Electronic Supplementary Information (ESI) for:

A heat-set lanthanide metallogel capable of emitting stable luminescence under thermal, mechanical and water stimuli

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Additional data

1. $^1$H-NMR spectra of H$_6$L

$^1$H-NMR spectrum of H$_6$L in DMSO-$d_6$ was recorded on a Bruker Avance III spectrometer operating at 400 MHz. 13.03 (6H), 9.70 (3H), 8.46 (6H), 8.11 (3H).

![Fig. S1 $^1$H NMR spectra of H$_6$L in DMSO-$d_6$.](image)

2. ESI-MS spectra of H$_6$L

H$_6$L was dissolved in DMF and diluted to $10^{-5}$ M with acetonitrile, and its ESI mass spectrum was recorded on a Bruker UltiMate 3000-microTOFII in positive-ion mode. MS m/z: calcd. For C$_{27}$H$_{18}$N$_6$O$_{12}$ [H$_6$L+H]$^+$: 619.1062; found: 619.1042.
3. Preparation of H₆L/Tb gel in varied solvents

H₆L (7.4 mg, 0.012 mmol) and TbCl₃·6H₂O (4.5 mg, 0.012 mmol) were dissolved in a predetermined volume of DMF or DMSO (mL) after which CH₃OH, H₂O or CH₃CH₂OH (predetermined volume, mL) was added with vortex blending. A total mixed solution of 1 mL was then placed in a closed vessel (5 mL) and heated for 2 h at 85°C to achieve gelation.

**Tab. S1** Gelation tests of H₆L and Tb³⁺ in different mixed solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>V/V</th>
<th>9:1</th>
<th>8:2</th>
<th>7:3</th>
<th>6:4</th>
<th>5:5</th>
<th>4:6</th>
<th>3:7</th>
<th>2:8</th>
<th>1:9</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF/CH₃OH</td>
<td>S</td>
<td>S</td>
<td>TS</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>TS</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>DMF/H₂O</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>DMSO/H₂O</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>DMF/CH₃CH₂OH</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>TS</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>DMSO/CH₃OH</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>S</td>
<td>S</td>
<td>TS</td>
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<td></td>
</tr>
<tr>
<td>DMSO/CH₃CH₂OH</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>TS</td>
<td>TS</td>
<td>P</td>
</tr>
</tbody>
</table>

S = solution; G = gel; TS = turbid solution; P = precipitation.

4. Preparation of H₆L/Tb gel with different H₆L or Tb³⁺ concentration

H₆L (predetermined weight, mg) and TbCl₃·6H₂O (4.5 mg, 0.012 mmol) were dissolved in DMF (0.5 mL) after which CH₃OH (0.5 mL) was added with vortex blending. The solution was then placed in a closed vessel (5 mL) and heated for 2 h at 85°C to achieve gelation.

**Tab. S2** Gelation tests of H₆L at a constant Tb³⁺ concentration
<table>
<thead>
<tr>
<th>H₆L (mg)</th>
<th>0.0</th>
<th>3.7</th>
<th>7.4</th>
<th>11.1</th>
<th>14:8</th>
<th>18.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results</td>
<td>S</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>TS</td>
</tr>
</tbody>
</table>

S = solution; G = gel; TS = turbid solution; P = precipitation.

H₆L (7.4 mg, 0.012 mmol, the minimum gelation weight of H₆L) and TbCl₃·6H₂O (predetermined molar weight) were dissolved in DMF (0.5 mL) after which CH₃OH (0.5 mL) was added with vortex blending. The solution was then placed in a closed vessel (5 mL) and heated for 2 h at 85°C to achieve gelation.

**Tab. S3** Gelation tests with different H₆L/Tb³⁺ molar ratio

<table>
<thead>
<tr>
<th>H₆L: Tb³⁺</th>
<th>1.0: 0.0</th>
<th>1.0: 0.5</th>
<th>1.0:1.0</th>
<th>1.0: 1.5</th>
<th>1.0: 2.0</th>
<th>1.0: 2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>TS</td>
</tr>
</tbody>
</table>

P = precipitation; G = gel; TS = turbid solution.

5. **FT-IR spectra of H₆L and H₆L/Tb³⁺ powder**

![Fig. S3 FT-IR spectra of H₆L (1) and H₆L/Tb³⁺ powder prepared from H₆L/Tb³⁺ solutions heated for various times: 0 min (2), 10 min (3), 30 min (4), 60 min (5), 90 min (6), and 120 min (7) at 85°C.](image)

6. **Schematic illustration of self-assembly of H₆L/Tb complex.**
7. The effect of solvents and H₆L/Tb³⁺ ratios on the luminescent intensity of H₆L/Tb gel

![Fig. S5](image)

**Fig. S5** Effect of solvents on luminescent intensity of H₆L/Tb gel (λ<sub>ex</sub>=333 nm) formation in 1/1 (v/v) solvent/solvent.

![Fig. S6](image)

**Fig. S6** The effect of the H₆L/Tb³⁺ ratios on luminescent intensity of H₆L/Tb gel (H₆L = 7.4 mg, λ<sub>ex</sub>=333 nm) formation in 1/1 (v/v) DMF/CH₃OH.

8. Thermal stability of H₆L/Tb gel
The H₆L/Tb gel was placed in the thermostat (DHG-9035AE) and maintained at 1 h for each temperature, and the gel was found stable in 0 and 100 °C.

**Fig. S7** Photographs of H₆L/Tb gel appearance in 0 and 100 °C.


**Fig. S8** Luminescence stability performance of collapsed H₆L/Tb gels by manual shaking treated by varied sonication time, where the ratio of I/I₀ is the luminescence intensities of the collapsed H₆L/Tb gel before and after sonication.

10. Luminescence decay curves
**Fig. S9** Luminescence decay curves of $^5D_4 \rightarrow ^7F_5$ (544 nm) from H$_6$L/Tb gel (red) and H$_6$L/Tb gel after manual shaking (blue).

11. **FT-IR spectra of H$_6$L/Tb xerogel and the powder of H$_6$L/Tb gel after manual shaking**

The powder of H$_6$L/Tb gel after shaking was prepared by centrifugally separating the H$_6$L/Tb gel after manual shaking and then drying at 40°C under vacuum for 24 hours.

**Fig. S10** FT-IR spectra of H$_6$L/Tb xerogel and the powder of H$_6$L/Tb gel after manual shaking.

12. **XRD pattern of powder of H$_6$L/Tb gel after manual shaking**

The powder of H$_6$L/Tb gel after shaking was prepared by centrifugally separating the H$_6$L/Tb gel after manual shaking and then drying at 40°C under vacuum for 24 hours.
13. FT-IR spectra of H₆L/Tb xerogel and the powder of H₆L/Tb xerogel after soaking in water

The solid powder of H₆L/Tb xerogel after soaking in water was prepared by centrifugally separating the H₆L/Tb xerogel after soaking in water of 18 h and then drying at 40°C under vacuum for 24 hours.

14. XRD pattern of solid powder of H₆L/Tb xerogel after soaking in water

The solid powder of H₆L/Tb xerogel after soaking in water was prepared by centrifugally separating the H₆L/Tb xerogel after soaking in water of 18 h and then by drying at 40°C under vacuum for 24 hours.
hours.

**Fig. S13** XRD pattern of H₆L/Tb xerogel after soaking in water.