Supporting Information

Self-healing supramolecular heterometallic gels based

on synergistic effect of the constituent metal ions

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1. General remarks

¹H NMR spectra were obtained with a Bruker AV II-400 (400 MHz). The ¹H NMR and ¹³C NMR chemical shifts were measured relative to CDCl₃ as the internal references. Mass spectra were obtained by Shimadzu LCMS-IT-TOF instrument. Elemental analyses were performed with a CARLO ERBA1106 instrument. Transmission electron microscopy (TEM) studies were carried out on a HITACHI H-600, operating at 100 kV. Tapping mode AFM imaging was performed under ambient conditions on a SEIKO SPA400 instrument by using BS-Tap 300Al levers (Budget Sensors, silicone cantilevers). Dynamic light scattering (DLS) experiment was performed with a Brookhaven BI-200SM instrument at 25 °C. Rheological characterisation was performed on a Bohlin CVO 200 produced by Malvern Instruments Ltd. A parallel plates viscometer (diameter: r = 35 mm) was used with a cap to prevent the evaporation of the solvent and the gap between the plates is 1 mm. Frequency sweep measurement was performed at 25 °C and the stress amplitude oscillations. The temperature was held at 25 °C. UV-Vis spectra were taken after stress amplitude oscillations. The

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Unless otherwise indicated, all syntheses and manipulations were carried out under dry N_2 atmosphere. Anhydrous solvents were dried by standard procedures. Ligand **1** were synthesized according to our previously reported methods. ^{S1}

Preparation of samples for AFM. Samples of the solution of metallogel **1**-Ni (0.1 wt %) and **1**-Co (0.2 wt %) in DMF were cast onto a freshly cleaved mica under ambient conditions, and then dried at room temperature for 0.5 h before making AFM images.

Preparation of samples for TEM. TEM specimens were prepared by gently placing a carboncoated copper grid on a surface of the metallogels sample. The TEM grid was removed, dried for 0.5 h at room temperature, and then subjected to observation.

Gelation tests for the monometallic gels and heterometallic gels. The ligand 1 and metal salts were dissolved in DMF respectively, then were mixed in a capped vial and placed at room temperature for a certain time. The sample was simply confirmed by the "stable to inversion of a

test tube" method, was formed. The heterometallic gels have been defined into 1-Co-Ni (x), x means the equivalents of Ni^{2+} to Co^{2+} .

2. Procedures for the preparation of 1, 5-dimethyl-1H-tetrazole 2

To a solution of **1** (0.2 g, 2.38 mmol) in dry DMF (5 ml) at 0 °C was added NaH (0.14 g, 60%, 3.57 mmol). The mixture was stirred at room temperature for 30 min, then CH₃I (0.51 g, 3.57 mmol) was added. After a total stirring of 4 h at 38 °C, the solvent was evaporated and the residue was diluted with CH₂Cl₂. The organic layer was washed with H₂O, and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by recrystallization from EtOAc and petroleum ether to afford **2** as a white solid (0.14 g, 62%). ¹H NMR (400 MHz, CDCl₃): δ 2.59 (s, 3H), 4.02 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 8.71, 33.33, 151.78 ppm; MS calcd for [M+1] ⁺: 99.0592; found: 99.0697; Anal. calcd for C₃H₆N₄: C, 36.73; H, 6.16; N, 57.11, found: C, 36.70; H, 6.20; N, 57.04.

[S1] L. Yan, S. Gou, Z. Ye, S. Zhang, L. Ma, Chem. Commun. 2014, 50, 12847.

	1 : Ni(OAc) ₂ ·4H ₂ O	1 : NiCl ₂ ·6H ₂ O	1: Ni(NO ₃) ₂ ·6H ₂ O
3:1	G	G (3.2 wt%)	S
2:1	G	G (2.6 wt%)	S
1:1	G	G (2.3 wt%)	S
1:2	S	G (3.7 wt%)	S
1:3	S	G (5.2 wt%)	S

Table S1 Gelation test of ligand 1 with Ni²⁺ with different anions in DMF at 25 $\,^\circ \mathbb{C}$

Table S2 Gelation test of ligand 1 with Co^{2+} with different anions in DMF at 25 $\,^{\circ}C$

	$1: Co(OAc)_2 \cdot 4H_2O$	1 : CoCl ₂ ·6H ₂ O	1 : Co(NO ₃) ₂ ·6H ₂ O
3:1	S	G (18.9 wt %)	S
2:1	S	G (13.2 wt %)	S
1:1	S	G (9.5 wt %)	S
1:2	S	G (12.4 wt %)	S
1:3	S	G (16.5 wt %)	S



Figure S1. The TOF-MS spectra of the metallogels (a) 1-Co and (b) 1-Ni.



Figure S2. (a) Tapping-mode AFM height image of metallogel **1**-Ni in DMF (0.2 wt %) on a freshly cleaved mica surface after the solvent was evaporated (scale bar: 200 nm), (b) TEM image of metallogel **1**-Ni (scale bar: 150 nm) in DMF (0. 3 wt %), (c) The intensity-weighted distribution of the aggregates obtained from the DLS measurement of the sample of metallogel **1**-Ni (0.3 wt %) in DMF at 25 °C.



Figure S3. The metallogel 1-Ni after adding TFA for 4 hours.



Figure S4. The reversible metallogel-sol transitions of the metallogel **1-**Co (10 wt%) triggered by pH- and thermo- stimuli.



Figure S5. The schematic illustration of the flexibility of coordination polymer chain of 1-Ni.



Figure S6. The UV-Vis spectra of a capped 1-Co solution after 1 day, 1 week and 1 month.



Figure S7. The stress sweep rheometry at a fixed frequency of 1.0 Hz (left) and the frequency sweep (right) of heterometallic gel **1**-Co- Ni (0.5).



Figure S8. A loop tests of heterometallic gels 1-Co-Ni (0.5) (left) and 1-Co-Ni (0.2) (right) via continuous step-stress measurements at 1 Hz. The 1-Co-Ni (0.1) was subject to 450 Pa stress for 2 mins, then back to 50 Pa in the linear regime for 2 mins, and this process could be repeated three times. Their original G' values were restored to 25% (left) and 39% (right) within 6 minutes, and another 10 minutes and 5 minutes were took to recover their original G' values, respectively.



Figure S9. The self-healing cycles of heterometallic gel **1**-Co- Ni (0.2). Heterometallic gel **1**-Co- Ni (0.1) also had the visual self-healing property, however, the wound was less obvious for taking pictures.



Figure S10. Images of injected letter "G" made by pure metallogel **1**-Co and heterometallic gel **1**-Co-Ni (0.2) (a) the fresh injected letter, (b) after 1 hour and (c) after 3 hours.

The preparation of the letter "G": First, the solutions of pure **1**-Co and heterometallic **1**-Co-Ni (0.2) were poured into a syringe respectively, then the gels would be formed after certain time. Subsequently, the letter "G" were made by injection of metallogel **1**-Co and heterometallic gel **1**-Co-Ni (0.2).



Figure S11. The UV-Vis spectra of heterometallic 1-Co-Ni (0.2) when exposed in air at 25 °C.



Figure S12. ¹H NMR spectrum of ligand **2** in CDCl₃ at 293K.



Figure S13. ¹³C NMR spectrum of ligand **2** in CDCl₃ at 293K.