Supporting information

Super Metal-Hydrogels Constructed from Simple Tripodal Gelator with Rare Earth Metal Ions and Its Application in Highly Selective and Ultrasensitive Detection Histidine

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Materials and General Methods:

**Materials:** 4-aminopyridine, trimesoyl chloride, DMF, triethylamine, ethyl alcohol, Tb$^{3+}$, Eu$^{3+}$, La$^{3+}$ and Ce$^{3+}$ and acids were reagent grade and used as received. Solvents were either employed as purchased or dried by CaCl$_2$. Fresh double distilled water was used throughout the experiment. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Study of scanning electron microscopy (SEM), Determination of the SEM images was performed on a JSM-6701F FE-SEM microscope.

**Preparation of water suspension of TP:** About 10 mg of TP was weighed out in a test bottle. Then, 2.0 mL deionized water was added into that test bottle followed by shaking for 1−3 min at room temperature, producing a viscous and milky suspension (0.5%).

**Preparation of hydrogel based on Tb$^{3+}$, Eu$^{3+}$, La$^{3+}$ and Ce$^{3+}$:** To a solution of Tb$^{3+}$, Eu$^{3+}$, La$^{3+}$ and Ce$^{3+}$ (20 μL, 0.1 M) was added into the emission of TP (200 μL, 0.5 %). The mixture of emission and Tb$^{3+}$, Eu$^{3+}$, La$^{3+}$ and Ce$^{3+}$ was heated to obtain a colorless solution, cooling the above solution to give white hydrogel.

**Fluorescence titration:** A serious of the gel with different equivalents guests were prepared by dissolving TP (2 mg) and proper equivalent of guest in water (400 μL). Then record their fluorescence intensity at 467 nm.

**Calculation formula of LOD:**
Linear Equation: \( y = Ax + B \)

\[
\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} (N = 20)
\]

\( S = A \delta 10^6 \),

\( LOD = K \delta S (K = 3) \)

**State**, \( F_i \): the fluorescence intensity of TP-Eu or TP-La with different concentration His at \( \lambda_{ex} = 467 \) nm; \( F_0 \): the average of 20 times fluorescence intensity of TP-Eu or TP-La at \( \lambda_{ex} = 467 \) nm; \( A \): Slope of linear fitting of fluorescence titration; \( B \): intercept of linear fitting of fluorescence titration.

**Results and Discussion:**

![Scheme S1. The synthesis of TP.](image)

The gelator TP was synthesized by simple classical reaction between 4-aminopyridine and trimesoyl chloride. To a solution of mixture of trimesoyl chloride (0.2639 g, 1.0 mmol) and triethylamine (1-2 d) was slowly dropwise added into the solution of 4-aminopyridine (0.3105 g, 3.3 mmol) in DMF (10 mL), the mixture was stirred at room temperature for 12 h, appearing a pale solid. The solid is vacuumed suction filtration and washed with cold ethyl alcohol (10 ml), finally the product solid was followed by drying in a vacuum oven at 40 °C for 24 h. Yield: 0.0421g (96%). M.P.: 167-168 °C.
$^1$H NMR (400 MHz, DMSO-$d_6$, room temperature) δ (ppm): 11.78 (s, 3 H), 8.99 (s, 3 H), 8.68 (m, 6 H), 8.25 (m, 6 H); $^{13}$C NMR (DMSO-$d_6$, 150MHz): 165.68, 149.58, 135.07, 131.36, 114.75; ESI-MS m/z: [M]$^+$ Calcd: C$_{24}$H$_{18}$N$_6$O$_3$: 439.14, found 439.19; IR (anhydrous KBr, cm$^{-1}$) v: 3421 (w) (N-H), 3080 (w) (C-H on pyridyl and phenyl group), 1710 (w) (C=O), 1508 (w) (C=N on pyridyl).

**Figure S1.** The $^1$H NMR Spectrum of TP.

**Figure S2.** The $^{13}$C NMR spectrum of TP.
Figure S3. Mass spectrum of TP.

Figure S4. IR spectrum of TP.
**Table S1.** Gelation property of super supramolecular metallo-hydrogels.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solution</th>
<th>State</th>
<th>CGC(%)</th>
<th>Tgel(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$^{3+}$</td>
<td>H$_2$O</td>
<td>G</td>
<td>0.5%</td>
<td>57-59 (0.5%)</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>H$_2$O</td>
<td>G</td>
<td>0.5%</td>
<td>75-77 (0.5%)</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>H$_2$O</td>
<td>G</td>
<td>0.5%</td>
<td>55-57 (0.5%)</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>H$_2$O</td>
<td>G</td>
<td>0.5%</td>
<td>52-54 (0.5%)</td>
</tr>
</tbody>
</table>

G=gelation

**Figure S5.** FT-IR spectra of His, xerogel of TP-Ms and TP-Ms+ His (TP-Ms: TP-Eu, TP-La).

**Figure S6.** FT-IR spectra of TP and xerogel of TP-Ms: (a) TP-Ce, (b) TP-Tb.
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Figure S8. The Powder XRD spectra of TP and xerogel of TP-Ce and TP-La.
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Figure S12. Fluorescence titration linear range of TP-Eu for His by addition various concentrations His into TP-Eu.

Figure S13. Fluorescence titration linear range of TP-La for His by addition various concentrations His into TP-La.