A ligand-chirality controlled supramolecular hydrogel†

Jiang-Shan Shen,*[a] Guo-Juan Mao,[a] Yu-Hua Zhou,[b] Yun-Bao Jiang[b] and Hong-Wu Zhang*[a]

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We report a novel example of ligand-chirality finely controlled *in situ* supramolecular hydrogel formation based on the coordination of phenylalanine (Phe) to Cu(II) with higher selectivity over other metal ions. As decreasing both enantiomeric excesses (ee%) of ligand Phe towards its D- and L-forms, the gelation ability of Phe-Cu(II) supramolecular metallogelator was found to be weakened and eventually disappeared, which likely resulted from the stereoselectivity of the ligand Phe. Intermolecular hydrogen bonding, hydrophobic and/or π–π stacking interactions were also found to be essential for forming the metallogel. We believe that the present work can open up a new entry for developing novel and promising chiral sensing and recognition platforms, *i.e.* visually sensing chiral molecules by naked eyes due to the feature of a sol-to-gel transition induced smartly by varying the ligand chirality.

1. Introduction

Biomolecules mostly take various weakly non-covalent interactions as driving forces to construct supramolecular architectures that are responsible for their biochemical functions and properties.[1] These driving forces, such as hydrogen bonding, coordination, hydrophobic interaction, and π–π stacking, can be elegantly balanced by nature to control the architectures and functions of the supramolecular assemblies. Therefore, artificially mimicking these naturally occurring superstructures and biochemical functions within the framework of supramolecular chemistry are interesting for a wide range of applications including sensing and catalysis.[2]

Supramolecular gels especially supramolecular hydrogels of low-molecular-weight gelators (LMWGs) have been recently explored as promising smart/intelligent soft materials for a series of potential applications, such as tissue engineering and drug delivery, as a result of smartly shrinking, swelling or degrading upon exposure to external stimuli including pH,[3] temperature,[4] light,[5] anions and/or cations,[6] and even biologically relevant molecules.[7] Despite considerable efforts which have been dedicated to developing these "smart" or "intelligent" soft materials, the range of stimuli responsive systems known is very limited. In general, the formation of supramolecular assemblies of these small gelators is mainly directed by hydrogen bonding in organogels and by hydrophobic and/or π–π stacking interactions in hydrogels.[8] Large amounts of solvent molecules can be entrapped to afford a solid-like appearance by a combination of capillary forces and interactions with the gelators themselves arising from self-assembling nano-/micro-scale fibers.[8a] Stimuli can induce the release of entrapped solvent molecules, resulting in shrinking or even a gel-to-sol transition of supramolecular gels. Although various LMWGs have been reported, those employing mainly metal–ligand interactions as an alternative weak driving force to construct supramolecular gels are less at present in comparison with other weak interactions driving gels of two-component systems.[9] Developing supramolecular hydro- and/or organogels involving metal coordination polymers, metal complexes and/or discrete organometallic molecules forming metallogels based on the concept of coordination chemistry are considerably attractive because metal coordination interaction can impart new chemical and physical properties to the resulted supramolecular gels.

It has been known for a long time that chirality plays a central role for controlling molecular recognition and interactions in living systems.[10] Developing and finding chirality-mediated supramolecular assemblies are undoubtedly significant for obtaining novel functional materials including chiral sensing platforms. Although the impact of chirality on self-assembled systems including fibrillar networks and even supramolecular gels has been found to be profound,[11] the formation of supramolecular metallogels finely controlled by ligand chirality has been hardly achieved so far,[12] at least to our knowledge. Supramolecular gel formation has indeed been found to be generally related to the chirality of gelators, yet it is difficult to fully understand the effect of the gelator stereostructure on supramolecular gel formation and properties at present. Therefore, it remains to be a challenging subject that deserves to be explored.

In the present report, we demonstrate an intriguing example that the gelation ability of supramolecular metallogelator was finely tuned by varying ligand chirality. It was found that phenylalanine (Phe) could coordinate to Cu(II) leading to *in situ* forming translucent and homogeneous supramolecular hydrogels under certain conditions (Scheme 1), featured by high selectivity. The formation of the supramolecular metallogel could be unprecedentedly controlled by varying enantiomeric excess (ee%) of the ligand Phe. As decreasing both ee% of Phe towards its D- and L-forms, the gelation ability of Phe-Cu(II) metallogelator is weakened and eventually disappears. Besides the chirality of the ligand, intermolecular hydrogen bonding, hydrophobic and/or π–π stacking interactions also play a critical role in the gelation

[a]*Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China. E-mail: jsshen@iue.ac.cn, hwzhang@iue.ac.cn; Fax: (+86)592-619-0773; Tel: (+86)592-619-0773*
[b]*Department of Chemistry, College of Chemistry and Chemical Engineering, and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen, 361005, China*

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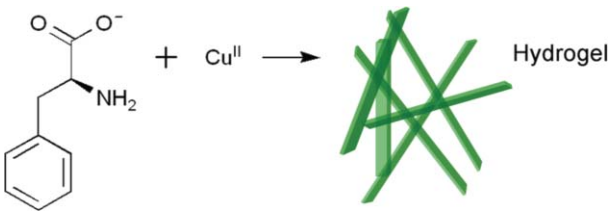

Scheme 1 Schematic illustration of supramolecular metallogel formation *via* Phe coordinating with Cu(II).

process. This system is considered to not only provide a novel class of metallogelator but also open a great opportunity for developing promising chiral sensing and recognition platforms, asymmetric catalysis, and even logic gate models.

2. Experimental

Chemicals and characterizations

D-Phe was purchased from Sigma. $Cu(NO_3)_2$, L-Phe and other chemicals, obtained from Shanghai Chemicals Group (China), were used without any further purification.

UV-visible absorption spectra were recorded on Thermo Evolution 300 absorption spectrophotometer using a 1 cm quartz cell. Circular dichroism (CD) spectra were measured on JASCO-810 CD spectrophotometer. Infrared (IR) spectra were conducted by Nicolet AVATAR FT-IR360 spectrophotometer. X-Ray powder diffractions (XRD) were performed on Panalytical X'pert PRO diffractometer equipped with Cu-Kα radiation ($\lambda = 1.5418$ Å) at room temperature. Field emission scanning electron microscopy (FESEM) experiments were carried out on HITACHI S-4800 working at an accelerating voltage of 20 kV. The tested samples for FESEM, XRD, IR, and solid CD experiments were prepared by freeze-drying the original hydrogels under vacuum at −80 °C.

Preparation of supramolecular hydrogels with varying Phe-Cu(II) content

One equivalent of $Cu(NO_3)_2$ and two equivalents of L-Phe containing two equivalents of NaOH were dissolved in pure water of certain volume, respectively. These two corresponding solutions were quickly mixed, leading to solutions containing L-Phe-Cu(II) by weight of 0.35%, 0.55%, 0.7%, and 1.4%, respectively. The mixed solutions were instantly transformed into homogeneous and translucent hydrogels.

The preparation of D-Phe-Cu(II) supramolecular metallogels were performed as the above operation procedure.

Gelation at varying ee% of Phe

The experiments of gelation at varying ee% of Phe were also performed as the above operation procedure. The molar ratio of Phe : Cu(II) : NaOH was 2 : 1 : 2 and 0.7% Phe-Cu(II) content was employed. In this case, total concentration of D- and L-Phe was fixed and the molar ratio of D- Phe to L-Phe was varied. ee% was calculated according to the following formula: ee% = (D − L)/(D + L) × 100%, in which D and L are relative content of D-Phe and L-Phe in the enantiomers mixtures, respectively.

3. Results and discussion

Phe, being a naturally occurring chiral α-amino acid, has previously been shown to have a unique chelating ability towards Cu(II) because it possesses amino and carboxylic groups.[13] The phenyl moiety can be expected to have intermolecular hydrophobic and/or π–π stacking interactions leading to facilitating supramolecular assembling, thereby creating efficient microrooms for immobilizing water molecules by means of hydrogen bonding and capillary force to form a gel. In fact, we found that when two equivalents of L-Phe were allowed to coordinate to one equivalent of Cu(II) *via* simply mixing, the resulted aqueous solution containing a L-Phe-Cu(II) content of 0.7% by weight led to the quick formation of a translucent hydrogel with moderate gelation capability. The gelation could be identified by the inverted tube method, which did not show fluid flowing down lasting for at least 20 min. It should be noted that before mixing two equivalents NaOH was required to deprotonate the originally protonated $-NH_3^+$ group in L-Phe for reversing its coordination ability. The optimal pH range for the gelation was found to be *ca.* 6.5–8.0. Control experiments demonstrated that L-Phe or Cu(II) solution employed alone could not self-assemble to form a gel state. We further found that the *in situ* gelation could still be observed at L-Phe-Cu(II) content as low as 0.35% by weight (Fig. 1), which is taken as the minimum gelator concentration (MGC). This also indicates that Phe-Cu(II) indeed is a so called "super gelator" since one metallogelator molecule can surprisingly immobilize *ca.* 16 000 water molecules in this case. Similarly, D-Phe-Cu(II) supramolecular metallogels could also be obtained by means of the same preparation procedures. Identical MGC was observed for the D-Phe-Cu(II) system. Field emission scanning electron microscopy (FESEM) images of the xerogels obtained by freeze-drying original hydrogels of varying Phe-Cu(II) content revealed that all metallogels contained well defined three-dimensional nanosized/even microsized structures of sheet-like supramolecular assemblies (Fig. 2 and Fig. S1 in ESI†).

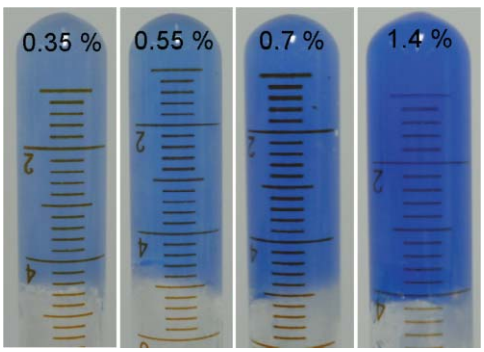

Fig. 1 Photos of the supramolecular metallogels of varying L-Phe-Cu(II) content (wt).

In order to understand the mechanism of the supramolecular metallogel formation, interaction of Phe with Cu(II) was thoroughly examined. Absorption spectra titration and Job plot clearly indicated a 2 : 1 of Phe to Cu(II) binding stoichiometry (Fig. 3 and 4). Note that the absorption at the wavelength range of 250 to 350 nm can be attributed to ligand-to-metal charge transfer (LMCT) transition of Phe-Cu(II) metallogelator.[14] ESI-MS analysis of the Phe-Cu(II) complex (Fig. S2, ESI†) offered

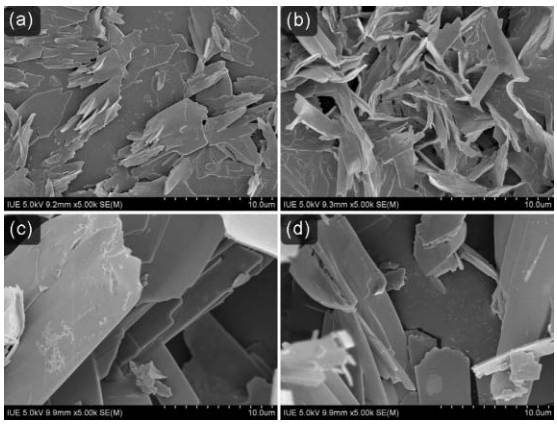

Fig. 2 FESEM images of xerogels from the original hydrogels containing L-Phe-Cu(II) of 0.35% (a), 0.55% (b), 0.7% (c), and 1.4% (d) by weight. Scale bar for (a–d) is 10 μm.

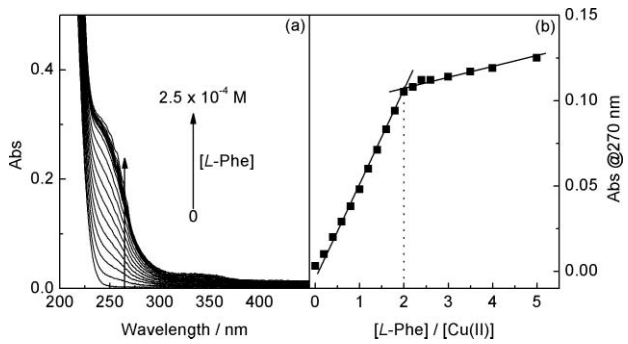

Fig. 3 (a) Absorption spectra of Cu(II) in the presence of increasing concentration of L-Phe. [L-Phe] = 0 – 2.5×10^{-4} M and [Cu(II)] = 5.0×10^{-5} M. (b) Plots of absorbance at 270 nm *versus* [L-Phe]/[Cu(II)] derived from Fig. 3(a).

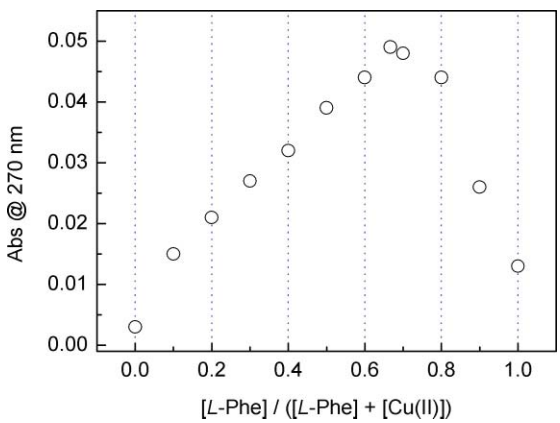

Fig. 4 Job plot of absorbance at 270 nm *versus* [L-Phe]/([L-Phe] + [Cu(II)]). Total concentration of [L-Phe] and [Cu(II)] was 1.0×10^{-4} M.

direct evidence for the binding stoichiometry. The main peak at *m/z* 413 corresponds to $[Cu(Phe)_2 + Na]^+$ along with *m/z* 393 peak for $[Cu(Phe)_2 + H]^+$. No gelation was observed when 0.5 or one equivalent of Phe was employed under similar preparation conditions. This appears to further indicate the requirement of a critical ligand to metal stoichiometry for the gelation. It was therefore made clear that the metallogel was mainly stabilized by the 2 : 1 of Phe to Cu(II) complex. Infrared (IR) spectra of the xerogels supported the coordination of carboxylic/amino groups to Cu(II) by the fact that the asymmetric stretching band of COO^- at 1620 cm^{-1} and the symmetric and asymmetric stretching bands of NH at 3251 cm^{-1} and 3337 cm^{-1} shift to higher frequencies and become more prominent compared to those of Phe alone (Fig. S3, ESI†).[15]

Density function theory (DFT) calculation[16] indicated that the optimized conformation of the complex $[Cu(Phe)_2]$ adopts a planar square tetrahedral coordination geometry, in which the central Cu atom employs a dsp2 hybridization pattern (Fig. 5). Two hydrophobic phenyl rings assumed an open form, a more stable structure that is good for intermolecular hydrophobic and/or π–π stacking interactions between two adjacent phenyl rings. This planar coordination conformation is favorable for constructing a sheet-like superstructure, which is significant for supramolecular hydrogel formation, because it was accordingly expected that a synergistic interaction among the intermolecular weak interactions such as hydrogen bonding, hydrophobic, and/or π–π stacking interactions would finally promote the effective 3D-networks formation. These micro-/nano-structures thereby provided enough cavities for holding a large amount of water molecules by means of hydrogen bonding and capillary force to form a metallogel (Scheme S1, ESI†). We also carried out a DFT calculation to model the IR spectrum at B3LYP/6-31G* level[16] (Fig. S4, ESI†), which is in accordance with that of Phe-Cu(II) xerogel measured. This further confirmed the assumed coordination geometry of Phe-Cu(II).

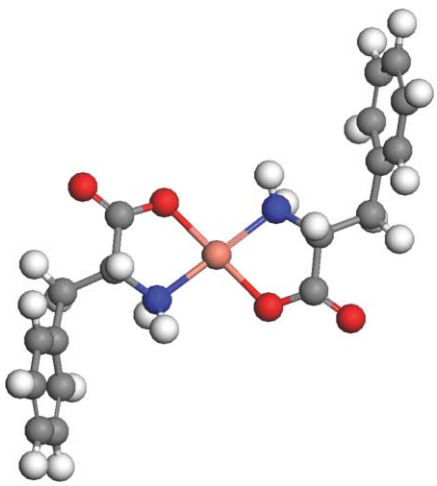

Fig. 5 DFT optimized conformation of Phe-Cu(II) complex.[16]

X-Ray powder diffraction patterns of the xerogels resulting from the original Phe-Cu(II) metallogels revealed that these coordination gels were of crystalline character as clearly evidenced by three distinct diffraction peaks at 2θ of 5.3°, 10.7°, and 16.1°. It should be noted that the three distinct diffraction peaks did not change as the Phe-Cu(II) content was lowered to 0.15% by weight, which is lower than its MGC (Fig. S5, ESI†).

To confirm the contribution of the hydrophobic phenyl ring of Phe for gelation, we successively changed X group in the α-amino acid of $X–CH_2CH(NH_2)(COO^-)$ form, which involving alanine, leucine, tryptophan, and histidine, were expected to coordinate to Cu(II) under the same preparation conditions, respectively (Scheme S2, ESI†). It was found that the coordination

complexes of these tested ligands with Cu(II) did lack the gelation ability. This is understandable for that, in the cases of alanine and leucine, the absence of intermolecular π–π stacking and/or hydrophobic interactions is responsible for the failure of gelation, however, in the cases of tryptophan and histidine, the participation of the backbone heteroatoms in the coordination with Cu(II), which might bring about unexpectedly disordered intermolecular hydrogen bonding, π–π stacking and/or hydrophobic interactions, unfavorable for the gelation. We should note that the *in situ* forming Phe-Cu(II) metallogel is distinct from the previously reported aspartic acids (Asp)-Cu(II) system which formed 1-D coordination polymer nanofibers and even gels were determined by coordinating both carboxylate groups of Asp to Cu(II).[9k]

The significance of intermolecular hydrogen bonding, hydrophobic and/or π–π stacking interactions for the gelation was further supported by ionic strength experiments. It was found that the gel formation was independent to the ionic strength maintained by NaCl (Table S1, ESI†). Stable hydrogels could still be obtained in the presence of the strong electrolyte over a wide concentration range, up to 500 mM, suggesting that the electrostatic interaction does not act as a critical role in the gelation.

Other metal ions instead of Cu(II) mixed with Phe were tested for the possibility of supramolecular metallogel formation. No obvious gelation, however, was observed under the same preparation conditions despite their complex abilities toward Phe (Table S2, ESI†).[17] The difference of coordination geometry among the tested metal ions were suggested to be responsible for the high selectivity of Cu(II) in the gelation because Cu(II) has a unique square planar coordination geometry that acts as a linker, together with hydrophobic and/or π–π stacking interactions, allowing the building blocks to take a linear pattern to aggregate. The aggregation model seems to be critical for the gelation.

The ligand Phe is able to induce "supramolecular chirality" in the gelation as demonstrated by circular dichroism (CD) spectra. Splitting CD signals with a crossing wavelength at 688 nm were observed for the coordination xerogels from the original hydrogels of D- and L-Phe-Cu(II), assignable for the known d–d transition of Cu(II)[18] (Fig. 6). For D- or L-enantiomeric form, CD signals of the xerogels show perfect mirror images, which are similar to that of the reported Asp-Cu(II) coordination polymer nanofibers.[9k]

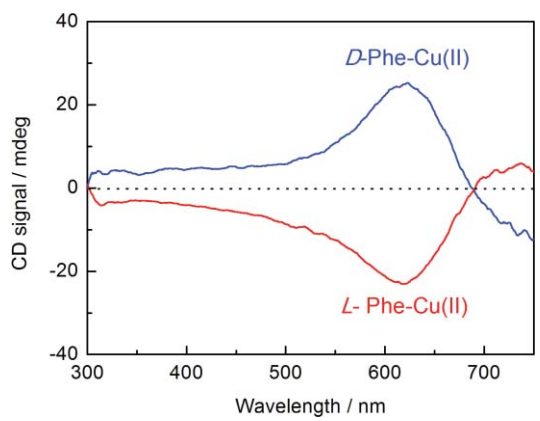

Fig. 6 CD spectra of xerogels from the original hydrogels containing D- or L-Phe-Cu(II) of 0.7% by weight.

Table 1 Gelation was controlled by varying ee% of Phe

ee (%)	Gelation, Y/N[a]
100 (L)	Y
80 (L)	Y
50 (L)	Semi-gelling
30 (L)	N
0	N
30 (D)	N
50 (D)	Semi-gelling
80 (D)	Y
100 (D)	Y

[a] The molar ratio of Phe to Cu(II) was 2 : 1 and two equivalents NaOH were used. The Phe-Cu(II) content was 0.7% by weight. "Y/N" represents "Yes or No".

Very intriguingly, we found that the chirality of Phe ligand was able to control the formation of Phe-Cu(II) supramolecular metallogels (Table 1). The enantiomer mixtures of L- and D-Phe of varying ee% were taken as ligands for coordinating to Cu(II) under the same preparation conditions. We observed that the gelation capability of the Phe-Cu(II) system was in general enhanced with increasing ee%. The Phe-Cu(II) system would lose its gelation ability when ee% was lower than 30%. At ee% of 50%, this system showed a semi-gel state, whereas a fully gel state was obtained at ee% higher than 80%. The gelation did not occur even when the DL-Phe-Cu(II) (ee% is equal to 0%) content was enhanced to 2% by weight. This indicates that the formation of the supramolecular metallogels could be modulated by varying the chirality of the Phe ligand. We believe that these observations mainly resulted from the stereoselectivity of inter-ligand interactions because efficient intermolecular hydrogen bonding, hydrophobic and/or π–π stacking interactions might be weakened as ee% lowered. It should be noted that the results are somewhat similar to that of previously reported tartrate acid-gemini based gelators.[11e]

In conclusion, we developed a novel *in situ* forming supramolecular metallogel system. The formation of Phe-Cu(II) metallogels could be controlled by varying the chirality of the Phe ligand. This hydrogel system may open up a new entry for developing promising chiral sensing and recognition platforms, asymmetric catalysis, and even logic gate models.

Acknowledgements

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