Supporting Information

A La$^{3+}$-selective metallohydrogel with a facile gelator of phenylalanine derivative containing an imidazole group

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1. Experimental Section

1.1 Reagents

Phenylalanine (Phe) and sodium borohydride (NaBH₄) were purchased from Aladin Reagent (Shanghai, China), 1H-Imidazole-4-carbaldehyde was purchased from Xiensi Reagent (Tianjin, China) and was used without further purification. All other reagents were of analytical grade, which include Na₂CO₃, HCl, KOH, NaBH₄, MgCl₂, CaCl₂, CdCl₂, Pb(Ac)₂, ZnSO₄·6H₂O, Ni(Ac)₂·6H₂O, CoCl₂·5H₂O, FeCl₃, Cu(Ac)₂·H₂O, MnSO₄, La(NO₃)₃·6H₂O, LaCl₃, La₂(SO₄)₃, Ce(NO₃)₃·6H₂O, Pr(NO₃)₃·6H₂O, Nd(NO₃)₃·6H₂O, Sm(NO₃)₃·6H₂O, Eu(NO₃)₃·6H₂O, Gd(NO₃)₃·6H₂O, Tb(NO₃)₃·5H₂O, Dy(NO₃)₃·5H₂O, Er(NO₃)₃·5H₂O, Y(NO₃)₃·5H₂O and Lu(NO₃)₃·6H₂O. Deionized water (MillQ, 18.2 MΩ) was used.

1.2 Synthesis of ImF ligands

Preparation of ImF: The compound ImF was prepared following a modified literature procedure[1,2]. To an aqueous solution (10 mL) of Phe (0.83 g, 5 mM) containing Na₂CO₃ (0.53 g, 5 mM), 1H-Imidazole-4-carbaldehyde (0.48 g, 5 mM) in CH₃CH₂OH (5 mL) was added slowly. The solution was stirred for 3 h at 40 °C. Then the solution was cooled in an ice bath. NaBH₄ (0.23 g, 6 mM) was added to the solution slowly. The mixture was stirred for 3 h, and 6mol·L⁻¹ hydrochloric acid was used to neutralize the basic (pH~10) reaction mixture and the pH was adjusted to 5.0-6.0. The mixture system was stirred further for 2 h. The resulting solid was filtered off, and was washed with ethanol and water, then dried.

ESI-MS (Q-TOF): calc. for C₁₃H₁₅N₃O₂ 245.11, observed 244.11 [M - H]⁺, 282.07 [M+K - 2H]⁻.

Scheme S1. Synthetic route of ImF.
$^1$H NMR (500 MHz, D$_2$O, ppm): -CH$_2$(2.93-2.94, d, 2H). -CH (3.35-3.38, 1H), -CH$_2$ (3.67-3.88, dd, 2H), Im-H (6.87, 1H), Phe-H (7.26-7.37, m, 5H), Im-H (7.47, 1H).

1.3 Preparation of La-ImF metallohydrogels

La-ImF metallohydrogel was prepared by mixing ImF solution (12 mM, ~pH 5-8) and La(NO$_3$)$_3$ solution with ratio of 2:1 (volume). The mixture was changed into a white metallohydrogel after shaking for several seconds.

1.4 ITC studies

Isothermal titration calorimetry (ITC) measurements were performed on a Microcal VP-ITC microcalorimeter (GE life sciences). Both ImF and La(NO$_3$)$_3$ solution were thoroughly degassed in a ThermoVal apparatus (Microcal). For titration experiments, ~1.5 mL La(NO$_3$)$_3$, LaCl$_3$ or La$_2$(SO$_4$)$_3$ (25 mM) solution was placed in the reaction cell, and a solution of ImF (1 mM) was injected over 20 s with a total of 25 injections (10 μL for per injection), with a 150 s interval between each injection. The reaction cell was continuously stirred at 502 rpm, and heat changes were recorded at 298.15 K. The data were analyzed and the binding isotherm was fitted to a single-site model in the Origin 7.0 software (GE life sciences).

1.5 UV-Vis studies

UV-Vis spectral changes of methyl orange (MO) and methylene-blue (MB) in presence of La-ImF complex were recorded in deionized water on a Hewlett-Packard 8453 diode array spectrometer. The reduction of MO and MB in La-ImF complex, respectively, was performed by monitoring the UV-Vis spectral changes for 0-30 h.

1.6 SEM, TEM, ESI-MS and NMR studies

Scanning electron microscope (SEM) images were obtained on a FEI HELIOS NanoLab 600i SEM (America). Transmission electron microscope (TEM) images were obtained from a FEI Titan microscope (America). La-ImF complex and ImF
complex mass spectrum measurement were obtained by using Xevo G2-XS QTof mass spectrometer (Waters, America). The La-ImF complex and ImF complex were dissolved in water and then passed through a 0.22 μm membrane filtration. NMR experiments were performed by using AMX-500 (Bruker, Switzerland).

1.7 Fluorescence spectral studies

Fluorescence spectral measurements were performed on a Fluorescence spectrometer (F-7000, Hitachi). The samples were prepared by mixing ImF solution (5 mM) and various lanthanide salt solutions (5 mM) with ratio of 2:1 (volume).

Reference


2. Supplementary Figures

**Fig. S1** ESI-MS spectra of compound ImF. Calculated: 245.1086 Da; Observed: 244.1113 Da ([ImF-H]), and 282.0748 Da ([ImF+K-2H]).

**Fig. S2** $^1$H NMR (500 MHz) spectrum of compound ImF in D$_2$O.
Fig. S3 The synthesis of ImF-Gel at MGC (C_{ImF} = 20 mM), pH 5-8.

Fig. S4 Digital photos of ImF in complex with different metal ions.

Fig. S5 Time-dependent UV-Vis spectra of ImF in complex with La(NO_3)_3 (The concentration of all solutions is 3 mM, n(ImF)/n(La^{3+}) = 2:1).
Fig. S6 Digital photos of La-ImF gels prepared by using LaCl$_3$ (left), La(NO$_3$)$_3$ (middle), and La$_2$(SO$_4$)$_3$ (right).

Fig. S7 Dynamic frequency sweep of fresh ImF-gel and La-ImF metallohydrogel at their respective MGC, measured at 0.1% strain.
**Fig. S8** Plot of T_{gel} of ImF-gel and La-ImF in different concentrations (12, 20, 40, 60, 80 and 100 mM).

**Fig. S9** The step strain experimental data obtained from La-ImF metallohydrogel. The concentration was maintained at MGC \( n(\text{ImF})/n(\text{La}^{3+}) = 2:1 \), strain = 0.1%. 
**Fig. S10** (A) TEM image of La-ImF metallohydrogel (MGC), SEM images of (B) ImF aqueous solution (10 mM), and (C) ImF-Gel (MGC).

**Fig. S11** Microcalorimetric titration of ImF with (A) La(NO$_3$)$_3$, (B) LaCl$_3$, and (C) La$_2$(SO$_4$)$_3$ in water at 298.15 K. (Top) Raw ITC data for 25 sequential injections (10 µL per injection) of La(NO$_3$)$_3$ solution (25 mM) into ImF solution (1 mM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.
Fig. S12 ESI-MS spectra of ImF-La(NO₃)₃: [(ImF)₂ + La] Calculated: 627.1235 Da; Observed: 627.0978 [(ImF)₂ + La]⁺, 872.1910 Da [(ImF)₃ + La]⁺ and 910.1393 Da [(ImF)₃ + La + K⁻ -H]⁺.

Fig. S13 Exitation spectrum of La-ImF complex.
**Fig. S14** Fluorescence spectra of ImF and its complexes with various lanthanide ions ($\lambda_{ex} = 315$ nm).

**Fig. S15** Digital photos of the absorption of MO and MB by the La-ImF metallohydrogel, and the corresponding UV-Vis spectral changes over time.