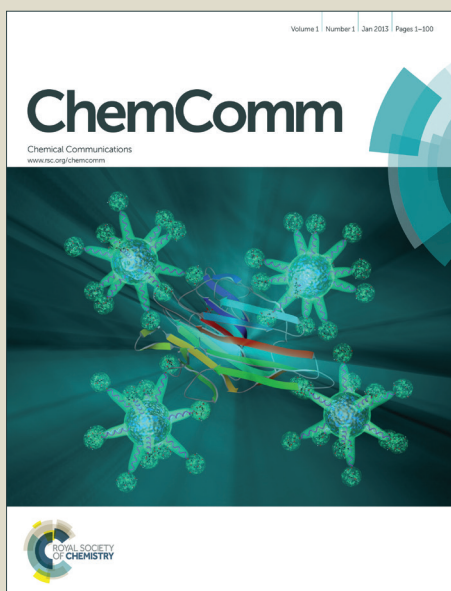


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COMMUNICATION

Supramolecular Copolymer from Two-component gels: Metal Ion-Mediated Cross-Linking, Enhanced Viscoelasticity and Supramolecular Yarn

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The hydrogels based on the co-assembly of bolaamphiphilic L-histidine and 2,2'-bipyridine-dicarboxylic acid have been transformed into viscoelastic supramolecular polymers by cross-linking with Cu(II) ions, and macroscopic supramolecular yarns were obtained by direct drawing from a dilute aqueous solution of the supramolecular polymers.

Supramolecular polymers¹ self-assembled from small molecules have been attracting great interest due to their reversible nature,² smart responsiveness³ and the ordered nanostructures,⁴ which show potential applications in stimuli-responsive systems,⁵ luminescent materials,⁶ gene transfection⁷ and drug-delivery.⁸ However, in comparison with the covalently bonded polymers, supramolecular assemblies generally lack mechanical strength and viscoelasticity due to the relatively weak non-covalent interactions.^{1b} Various efforts have been devoted to overcome such shortcomings of the supramolecular polymers,^{1, 4a, 9} such as increasing the H-bond sites,^{1, 10} combining them with covalently bonded polymers.¹¹ One of the most distinguished viscoelastic supramolecular polymers systems can be from the assembly of small molecular building blocks containing 2-ureido-4-pyrimidone.¹² The quadruple hydrogen bonding helped those small organic molecules reversibly self-assemble into linear supramolecular polymers with viscoelasticity in organic solvent.¹² In addition, the cross-linking of supramolecular polymer is particularly noteworthy for increasing the mechanical properties.^{3b, 3c, 13}

However, most of the known viscoelastic supramolecular polymers were produced in organic solvent or ionic liquid with relatively high concentrations.^{9c, 10} It still remains a challenge to fabricate similar supramolecular polymers in aqueous solution,^{9a, 14} especially with diluted aqueous solutions. Definitely, constructing supramolecular polymers with good mechanical properties in water could be very important for biomedical applications.¹⁵ However, the cross-linking of supramolecular polymers in aqueous solution, which may gigantically change the nanostructures or macroscopic properties of those supramolecular polymers, is rarely reported. In this communication, by using the two-component hydrogels and the crosslinking by metal ions, we have successfully fabricated a supramolecular copolymer with good

viscoelasticity, which can be further drawn into supramolecular yarn.

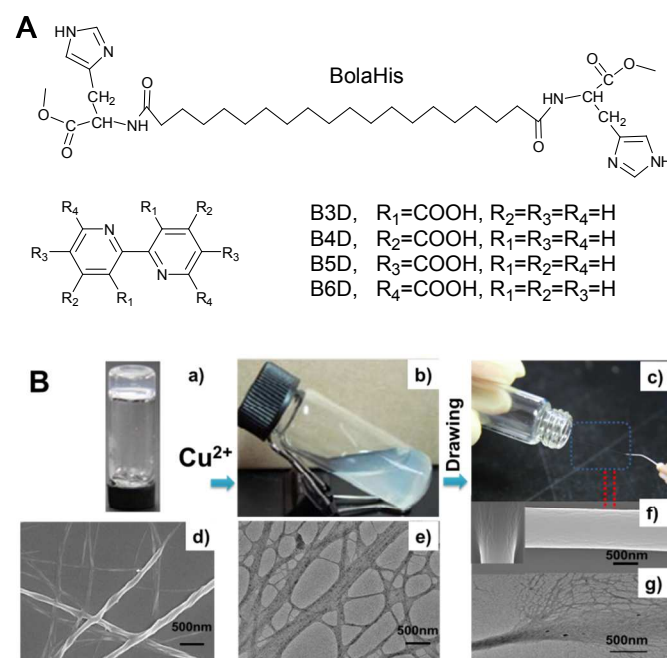


Figure 1. (A) Molecular structure of **BolaHis** and various dipyrindine-dicarboxylic acids; (B) Changes on both nanostructures and macroscopic properties of supramolecular polymers, from hydrogels to viscoelastic solution until the macroscopic supramolecular yarn from direct drawing. a) Photograph and d) SEM images of supramolecular polymer hydrogels formed by **BolaHis**/**B5D**=1/1; b) Photograph and e) TEM images of viscoelastic solution formed by Cu²⁺/**BolaHis**/**B5D**=0.5/1/1; c) Photograph of drawing supramolecular yarn from viscoelastic solution, f) SEM and g) TEM images of macroscopic yarns. (The concentration of **BolaHis**=0.1 wt%)

Previously, we have found that a bolaamphiphilic L-histidine (**BolaHis**, Fig.1) could self-assembly with benzene dicarboxylic acids to form two-component hydrogels.^{6d} We have further found that many other dicarboxylic acids have similar properties and supramolecular polymers with tuneable properties can be expected. Herein, we introduced 2,2'-bipyridine-dicarboxylic acids (**BD**), instead of benzene

dicarboxylic acids, to co-assemble with BolaHis. The 2, 2'-dipyridine units provide additional binding sites for coordination, which give more possibility for modulating the assemblies. Although neither bolaamphiphile nor individual **BD** molecules (Figure 1A) could form hydrogels themselves, some of the one to one mixtures showed the gelation ability, which depended on the substituent positions of the carboxylic acid. Heating the **BolaHis** together with **B5D** or **B4D** in water and slowly cooling down would produce nice hydrogels and supramolecular polymer. And 0.1 wt% bolaamphiphile in the system is good enough to make stable hydrogels. While **B3D** and **B6D** cannot form hydrogels (Table S1), presumably due to the relative positions of two carboxylic acids are not favourable for ordering molecular packing. Interestingly, simple addition of Cu(II) ions to the **B5D/BolaHis** hydrogels could lead an aqueous solution with enhanced viscoelasticity at very low concentration. Furthermore, the macroscopic yarns with the length about several centimeters can be obtained from the viscoelastic solution by direct drawing (Figure 1c).

While comparing with the **BolaHis/B4D** system, the **BolaHis/B5D** hydrogels with different molar ratios always have better thermal stability; as confirmed by the sol-gel transition temperature (T_{gel}) (Figure S2) and the critical gelation concentration (CGC) of these hydrogels. For **B5D/BolaHis**=2/1, 0.034 wt% bolaamphiphile in the system can already produce stable hydrogels; while for **B4D/BolaHis**=2/1 system, the critical gelation concentration of **BolaHis** was determined as 0.067 wt%. Although **B5D/BolaHis**=1/1 already can form nice transparent hydrogels, addition of more dicarboxylic acid into the systems could increase the sol-gel transition temperature (T_{gel}) gradually (Figure S2). However, too much **B5D** in the systems cannot be dissolved well upon heating and also cannot form hydrogels.

For **B5D/BolaHis** and **B4D/BolaHis** systems, the interlaced helical nanofibers can be observed from the SEM images (Figure 1, S3). These fibers appear to be several micrometers long with the diameter about 40-50 nm. And the entanglement of these nanofibers could further gel water.^{6d}

On the other hand, the 2, 2'-bipyridine units are good binding sites for different metal ions, which could change the structural and functional properties of the assemblies. Different metals ions, such as Cu^{2+} , Ag^+ , Co^{2+} , Ni^{2+} , Zn^{2+} , Fe^{2+} and Fe^{3+} were studied. The results show that only the interactions between **B5D/BolaHis** hydrogel and Cu^{2+} or Zn^{2+} can form viscous solution. Adding Ag^+ cannot change the properties of **B5D/BolaHis** hydrogels. While when Ni^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} were added into the **B5D/BolaHis** hydrogels, the solution without viscosity were formed (Figure S4). Thus, only the metal ions with preferred geometries and appropriate binding strengths for forming complex can change **B5D/BolaHis** hydrogel to viscous solution. Notably, the quantity of Cu^{2+} or Zn^{2+} should be carefully controlled; too much metal ions in the systems would lead precipitation. The Cu(II)-coordinated supramolecular polymers have viscoelastic properties; and macroscopic supramolecular yarns can be obtained by direct drawing from the aqueous solution of $Cu^{2+}/B5D/BolaHis$ supramolecular polymers. Thus, when a needle was put into the solution with gentle stirring and then carefully lifted out of the water surface, a visible thin fiber with the length about centimeters can be obtained (Figure 1c).

For the Cu(II)-coordinated supramolecular polymers ($CuCl_2/B5D/BolaHis$), interlaced thin nanoribbons were detected from TEM measurement (Figure 1b, S5). For the macroscopic supramolecular yarns, the SEM images show that

the diameters of these centimeter length fibers are about 1.5-5 μm (Figure 1c), and aligned nanofibers can be detected from the end of yarns. Moreover, the TEM images of the divergent end on macroscopic fibers clearly show thin nanoribbons, which are similar like the morphologies observed from the original Cu(II)-coordinated supramolecular polymers. These results indicate that the macroscopic supramolecular yarns are constructed by ordering arranged nanoribbons, which can be further demonstrated by cross-polarized microscope measurements. Thus, the anisotropic entities can be detected throughout the supramolecular yarns, with length in the scale of several centimeters (Figure S6).

The viscoelasticity of these supramolecular polymers was characterized by rheological measurements, which were performed at 298 K with **BolaHis** at a concentration of 0.1 wt%. First, to detect the tolerance performance of **B5D/BolaHis** hydrogel, a strain sweep was conducted (Figure S7). Both moduli G' (storage modulus) and G'' (loss modulus) remained roughly constant below a critical strain value of 0.3 %, known as the upper limit of the linear viscoelastic regime. Above this strain value, a sharp decrease of G' and G'' was observed and the value of G'' became larger than that of G' , representing a partial broken of the hydrogels. We choose the strain value of 0.1% in the frequency sweeps, by recording the evolution of storage and loss moduli.

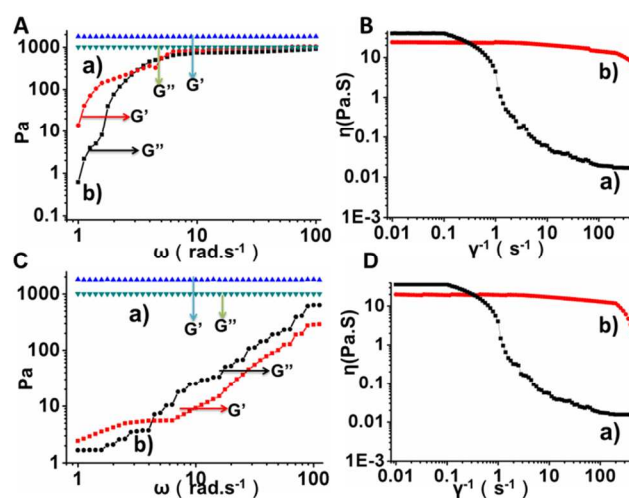


Figure 2. (A, C) Storage modulus G' and loss modulus G'' versus frequency ω (from 1 to 100 $rad\ s^{-1}$), measured at 0.1% strain; (B, D) Shear viscosity determined by steady shear rate sweep performed at 25°C. a) Molar ratios of **BolaHis/B5D** equal to 1/1 (A, B) or 1/2 (C, D); b) Molar ratios of $CuCl_2/B5D/BolaHis$ equal to 0.5/1/1 (A, B) or 1/2/1 (C, D).

For two-component supramolecular hydrogels with **BolaHis/B5D**=1/1 or 1/2, the G' and G'' versus frequency plot are nearly linear and invariant with angular frequency (ω). And G' is always higher than G'' over the entire range of frequency (from 1 to 100 $rad\ s^{-1}$), showing the stability of the hydrogels (Figure 2A, C). For $CuCl_2/B5D/BolaHis$ =0.5/1/1 supramolecular polymer with the concentration of **BolaHis**=0.1wt%, the rheological measurements clearly suggest the viscoelasticity (Figure 2A). When the scanning frequency ω was changed from 1 to 100 $rad\ s^{-1}$, both G' and G'' increased progressively. And G' is higher than G'' at lower frequency, indicating the elastic is the predominant property. However, when ω was increased to the crossover point (about 5.5 $rad\ s^{-1}$), G'' became higher than G' , showing the properties

are closer to liquid. Interestingly, when ω was further increased, the G' again became higher than G'' . In contrast, although the rheological measurements on $\text{CuCl}_2/\text{B5D}/\text{BolaHis}=1/2/1$ systems also showed the viscoelasticity at lower frequency, the assemblies quickly changed into liquid upon increasing ω values (Figure 2C).

The shear rate dependent viscosity of these supramolecular polymers were also studied (Figure 2B, D). At low shear rates, the viscosity of **B5D/BolaHis** hydrogels is larger. Interestingly, when the shear rate was increased, the viscosity of Cu(II) -coordinated supramolecular polymer became larger than that of two component supramolecular hydrogels. Moreover, the viscosity of hydrogels decreased exponentially upon increasing the shear rate from 0.1 S^{-1} to 100 S^{-1} , indicating the disassembly of the gels. In contrast, although the viscosity of Cu(II) -coordinated supramolecular polymers can also decrease along with the increasing of shear rates, the changes of η values are relatively small within the shear rate range from 0.01 S^{-1} to 100 S^{-1} .

Although **B5D/BolaHis** hydrogel can also form viscous aqueous solution with Zn^{2+} , the rheological measurements on $\text{ZnCl}_2/\text{B5D}/\text{BolaHis}$ systems cannot show any viscoelastic properties (Figure S8). Thus, G' is always lower than G'' , and the viscosity of $\text{ZnCl}_2/\text{B5D}/\text{BolaHis}$ systems also decrease rapidly upon increasing the shear rate. Therefore, no macroscopic supramolecular yarn can be drawn from $\text{ZnCl}_2/\text{B5D}/\text{BolaHis}$ solution.

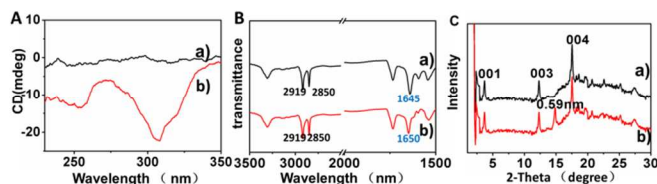


Figure 3. (A) CD spectra, (B) FT-IR spectra and (C) XRD pattern of supramolecular polymers. a) **BolaHis/B5D**=1/1; b) $\text{CuCl}_2/\text{B5D}/\text{BolaHis}=0.5/1/1$.

The **B5D/BolaHis** hydrogels do not show optical activity upon CD measurements, even though **BolaHis** is chiral molecule. However, for the Cu(II) -coordinated supramolecular polymers, the strong negative Cotton effect can be observed (Figure 3A) at about 303 nm, which corresponds to the UV-Vis absorption of **B5D** (Figure S9), indicating ordered packing of bipyridine rings upon binding with Cu(II) ions. Interestingly, even though very small amount of Cu^{2+} in the systems already can give strong CD signals, larger amount of Cu(II) ions only produce weak CD signal (Figure S10A), presumably due to the disturbing of the molecular packing. It is worth mentioning that, the CD spectra of $\text{ZnCl}_2/\text{B5D}/\text{BolaHis}$ supramolecular polymers with different molar ratios do not show any clear Cotton effect (Figure S11), suggest that bipyridine molecules cannot form ordering aggregation after binding with Zn^{2+} , presumably due to the weak binding capability between Zn^{2+} and pyridine ligands¹⁶ as well as the larger diameter of zinc cations.

The XRD patterns of two-component hydrogels (Figure 3C) clearly show periodical diffraction peaks, suggest the monolayer lipid membranes (MLM) formed from the self-assembly of **BolaHis**.^{6d} While the XRD patterns (Figure 3C) of $\text{CuCl}_2/\text{B5D}/\text{BolaHis}$ cross-linked supramolecular polymer show a new diffraction peak at 2θ value of 14.9° . The corresponding long spacing ($d=0.59\text{nm}$) of the assemblies can

be assigned to ordered packing of bipyridines upon forming complex with Cu(II) ions.

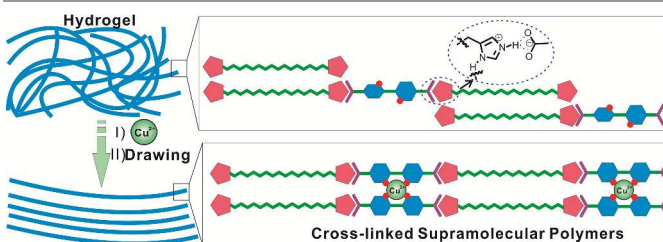


Figure 4. Possible mechanism for the formation of cross-linked supramolecular polymer with viscoelasticity and optical activity

For the FT-IR spectra of **B5D/BolaHis** hydrogels, the asymmetric (2919 cm^{-1}) and symmetric (2850 cm^{-1}) stretching vibrations of CH_2 indicate the ordering packing of long alkyl spacers. And the amide I (1645 cm^{-1}) and II (1542 cm^{-1}) peaks clearly show the amide hydrogen bonding between the bolaamphiphiles.¹⁷ While interactions between imidazole and carboxylic acid groups can be proved by the broad band around $1940\text{--}1960 \text{ cm}^{-1}$, which illustrates the formation of imidazolium carboxylate salts (Figure 3B, S12).¹⁸ On the other hand, the FT-IR spectra of $\text{CuCl}_2/\text{B5D}/\text{BolaHis}$ supramolecular polymers are very similar like that of the **B5D/BolaHis** hydrogels, indicating the linear supramolecular polymer chains as well as the layered nanostructures preserved upon adding Cu(II) ions. However, the only exception is that the amide I band changed from 1645 to 1650 cm^{-1} upon adding Cu^{2+} , indicate the amide hydrogen bonding between different parallel packed **BolaHis** molecules changed after the cross-linking from the Cu(II) ions (Figure 3B, S10C, D).

These results suggest that COOH on **B5D** could interact with the histidine head-groups of **BolaHis** to form linear assemblies.^{6d} When Cu^{2+} was introduced, the metal ions would interact with the nitrogen atom on pyridine (Figure 4). Because two nitrogen atoms in 2, 2'-bipyridine are close to each other, there are strong cooperative effects for binding Cu(II) ions. On the other hand, the XRD pattern and FT-IR spectra also suggest that the bolaamphiphiles always self-assemble into monolayer lipid membranes (MLM),^{6d} even though bipyridine-dicarboxylic acids and metal ions were introduced into the systems. For $\text{CuCl}_2/\text{B5D}/\text{BolaHis}$ supramolecular polymers, the **BolaHis** MLM would render linear supramolecular polymers chains align parallel with each other. Moreover, binding with identical Cu(II) ions from different 2, 2'-bipyridine molecules would produce cross-linked supramolecular polymers, which would produce further hierarchically organized nanostructures. Therefore, the assemblies would become much more aligned manner in the presence of copper ions, and show viscoelasticity for drawing macroscopic yarns.

In summary, the co-assembly of bolaamphiphilic L-histidine and 2, 2'-bipyridine-dicarboxylic acids form supramolecular hydrogels, while simply adding Cu(II) ions changed the hydrogels into viscoelastic supramolecular polymers, which produce macroscopic supramolecular yarn via direct drawing. These viscoelastic supramolecular polymers are based on the hierarchical self-assembly of simple organic molecules in water with very low concentration. The hydrogen bonding, hydrophobic interactions between organic molecules played an important role in forming the linear supramolecular polymer, while the Cu(II) ion-mediated cross-linking between linear polymer contribute to the viscoelasticity of the polymer.

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Notes and references

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