

Electronic Supplementary Information (ESI) for:

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

Binbin Zhang^a, Xuelin Dong,^{ab} Yuxing Xiong^b, Qi Zhou,^a Shan Lu,^a Yonggui Liao,^a Yajiang Yang^a and Hong Wang^{*a}

Additional data

1. ¹H-NMR spectra of H₆L

¹H-NMR spectrum of H₆L 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).

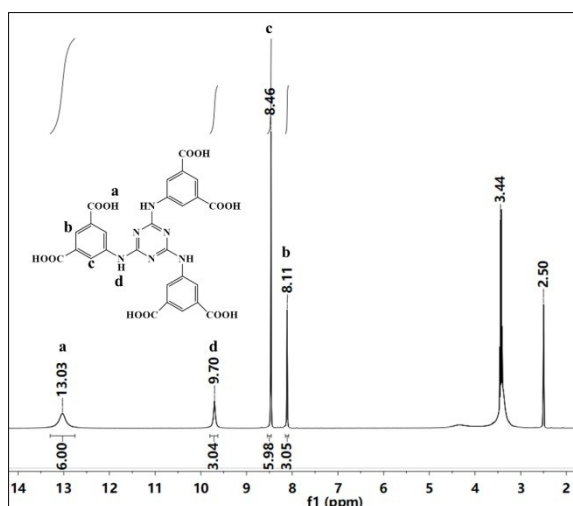


Fig. S1 ¹H NMR spectra of H₆L in DMSO-*d*₆.

2. ESI-MS spectra of H₆L

H₆L 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 C₂₇H₁₈N₆O₁₂ [H₆L+H]⁺: 619.1062; found: 619.1042.

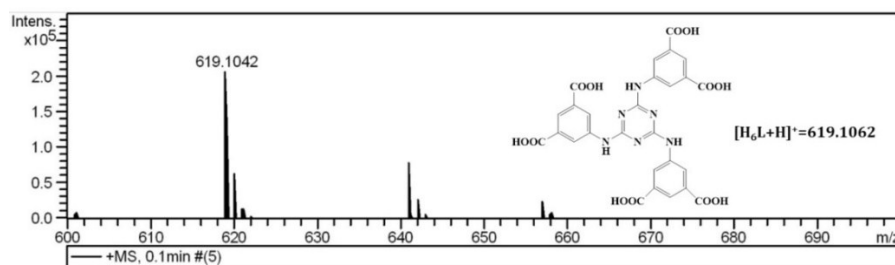


Fig. S2 ESI-MS spectra of H₆L.

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

Solvents \ Results	V/V									
	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8	1:9	
DMF/CH ₃ OH	S	S	TS	G	G	G	TS	P	P	
DMF/H ₂ O	P	P	G	G	G	G	G	P	P	
DMSO/H ₂ O	S	S	S	S	G	G	G	G	G	
DMF/CH ₃ CH ₂ OH	S	S	S	S	S	S	S	TS	TS	
DMSO/CH ₃ OH	S	S	S	S	S	S	S	TS	TS	
DMSO/CH ₃ CH ₂ OH	S	S	S	S	S	S	TS	TS	P	

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

H ₆ L (mg)	0.0	3.7	7.4	11.1	14: 8	18.5
Results	S	P	G	G	G	TS

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

H ₆ L: Tb ³⁺	1.0: 0.0	1.0: 0.5	1.0:1.0	1.0: 1.5	1.0: 2.0	1.0: 2.5
Results	P	P	G	G	G	TS

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

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

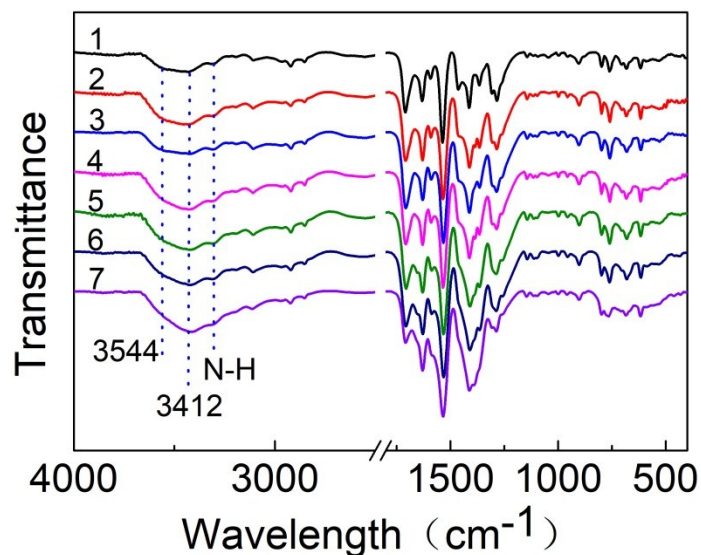


Fig. S3 FT-IR spectra of H₆L (1) and H₆L/Tb³⁺ powder prepared from H₆L/Tb³⁺ solutions heated for various times: 0 min (2), 10 min (3), 30 min (4), 60 min (5), 90 min (6), and 120 min (7) at 85°C.

6. Schematic illustration of self-assembly of H₆L/Tb complex.

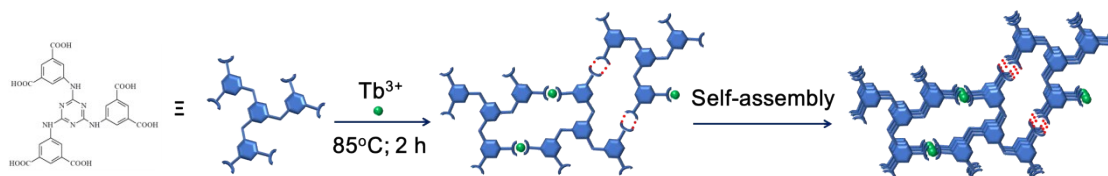


Fig. S4 Schematic illustration of self-assembly of H_6L/Tb complex.

7. The effect of solvents and H_6L/Tb^{3+} ratios on the luminescent intensity of H_6L/Tb gel

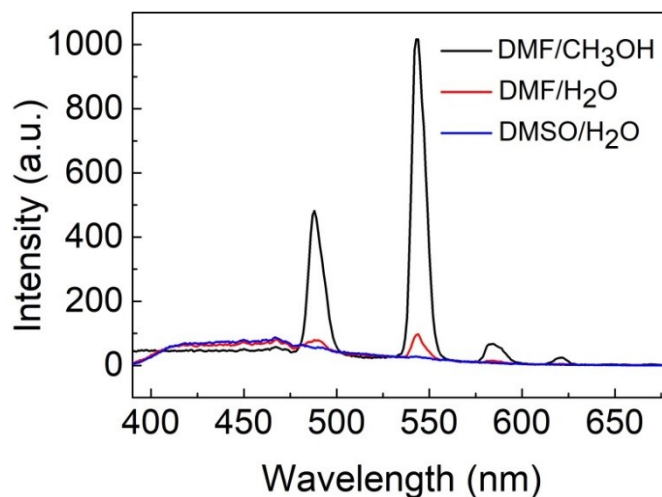


Fig. S5 Effect of solvents on luminescent intensity of H_6L/Tb gel ($\lambda_{ex}=333$ nm) formation in 1/1 (v/v) solvent/solvent.

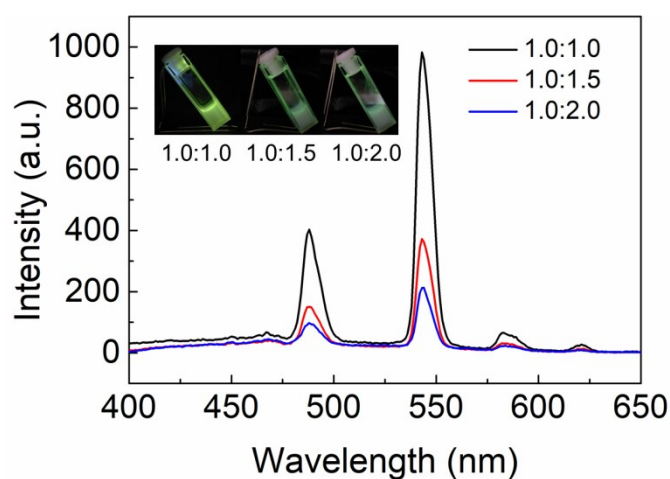


Fig. S6 The effect of the H_6L/Tb^{3+} ratios on luminescent intensity of H_6L/Tb gel ($H_6L = 7.4$ mg, $\lambda_{ex}=333$ nm) formation in 1/1 (v/v) DMF/ CH_3OH .

8. Thermal stability of H_6L/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.

9. Stable luminescence of collapsed H₆L/Tb gels by manual shaking treated by varied sonication time.

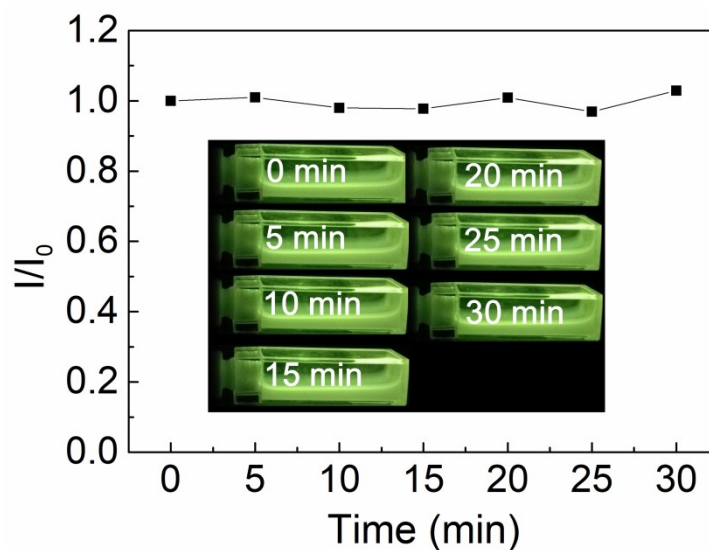


Fig. S8 Luminescence stability performance of collapsed H₆L/Tb gels by manual shaking treated by varied sonication time, where the ratio of I/I_0 is the luminescence intensities of the collapsed H₆L/Tb gel before and after sonication.

10. Luminescence decay curves

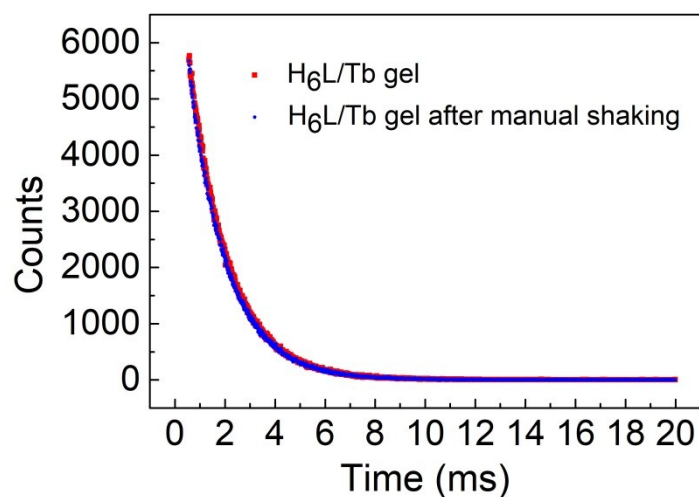


Fig. S9 Luminescence decay curves of $^5D_4 \rightarrow ^7F_5$ (544 nm) from H₆L/Tb gel (red) and H₆L/Tb gel after manual shaking (blue).

11. FT-IR spectra of H₆L/Tb xerogel and the powder of H₆L/Tb gel after manual shaking

The powder of H₆L/Tb gel after shaking was prepared by centrifugally separating the H₆L/Tb gel after manual shaking and then drying at 40°C under vacuum for 24 hours.

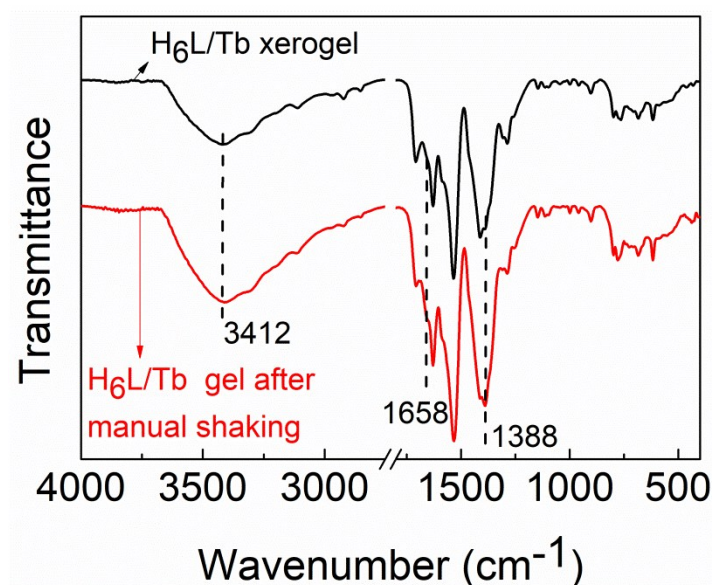


Fig. S10 FT-IR spectra of H₆L/Tb xerogel and the powder of H₆L/Tb gel after manual shaking.

12. XRD pattern of powder of H₆L/Tb gel after manual shaking

The powder of H₆L/Tb gel after shaking was prepared by centrifugally separating the H₆L/Tb gel after manual shaking and then drying at 40°C under vacuum for 24 hours.

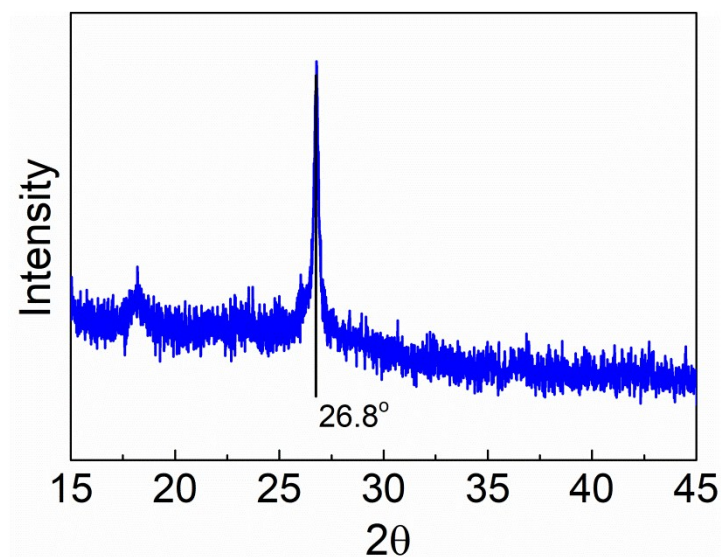


Fig. S11 XRD pattern of H₆L/Tb gel after manual shaking.

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.

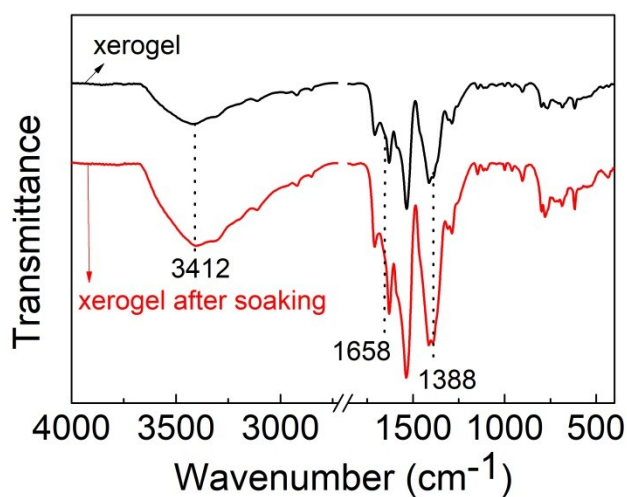


Fig. S12 FT-IR spectra of H₆L/Tb xerogel and H₆L/Tb xerogel upon the treatment of soaking in water.

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

The solid power 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.

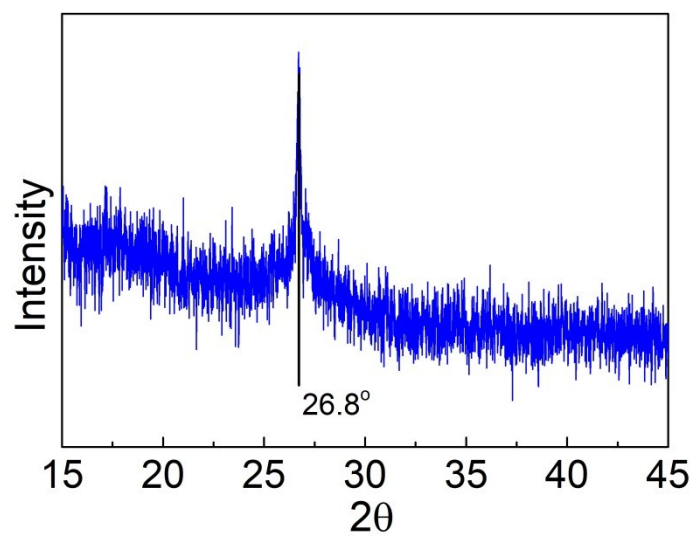


Fig. S13 XRD pattern of H₆L/Tb xerogel after soaking in water.