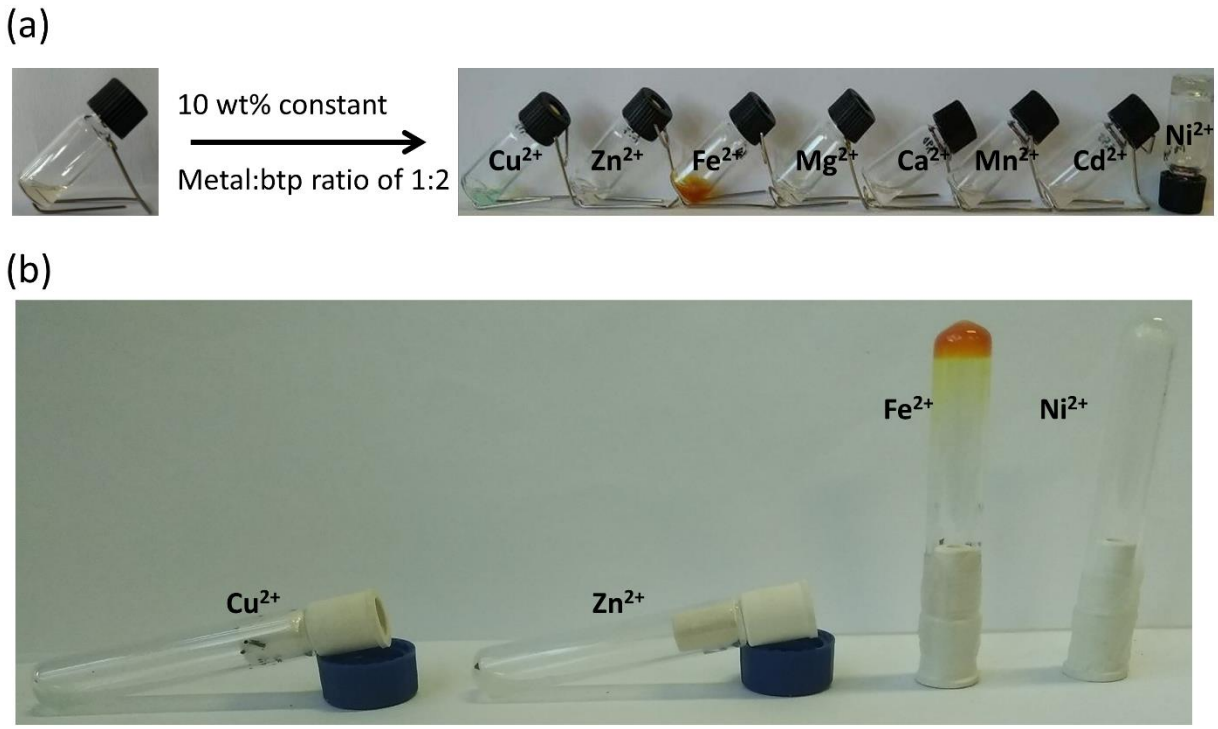



Figure 2. (a) Photographs of 10 wt% of **L1** in the presence of 0.5 equivalents (compared to btp) to metal ions in water, from left to right: chloride salts of $Cu^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Mn^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ and (b) in acetonitrile.

Subsequently, the influence of the metal to ligand ratio and polymer concentration on the hydro-gelation process and mechanical stability of the resulting metallo-supramolecular hydrogels was investigated. To assess the effect of the amount of $NiCl_2$ on the formation of the metallo-supramolecular hydrogels, various $Ni^{2+}$:btp ratios (e.g., 0.125:1, 0.25:1, 0.5:1, 1:1 and 2:1) were used in the system. Figure 3a illustrates the 10 wt% solutions of **L1** in the presence of various $Ni^{2+}$ to btp ratios. Preliminary hydro-gelation experiments were performed by the inverted test tube

method (Figure 3a). Stable hydrogels were obtained when 0.5 equivalents of $Ni^{2+}$ were added, in accordance with the 1:2 $Ni^{2+}$:btp binding ratio. The gelation was hampered at lower $Ni^{2+}$ content due to the insufficient number of cross-links while increasing the $Ni^{2+}$:btp ratio to 1:1 did not affect the hydrogel formation. However, when higher equivalents of $Ni^{2+}$ were used, the gelation was prevented because of the prevalence of the formation of mono-complexes. Rheology investigations provided more insights into the stability of the metallo-supramolecular hydrogels. As expected, the hydrogel formed in the presence of 1 equivalent of $Ni^{2+}$ has a lower G' value compared to the hydrogel obtained with 0.5 eq, due to the formation of more mono-complexes, thus leading to a lower effective cross-linking density (Figure 3b). Next, frequency-dependent oscillatory rheology was used to probe the dynamic mechanical properties of metallo-supramolecular hydrogels under shear. As shown in Figure 3c, at the lowest frequency area, G' is lower than G'', with moduli crossing at 0.04 rad $s^{-1}$ for 1:1 $Ni^{2+}$:btp sample, suggesting a finite lifetime of the crosslinks in the $Ni^{2+}$ based hydrogels in the order of tens of seconds, as a result of dynamic metal-ligand exchange. In contrast, the crossover for the 0.5:1 $Ni^{2+}$:btp hydrogel is higher than that of the 1:1 $Ni^{2+}$:btp hydrogel (0.02 rad $s^{-1}$), which can ascribed to a longer lifetime of the crosslinks, which is consistent with a slower exchange of $Ni^{2+}$:btp bonds upon formation of a more stable bis-complex. Moreover, the results are in agreement with the theory that the btp units typically form stable 1:2 (metal: ligand) complexes. Thereby, the dynamic nature of the crosslinks of $Ni^{2+}$ induced hydrogels can be captured by frequency-dependent oscillatory rheology, which is consistent with the previous work of Sakai et al.[37] Additionally, the viscoelasticity of the obtained hydrogels was investigated by a strain sweep test. Figure 3d illustrates the moduli as a function of applied strain amplitude. Both hydrogel samples showed linear viscoelastic regions, where G' and G'' remain constant up to 10% a strain, after which *G'* begins to decrease. The cross-over point of G' and G'' was found at 153% and 64% strain when 1 eq. and 0.5 eq. of $Ni^{2+}$ ions vs btp were used, respectively, thus

suggesting the formation of a more cross-linked network when a $Ni^{2+}$:btp ratio of 1:2 is used. It may be speculated that the excess of $Ni^{2+}$ ions at a 1:1 $Ni^{2+}$:btp ratio results in a lower coordination number of $Ni^{2+}$ and reduce the stiffness of the crosslinked network.

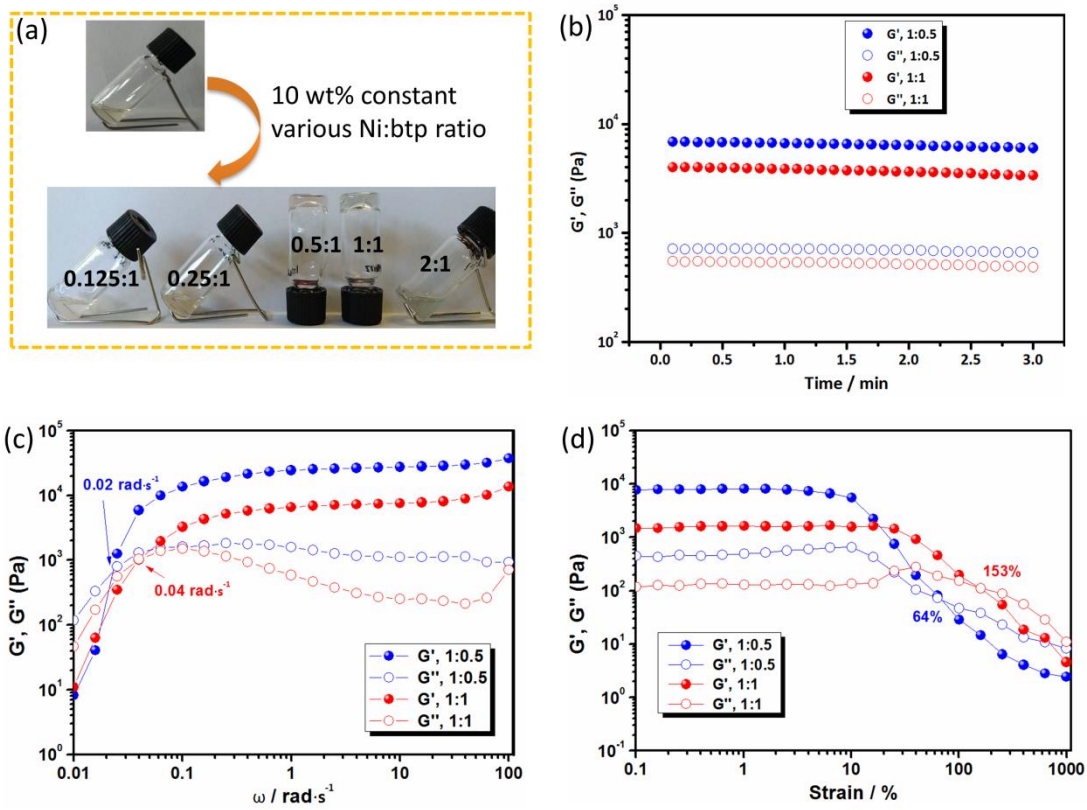



Figure 3. (a): Photographs of the metallo-supramolecular hydrogels at 10 wt% L1 concentration with various amounts of $Ni^{2+}$ (from left to right $Ni^{2+}$:btp 0.125:1, 0.25:1, 0.5:1, 1:1, and 2:1); (b) time sweep experiments of the metallo-supramolecular hydrogels using a fixed strain of 1% and a frequency of 1 rad/s at 25 °C for 3 min; (c) frequency sweep measurements performed using a fixed 1% strain; and (d) strain sweep measurements performed using a fixed 1 rad/s frequency.

Finally, the concentration of the polymer, was varied between 1 and 10 wt%, while keeping a constant $Ni^{2+}$:btp ratio of 1:2 to investigate the influence of this factor on the mechanical properties of the formed metallo-supramoleular hydrogels. Preliminary tests were performed using the inverted test tube method. At ambient temperature, stable hydrogels were obtained starting from 4 wt% polymer concentration (Figure 4a). While metallo-supramolecular hydrogels are obtained in a constant $Ni^{2+}$:btp ratio of 1:2, increasoffing the polymer concentration leads to a significant increase in the slow relaxation time revealing the dynamic exchange of complexes. As shown in Figure 4b, the modulus crossover marking the terminal relaxation of the hydrogel is indeed gradually shifted by two orders of magnitude to higher frequency as the polymer concentration is decreased from 10 wt% to 4 wt%, as expected.[35]. The plateau G' is reached at high frequencies indicating that the $Ni^{2+}$-btp complex yields a physically crosslinked network that displays a viscous fluid characteristic at low frequencies and an elastic solid behavior at high frequencies. Those rheological behaviors are in good agreement with other metallo-supramolecular hydrogels based on metal coordination.[38] In spite of the dynamic nature, the sample with 10 wt% polymer has high stiffness with outstanding elasticity as evidenced by the plateau value of G' = 7 kPa, suggesting that the Ni-btp complex in this star-shaped back bone can give access to relatively strong hydrogels, especially compared to our previously reported system based on linear PEG with multiple btp-ligands in the main chain. At lower polymer concentration the entanglements between polymer chains are suppressed, thus favoring the intramolecular crosslinking reaction and loop formation resulting in ineffective connections between the chains. However, increasing the polymer concentration to 10 wt%, leads to the formation of homogeneous network structures. The results are in accordance to Sakai observations, suggesting that 10 wt% concentration is in the region of the overlap concentration.[39-42] The variation of the moduli with frequency suggests that part of the btp units do not form transient interactions with metal ions and have time to relax. Thus, at a

polymer concentration lower than 10 wt%, a large fraction of star arms is free and does not participate in the formation of the supramolecular network.

The strain sweep experiments revealed that the mechanical resistance of the hydrogels could be easily controlled between 20 and 9000 Pa by adjusting the concentration of the polymer solution. Metallo-supramolecular hydrogels with higher elasticity (i.e., longer viscoelastic linear regime and higher cross-over point) are obtained at lower polymer concentration, but with lower mechanical resistance (i.e., lower G' value) (Figure 4c).

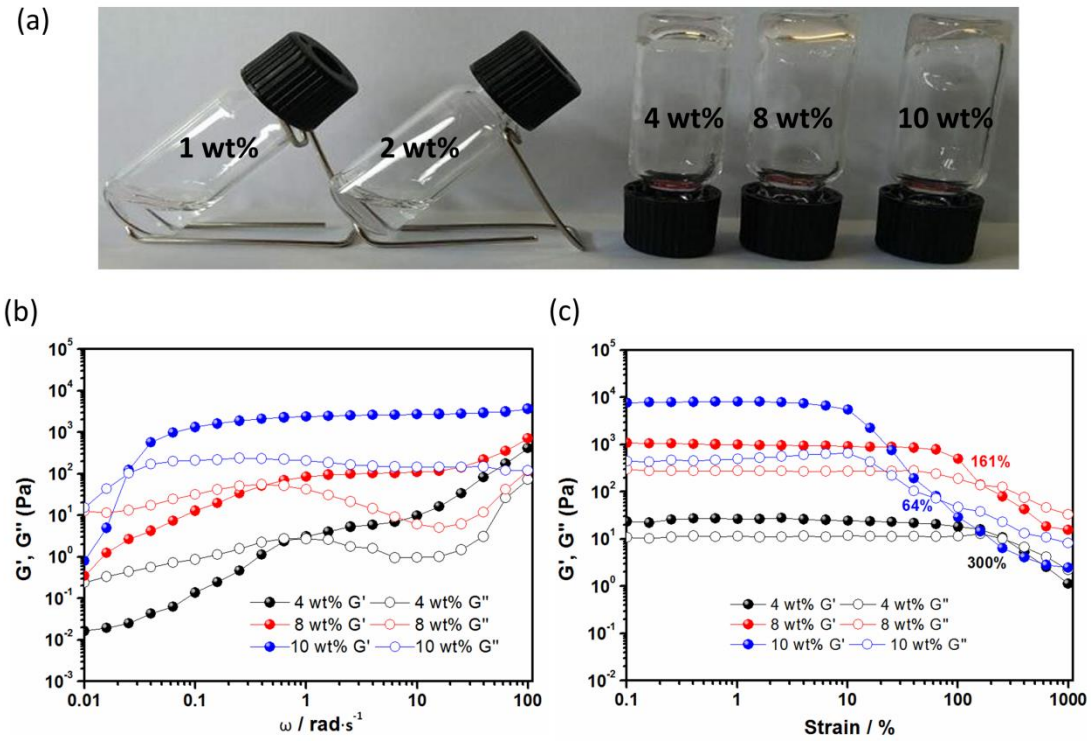



Figure 4. Metallo-supramolecular hydrogels with various **L1** concentrations at fixed $Ni^{2+}$:**L1** ratio of 0.5:1: (a) photographs, (b) frequency sweep experiments performed using a fixed 1% strain, and (c) strain sweep measurements performed using a fixed 1 rad/s frequency

The rheological properties of the organogels obtained at 10 wt% of polymer concentration in acetonitrile by the addition of $Fe^{2+}$ or $Ni^{2+}$ at a fixed metal: L1 ratio of 0.5:1 in acetonitrile were also explored (Figure 5). The obtained organogels were referred as Fe-Gel and Ni-Gel, respectively. A preliminary frequency sweep measurement was performed to investigate the dynamic nature of the metal coordination on the mechanical properties and the result is given in Figure 5a. It was found that the G' is always larger than the G'', consistent with the formation of gels. The G' and G'' are both largely frequency-independent, suggesting the formation of a stable physically crosslinked network. The strain sweep studies disclosed that the rheology properties can be easily changed from ~1500 to ~3000 Pa by simply switching the $Fe^{2+}$ to $Ni^{2+}$ (Figure 5b). The $Ni^{2+}$-induced organogel showed a higher G' than that of Fe-Gel, which is in accordance with the higher thermodynamic stability of $Ni^{2+}$-btp in organic solvent. The yield point is shifted from 3% to 15% with decreasing strength of metal complexes from $Ni^{2+}$ to $Fe^{2+}$ ions due to the higher kinetic network flexibility. Over this area, G' decreased down rapidly and crossed over with G'' at ca. 250% for both organogels. The 250% strain was the critical strain of both organogel, indicative of rupture of the gel network, and at a strain higher than this critical value the organogels transferred to viscoelastic states. Compared to the hydrogels obtained by the addition of $Ni^{2+}$ ions to the btp star-PEG in water, Ni-Gel showed a lower mechanical strength while possessing a higher elasticity as evidenced by the higher values of the flowing point. This higher mechanical strength of the hydrogel might indicate a higher thermodynamic stability of the $Ni^{2+}$-btp complexes or a lower extent of intramolecular complexation in water.

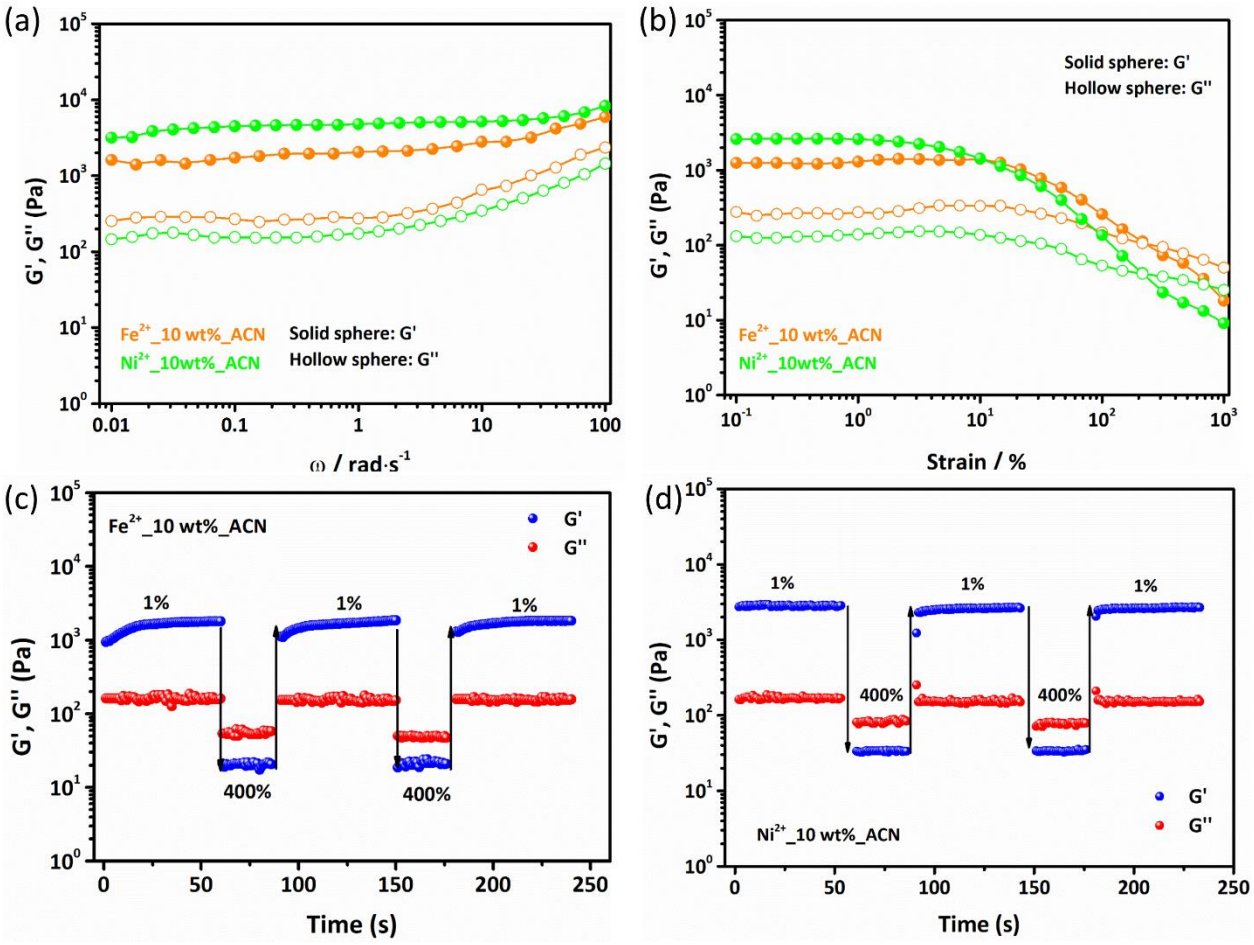



Figure 5. Rheology measurements of organogels obtained from 10 wt% polymer solution by the addition of $Fe^{2+}$ and $Ni^{2+}$ at a fixed metal: **L1** ratio of 0.5:1 in acetonitrile, respectively. (a) Frequency sweep experiments performed using a fixed 1% strain; (b) strain sweep measurements performed using a fixed 1 rad/s frequency; cyclic strain time sweep rheology of organogel in the presence of (c) $Fe^{2+}$ ions and (d) in the presence of $Ni^{2+}$ ions.

To get more insight into the self-repairing properties of the hydrogels, a time sweep experiment was performed under oscillatory shear to investigate the breakup as well as the reformation of the hydrogel network (Figure S2). The **L1** concentration was 10 wt%, while the **L1**: $Ni^{2+}$ ratio was 1:0.5. When the pre-shear experiment with a strain of 400% and a frequency of 1 rad/s was employed, the hydrogel was effectively broken into a solution, as demonstrated by the G''>G'. After the large strain shear was release and adjusted back to 1%, an instantaneous crossover of G' and G'' (i.e., G'>G'') was observed, indicative of the reconstruction of the hydrogel network. Moreover, the initially value of G' is almost immediately recovered after ending the high strain indicating the high reversibility of the metallo-supramolecular hydrogel formation. The dynamic properties of the organogels were also determined by imposing alternating strain of 1% and 400% at a constant regular frequency of 1 rad/s as shown in Figure 5c and 5d. Similar to the $Ni^{2+}$ ion induced hydrogel, both organogels are also able to recover instantly with a fast and almost full recovery of the original modulus in a short span after three cyclic strain time sweeps. This rheology behavior further confirmed the excellent and autonomous rapid self-healing properties of these organogels and highly dynamic $Fe^{2+}$ or $Ni^{2+}$-btp complexes even in organic solvents. Such effective recovery demonstrates the thermodynamically stable yet kinetically labile nature of the $Fe^{2+}$:btp and $Ni^{2+}$: btp complexes and could be potentially useful for applications that require a fast response.

## Conclusions

Supramolecular metallo-hydrogels were prepared by metal-ligand coordination of a tetra-arm PEG functionalized with btp units at each chain-end. The hydrogelation was specifically induced by $Ni^{2+}$, while the addition of other divalent metals (e.g., $Cu^{2+}$, $Zn^{2+}$, and $Fe^{2+}$ ions) resulted only in an increase of the solution viscosity. Studies regarding the hydrogelation revealed that the minimum polymer concentration is 4 wt%, while the optimal ratio between $Ni^{2+}$ and btp is 0.5:1. The specific hydrogelation with $Ni^{2+}$ ion coordination results from the strong binding constant between the btp units and the $Ni^{2+}$ ions, while the inability to induce hydrogelation with $Fe^{2+}$ was mainly ascribed to the oxidation of $Fe^{2+}$ ions to $Fe^{3+}$ ions in aqueous solution. The successful organogelation of the btp star-PEG in acetonitrile in the presence of both $Ni^{2+}$ ions and $Fe^{2+}$ ions, indirectly confirmed this hypothesis of aqueous oxidation of $Fe^{2+}$. The mechanical properties of the organogels were also investigated revealing that the $Ni^{2+}$ organogels were stronger that the $Fe^{2+}$ organogels. Moreover, both the hydrogel and the organogels showed rapid self-healing properties and good repeatable autonomic healing capability. The high strain resistance and fast self-healing properties make, especially the $Ni^{2+}$ metallo-hydrogel a promising platform for designing materials with potential applications in supramolecular chemistry, coordination chemistry, and the catalysis field.

## Acknowledgements

R.H. thanks Ghent University and FWO for continuous financial support.

## Conflict of Interest

The authors declare no conflict of interest.

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