

Supporting Information for:

Pb²⁺-specific Metallohydrogel Based on Tryptophan-Derivatives: Preparation, Characterization, Multi-stimuli-responsiveness and Potential Applications in Wastewater and Soil Treatment

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1. Experimental Section

1.1 Reagents

1,4-Benzenedicarboxaldehyde Terephthalaldehyde and Benzaldehyde were purchased from Alading (Shanghai, China); sodium borohydride was purchased from Xiya Reagent (Chengdu, China); L - typtophan, was purchased from Xiensi Reagent (Tianjin, China). All other reagents were of analytical grade and deionized water (MillQ, 6.8M Ω) was used.

1.2 Instrumentation

Field emission scanning electron microscopic (FE-SEM) study: Scanning electron microscope (SEM) images were obtained on a FEI HELIOS NanoLab 600i SEM (America).

Transmission electron microscopy (TEM) study: Transmission electron microscope (TEM) images were carried out on a FEI Titan G2 60-300 TEM (America)

FTIR spectroscopy: FT-IR spectra were recorded with a Perkin Elmer Spectrum One instrument (America). Firstly, KBr crystals baked by infrared light were used as the matrix for sample preparation, and then KBr was mixed with the powdered samples to prepare the thin films.

UV/Vis spectroscopy: were recorded on Shimadzu UV-2450 spectrometer (Japan).

Fluorescence spectroscopy: The samples were detected by using Hitachi F-7000(Japan)

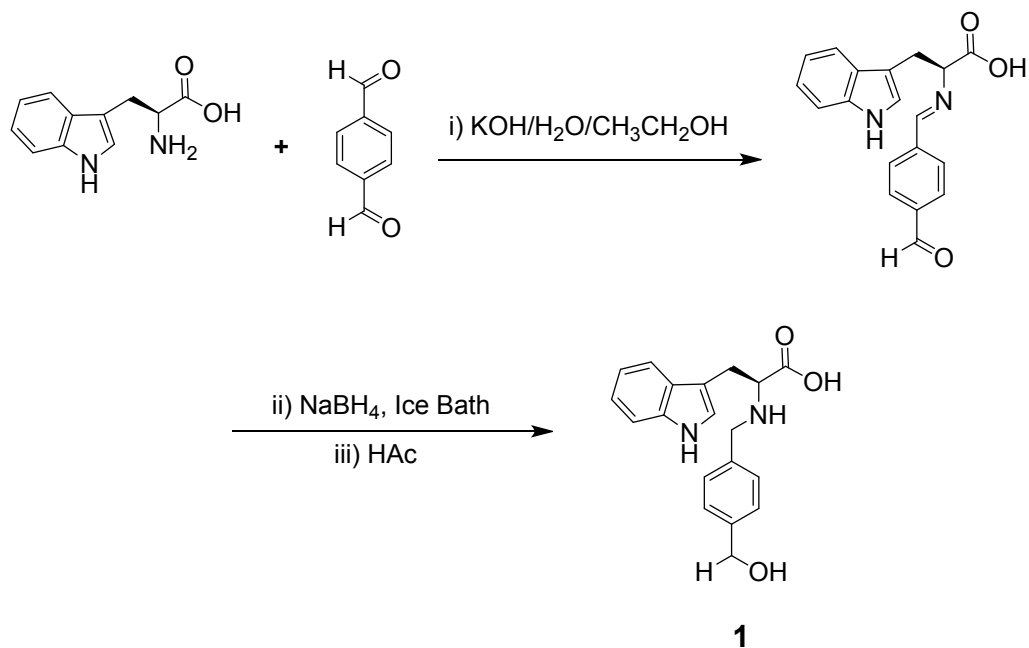
Rheology: The rheological studies were carried out on a rotated rheometer (AR 2000ex, TA Instrument, America).

NMR experiments: The samples were obtained by using AMX-500 (Bruker, Switzerland)

Circular dichroism (CD) study: Circular dichroism spectra of different samples were obtained by using Jasco-815 CD spectrometer (Japan). The samples were detected by using 1mm quartz cell.

1.3 Synthetic Procedures

1.3.1 Synthetic route of compound 1

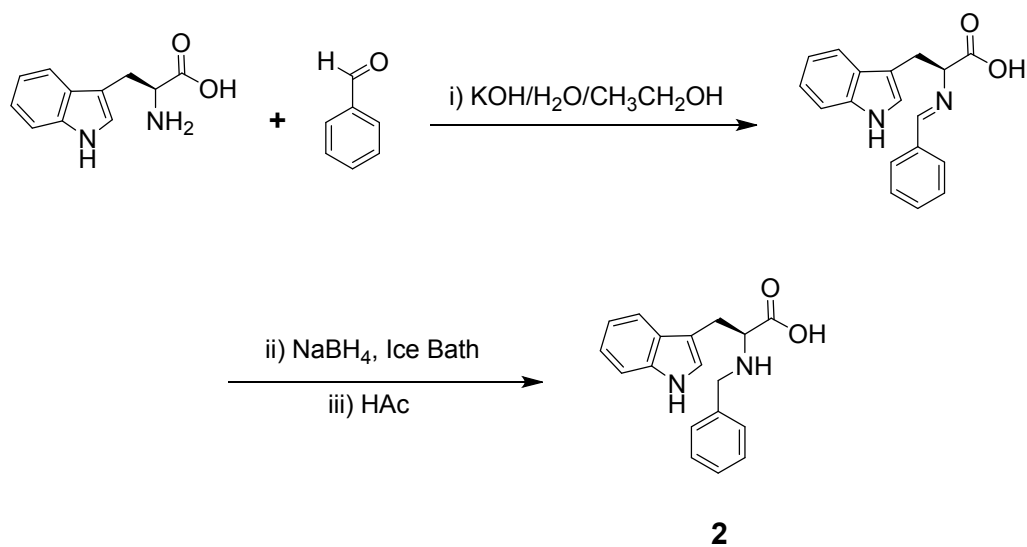


(S)-2-((4-(hydroxymethyl)benzyl)amino)-3-(1H-indol-3-yl)propanoic acid

Scheme 1 Synthetic route of compound 1

Preparation of compound 1 (**HAIP**): The compound 1 was prepared following a modified literature procedure.¹ To an aqueous solution (10 mL) of L - tryptophan (1 g, 5 mmol) containing KOH (0.28 g, 5 mmol), 1,4-Benzenedicarboxaldehyde Terephthalaldehyde (0.67 g, 5 mmol) in ethanol (5 mL) was added slowly. The solution was stirred for 3 h at room temperature, and during this period the color of the solution was more and deeper. Then the solution was cooled in an ice bath. NaBH₄ (0.23 g, 6 mmol) was added to the solution slowly. The mixture was stirred for 3 h, and 50% acetic acid was used to neutralize the basic (pH~10) reaction mixture and adjusted the pH to 4.0-5.0. The mixture system was stirred further for 3 h. The resulting solid was filtered off, and washed with ethanol and water, dried, and recrystallized from water/ethanol (3:1). Yield (compound 1): 1.1 g, 65.0%. ¹H NMR (500 MHz, (CD₃)₂SO, ppm): -CH₂ (1.88, s, 2H), -CH₂OH (4.45, s, 2H), In-H and Phe-H (6.94-7.50, m, 10H), -NH(10.79, s, 1H), -COOH(10.89, s, 1H) MS (ESI): calc. for C₁₉H₂₀N₂O₃ 324.15; observed 325.16 [M + H]⁺.

1.3.2 Synthetic route of compound 2



Scheme 2 Synthetic route of compound 2

Preparation of compound 2 (**BAIP**) : The compound 2 was prepared following a modified literature procedure.¹ To an aqueous solution (10 mL) of L/D-tryptophan (1 g, 5 mmol) containing KOH (0.28 g, 5 mmol), 1,4-Benzenedicarboxaldehyde Terephthalaldehyde (0.53 g, 5 mmol) in ethanol (5 mL) was added slowly. The solution was stirred for 3 h at room temperature, and during this period the color of the solution was more and deeper. Then the solution was cooled in an ice bath. NaBH₄ (0.23 g, 6 mmol) was added to the solution slowly. The mixture was stirred for 3 h, and 50% acetic acid was used to neutralize the basic (pH~10) reaction mixture and adjusted the pH to 4.0-5.0. The mixture system was stirred further for 3 h. The resulting solid was filtered off, and washed with ethanol and water, dried, and recrystallized from water/ethanol (3:1). Yield (compound 2): 1.2 g, 78.4%. ¹H NMR (500 MHz, D₂O, ppm): -CH₂ (2.82, d, 2H). -CH (3.17, t, *J* = 6.7 Hz, 1H), -CH₂ (3.55, d, 2H), In-H and Phe-H (6.94-7.44, m, 11H) MS (ESI): calc. for C₁₈H₁₈N₂O₂ 294.15; observed 293.35 [M - H]⁺.

1.4 Characterization Data

1.4.1EI-MS

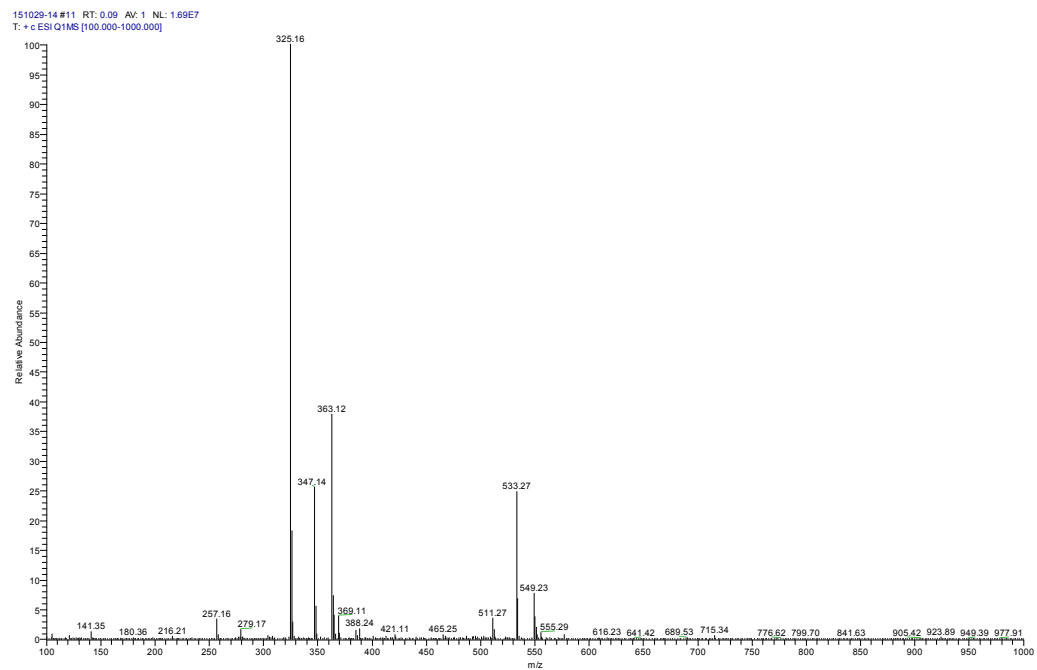


Fig. S1 Electrospray ionization mass spectra of Compound 1(HAIP).

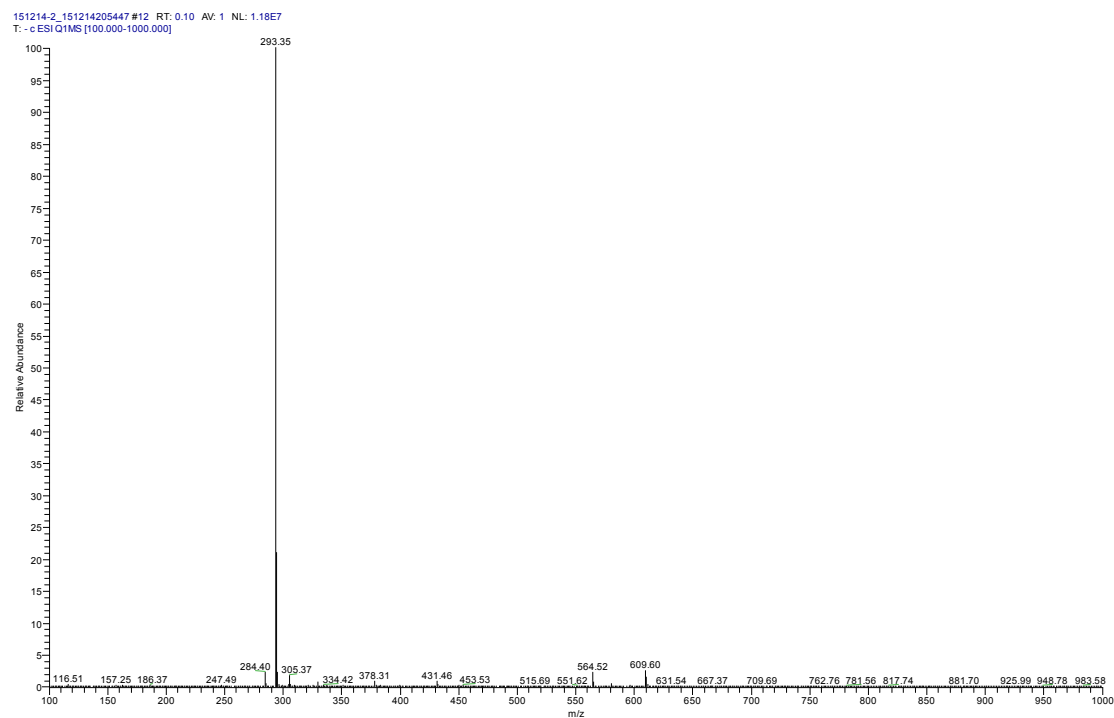


Fig. S2 Electrospray ionization mass spectra of Compound 2(BAIP).

1.4.2 ^1H NMR spectrum

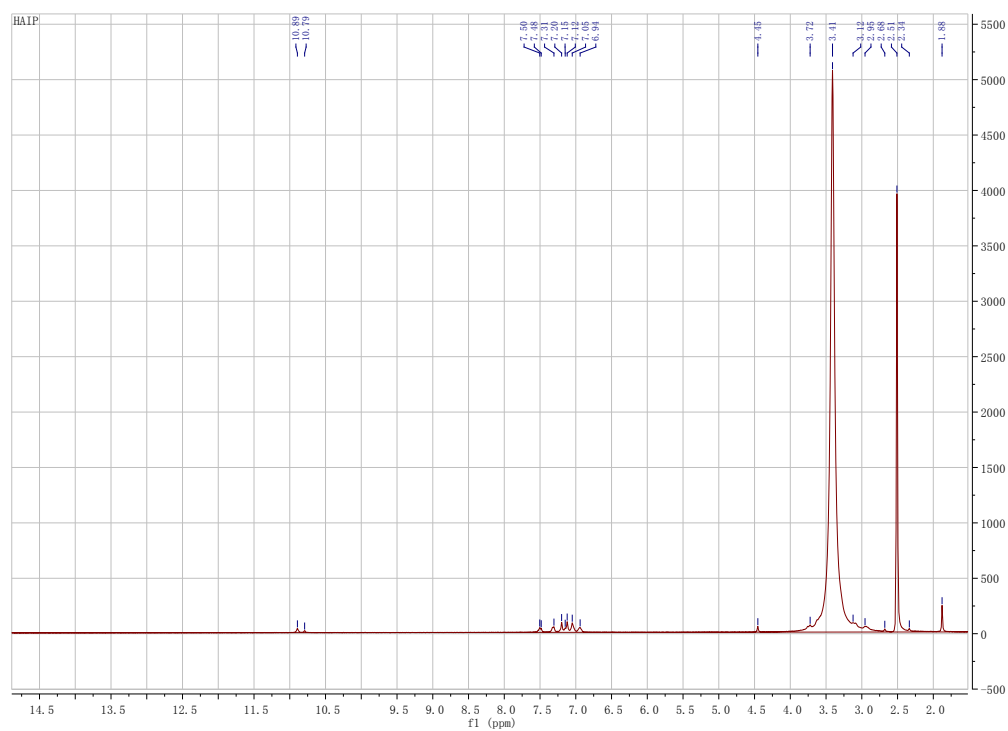


Fig. S3 ^1H NMR (500 MHz) Spectra of Compound 1(HAIP) in $(\text{CD}_3)_2\text{SO}$.

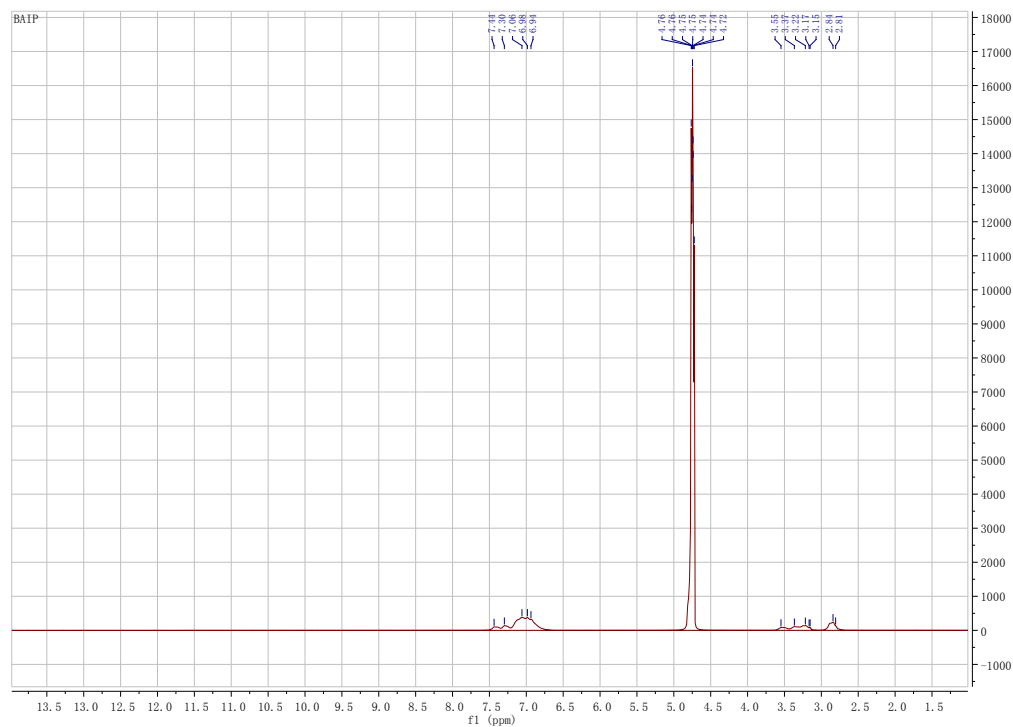


Fig. S4 ^1H NMR (500 MHz) Spectra of Compound 2(BAIP) in D_2O .

2. Supplementary Figures

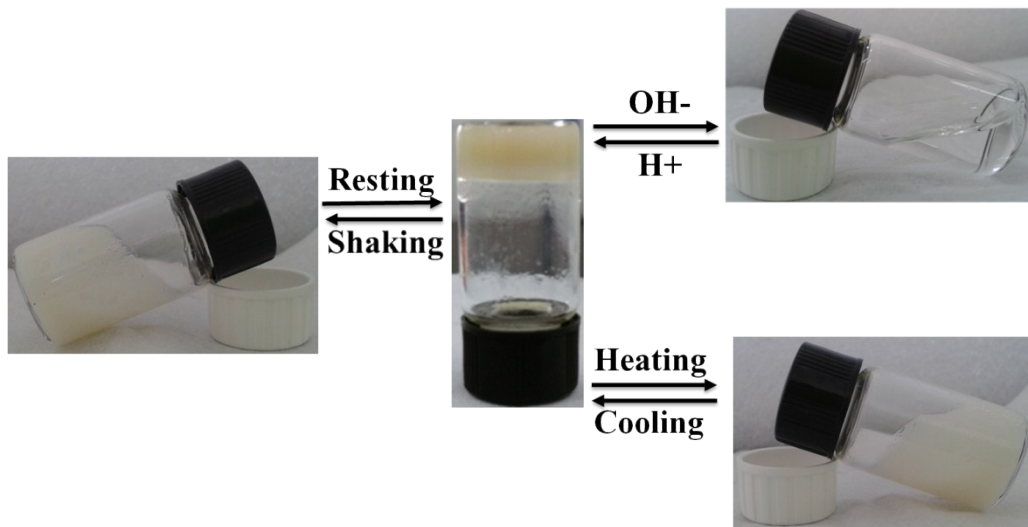


Fig. S5 Reversible gel-sol transitions of the HAIP-gel triggered by multiple stimuli (shear stress, temperature, and pH).

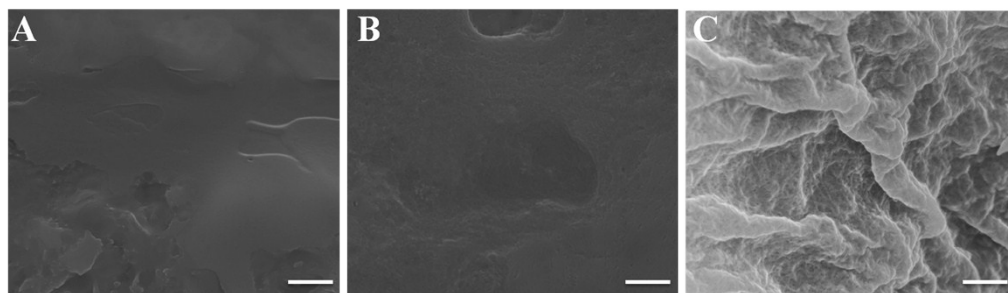


Fig. S6 A) SEM images of HAIP solution ($\text{pH} > 9$) B) HAIP suspension ($\text{pH} \leq 8$) without ultrasound C) As prepared HAIP-gel by sonication. The scale bars are $2 \mu\text{m}$, $1 \mu\text{m}$, $1 \mu\text{m}$, respectively.

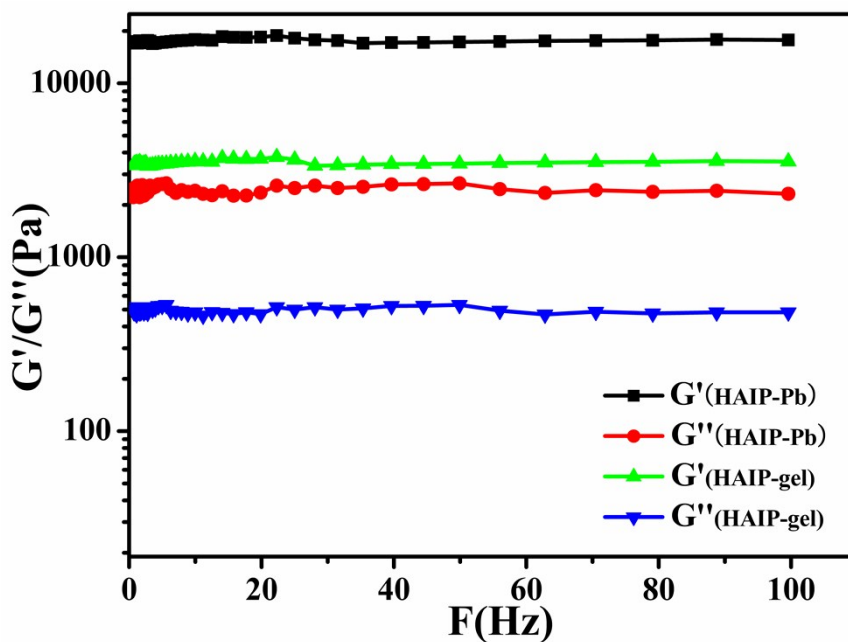


Fig. S7 Dynamic frequency sweep of fresh HAIP-gel and HAIP-Pb metallohydrogel, measured at 0.1% strain, respective MGC.

From Fig. S7, we found that the average values of storage modulus G' of HAIP-gel and HAIP-Pb were always higher than the loss modulus (G'') respectively. G' and G'' values exhibited slight dependence on frequency over the entire measurement range (0.1–100 Hz). All these results illustrated the presence of gel phase. Moreover, the G' values of HAIP-Pb are larger than that of HAIP, indicating that the mechanical strength of the gel greatly improved because of introduction of Pb^{2+} .

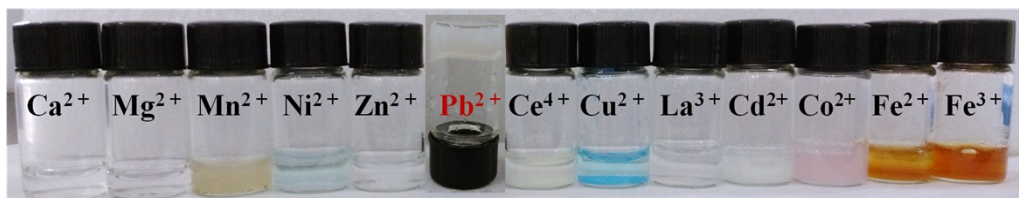


Fig. S8 Photos of complexes of HAIP and different metal ions (from left to right: Mn^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Ce^{4+} , Cu^{2+} , La^{3+} , Cd^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+}).

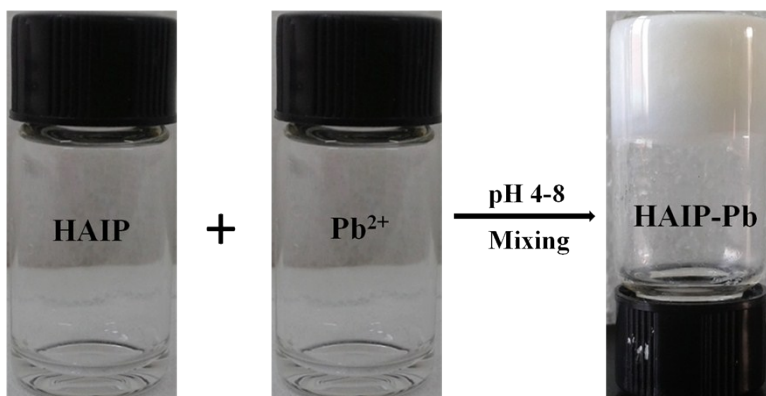


Fig. S9 Schematic diagram of Synthesis of HAIP-Pb at the MGC. $n(\text{HAIP})/n(\text{Pb}) = 2:1$.



Fig. S10 Schematic diagram of Synthesis of BAIP-Pb. $n(\text{BAIP})/n(\text{Pb}) = 2:1$.

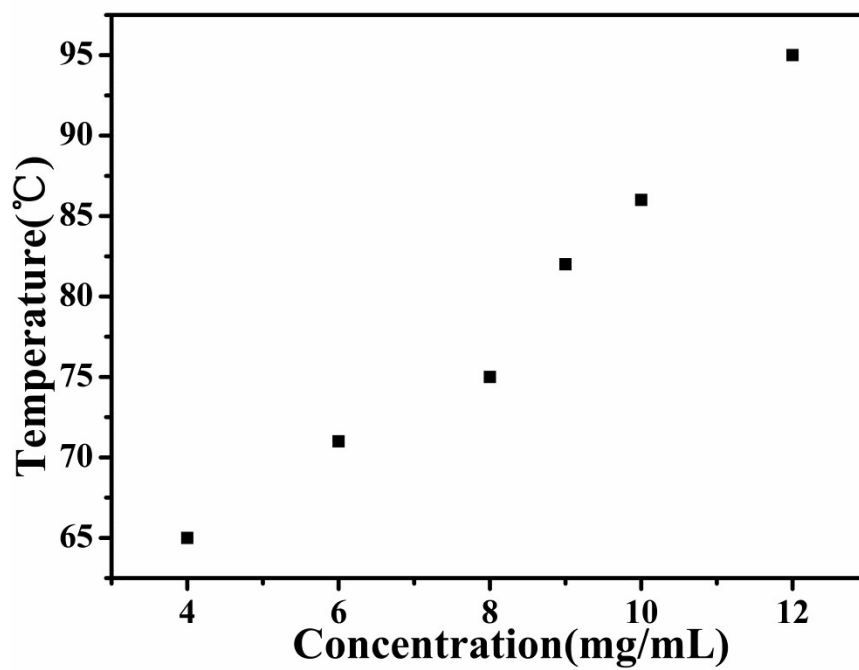


Fig.S11 Plot of Tgel of HAIP-Pb metallohydrogels with different concentrations (4 mg/mL, 6 mg/mL, 8 mg/mL, 10 mg/mL, 12 mg/mL).

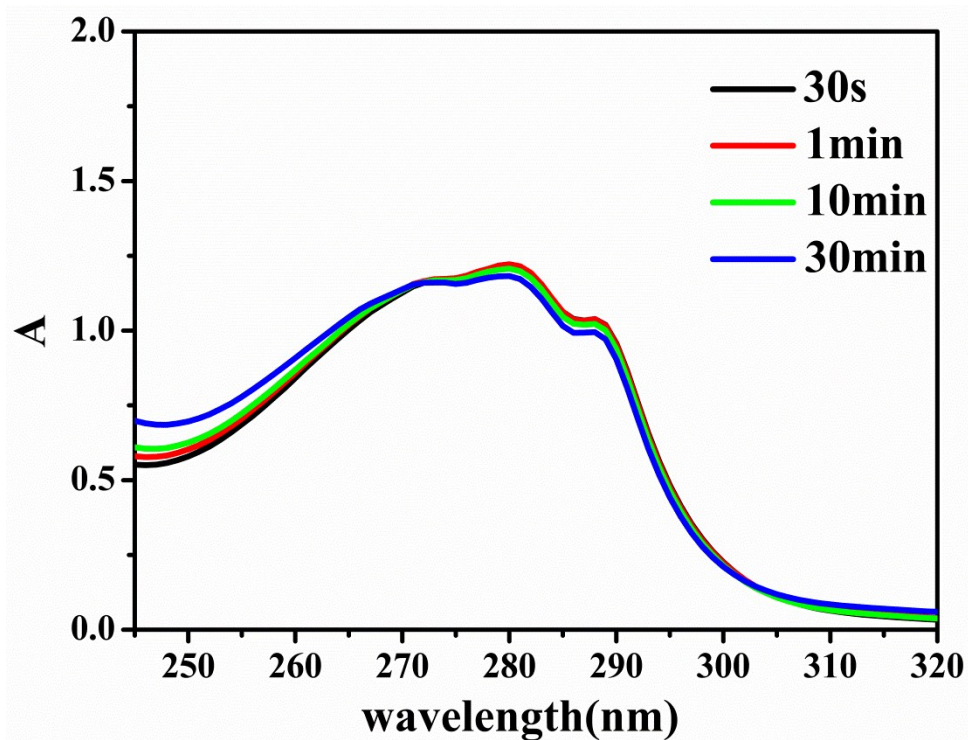


Fig. S12 The time-dependent UV-Vis spectra of the mixture of HAIP and Pb^{2+} (The concentration of all solutions is $200 \mu M$, $n(HAIP)/n(Pb) = 2:1$).

To identify the dynamic gelation behavior of HAIP-Pb gel, we conducted time-dependent UV-vis absorption investigations (Fig. S12[†]); the results suggested that the coordination reaction between HAIP and Pb^{2+} is a rapid process.

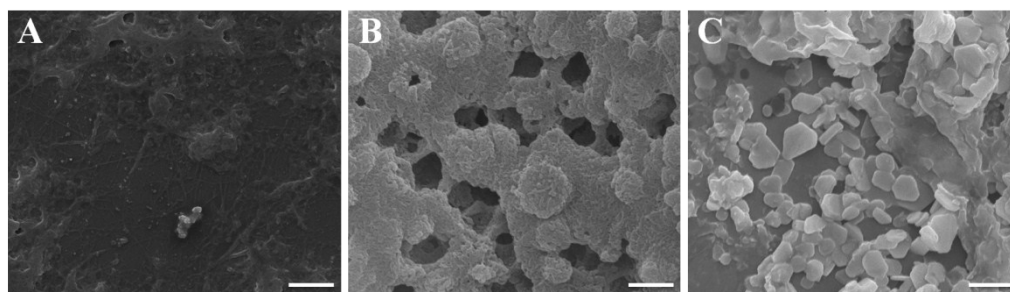


Fig. S13 SEM images of HAIP-Pb A) after heating, B) after shaking, C) adding KI. The scale bars are $2 \mu m$, $1 \mu m$, $1 \mu m$, respectively.

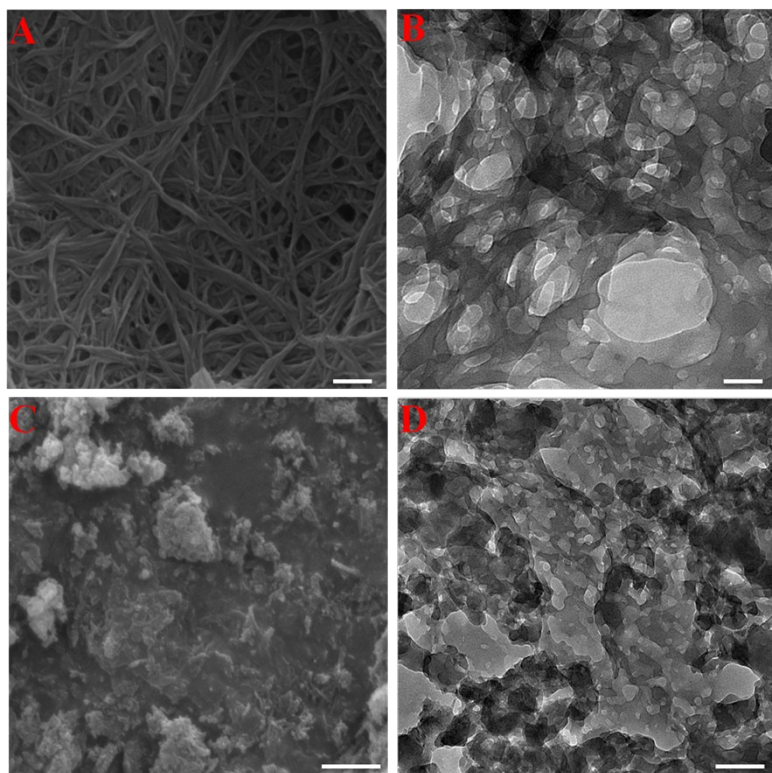


Fig. S14 A) SEM and B) TEM images of the cryo-dried HAIP-Pb metallohydrogel. C) SEM and D) TEM images of the cryo-dried HAIP-Pb-MB metallohydrogel. The scale bars are 1 μm , 100 nm, 2 μm , 200 nm, respectively.

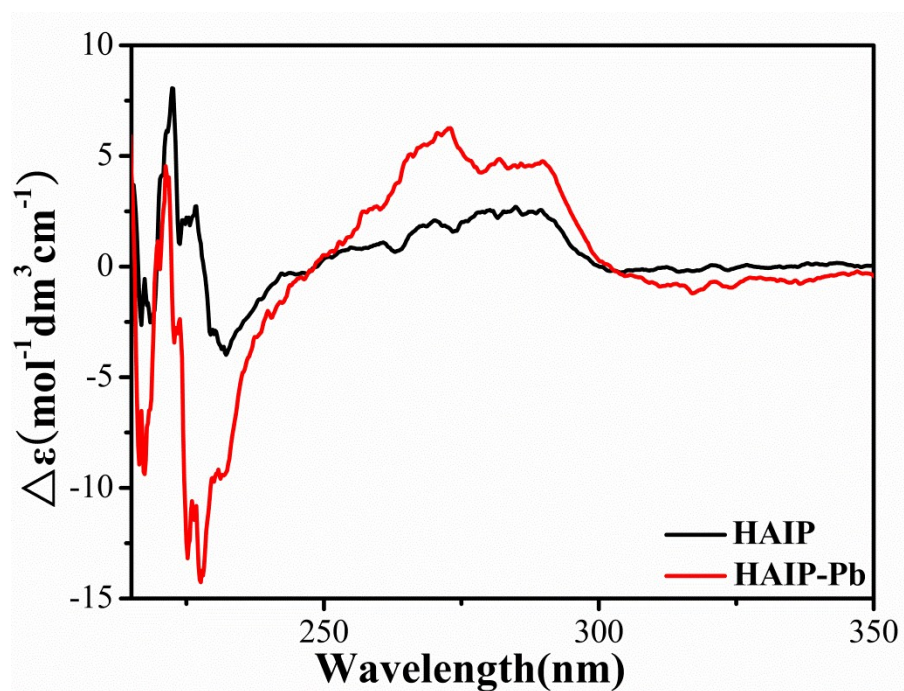


Fig. S15 CD signals for HAIP (black) and HAIP-Pb (red), respectively (The concentration of all solutions is 2.5 Mm, $n(\text{HAIP})/n(\text{Pb}) = 2:1$.).

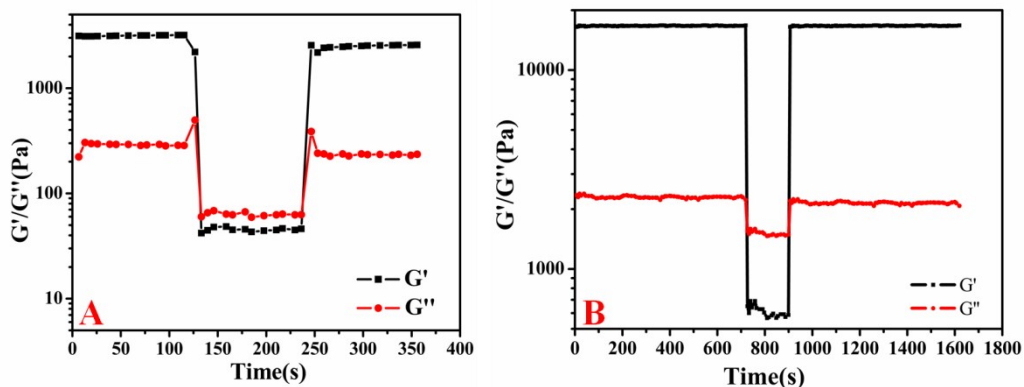


Fig. S16 The step strain experimental data obtained from the gels A) HAIP-gel (The concentration was maintained at MGC) and B) HAIP-Pb (The concentration was maintained at MGC and the ratio of HAIP and Pb^{2+} was 2:1.) at strain = 0.1%.

A time dependent step-strain rheological experiment of HAIP-gel (Fig.S16A) was performed at a constant frequency of 1 Hz. The storage modulus (G') was higher than the loss modulus values (G'') at the constant strain 0.1%, indicating a gel nature. Nevertheless, at constant strain 35%, the value of G'' was larger than G' , which implied a disruption of the network of the gel. After removing of 35% strain, the gel restored 95% of its original mechanical strength after 30 minutes. A similar viscoelastic behavior (Fig.S16B) was observed for HAIP-Pb metallogel. However, the difference between HAIP and HAIP-Pb is that the HAIP-Pb gel immediately restored 95% of its original mechanical strength and recovered to 100% in several seconds after removing of 35% strain. This process could be repeated for at least 5 cycles without an obvious reduction in the average magnitude of G' and G'' .

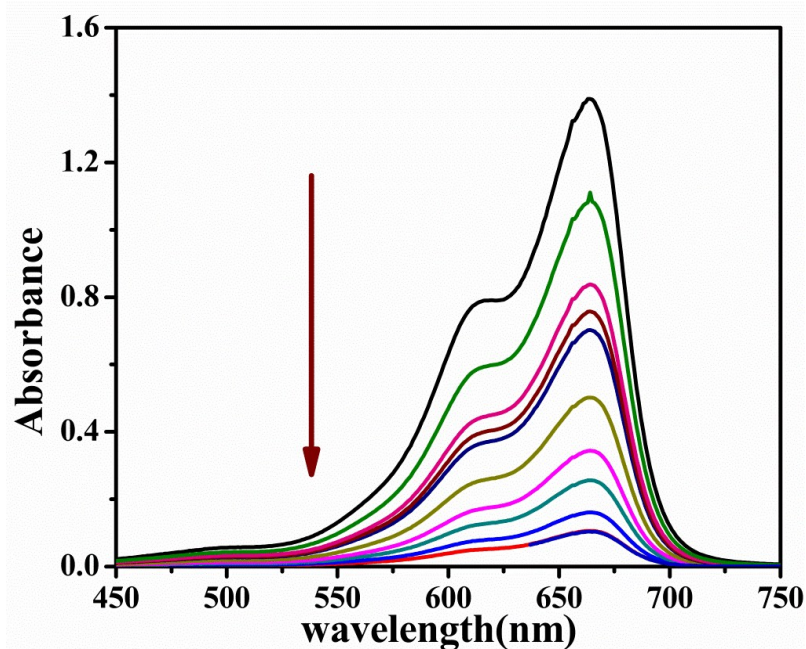


Fig. S17 UV-Vis study of MB on HAIP-Pb hydrogel sampling the supernatant at time 0 h, 3 h, 5 h, 10 h, 13 h, 15 h, 17 h, 20 h, 25 h, 30 h, 35 h (top to bottom).

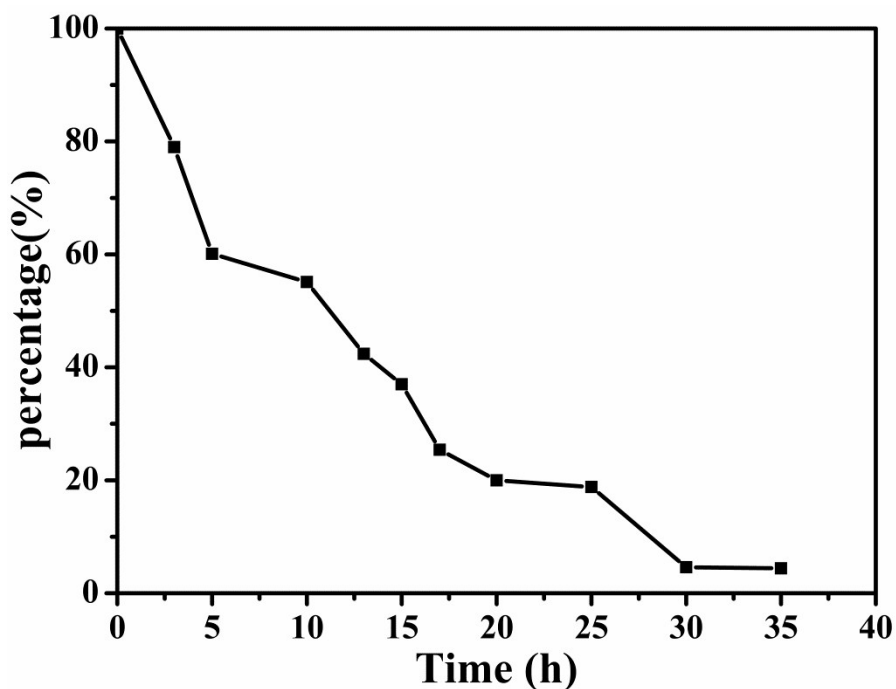


Fig. S18 Plots of λ_{\max} vs. time (methylene-blue absorption at $\lambda_{\max} = 664$ nm)

Adding 500 μ L 1 mM aromatic dye MB to 1 mL gel HAIP-Pb (MGC), the gel was covered with MB aqueous solution on the surface of it in an incubator. A few minutes later, the gel layer gradually turned blue. Kinetic-study was conducted, a small amount of the supernatant was taken out every once in a while, and their UV spectra (Fig. S17†) were measured to note the value of absorbance at 664 nm. After 30 h, the gel layer was dark blue, while aqueous solution layer was almost colorless. And the absorbance value was very low, showing that the adsorption efficiency of MB was large (95.36%) (Fig. S18†) and the uptake is 380 mg(MB)/1g gelator.

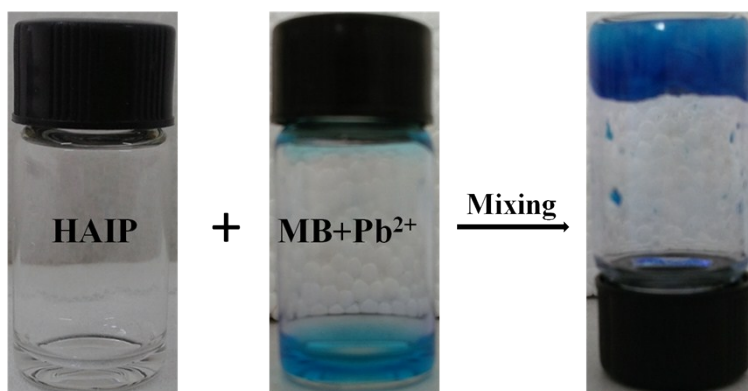


Fig. S19 The gelation process of HAIP(MGC) and the mixture of (MB + Pb²⁺), n(HAIP)/n(Pb) = 2:1.

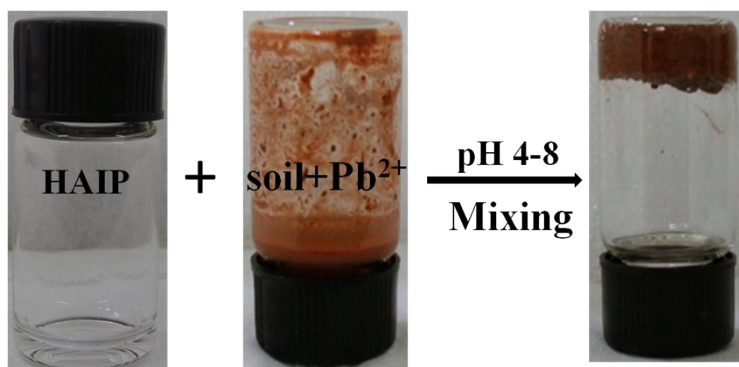


Fig. S20 Digital photos on gelation of HAIP(MGC) and the soil containing Pb²⁺ ions, n(HAIP)/n(Pb) = 2:1.

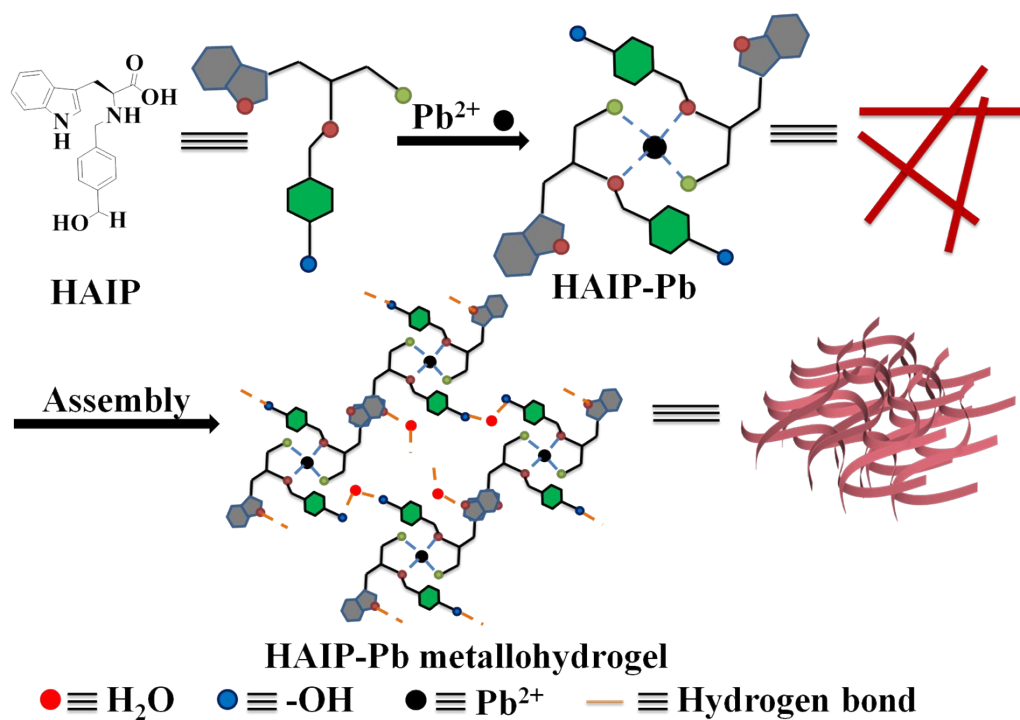


Fig. S21 Schematic representations of the probable local structure of HAIP-Pb metallohydrogel.

References

- 1 L. L. Koh, J. O. Ranford, W. T. Robinson, J. O. Svensson, A. L. C. Tan and D. Wu, *Inorg. Chem.*, 1996, **35**, 6466.