

Information

A tripodal acylhydrazone derivative AIE gel for highly selective sensing of Al³⁺ and Al@gel detection for oxalic acid

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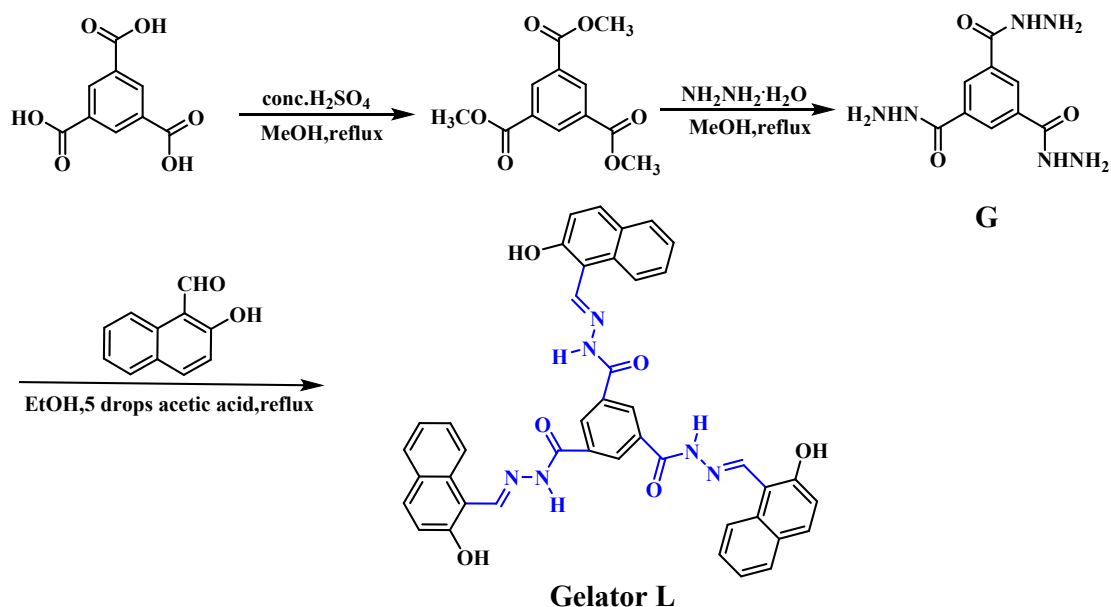
Materials

1,3,5-benzenetricarboxylic acid was purchased from Shanghai Energy Chemical Co., Ltd. Hydrazine hydrate (80%) were purchased from Shanghai Tansoole Chemical Co., Ltd. All the solvents were purchased from Chengdu Chron Chemical Co., Ltd. All chemical agents were used without further purification, unless otherwise noted.

Measurements

¹H NMR spectra were measured by using a Bruker Ascend™ 400MHz. UV-vis absorption spectra were performed with a UV 2600. Fluorescence measurements were carried out by Cary Eclipse. Fluorescence images of the samples were conducted with an unfocused UV radiation (365nm). XRD (X-ray diffraction patterns) measurements were carried out with Ultima IV over the 2θ range of 5-80°. FT-IR (Fourier transform infrared) spectra were determined by Nicolet 670 spectrometer with the KBr pellet technique. SEM measurements were performed by Gemini 500. Atomic Force Microscopy (AFM) investigation were taken by Dimension Icon with ScanAsyst-air mode. All measurements were carried out at room temperature.

Synthesis of gelator L



Scheme S1. Synthesis of Gelator L

Synthesis of Trimethyl 1,3,5-benzenetricarboxylate

Trimesic acid (5.00 g, 0.0238 mol) was dissolved in MeOH (50 mL) and concentrated H_2SO_4 (2 mL) was added dropwise under stirring. Then the mixture solution was refluxed for 24 h. After cooling to room temperature, the white solid was collected by vacuum filtration. The crude product was dissolved in CH_2Cl_2 (20 mL) followed by washing with saturated NaHCO_3 (aq) (2×15 mL) and drying over anhydrous Na_2SO_4 . The organic solvent was removed under reduced pressure to give the target compound (5.92 g, 98.6%).

Synthesis of Benzene-1,3,5-tricarboxylic acid trihydrazide (G)

1,3,5-benzenetricarboxylic acid trimethyl ester (5.04 g, 0.02 mol) and hydrazine hydrate (80%, 13 mL, 12 eq) were added to a round-bottom flask with 100 mL MeOH , and the solution was refluxed for 48 h. After cooling to room temperature, excess solvent was removed by filtration. The residue was washed three times with water. Further purification was done by recrystallization from ethanol to give **G** (3.84g, 74.48%).

Synthesis of gelator L

The solution of **G** (2.52 g, 0.01 mol) in ethanol (70 mL) was mixed with 2-hydroxy-1-

naphthaldehyde (5.16 g, 0.03 mol) and 5 drops of acetic acid. Then the solution was refluxed for 48 h. The crude yellow-green powder was isolated by filtration and washed with hot (MeOH/CHCl₃ =1:4) solution for several times. The crude product was then dissolved in DMF and the solution was poured into saturated aqueous NaCl_(aq). After several days, the target product was precipitated (4.48 g, 63.24%). ¹H NMR (400 MHz, DMSO-d₆): δ 12.74 (s, 3H), 12.62 (s, 3H), 9.60 (s, 3H), 8.89 (s, 3H), 8.32 (s, 3H), 7.96 (d, *J* = 8.9 Hz, 3H), 7.91 (d, *J* = 8.0 Hz, 3H), 7.64 (s, 3H), 7.43 (s, 3H), 7.28 (d, *J* = 8.9 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆): δ 161.83, 158.64, 148.23, 134.25, 133.51, 132.16, 130.47, 129.49, 128.36, 124.10, 121.34, 119.36, 109.09. ESI-MS: *m/z* [L + Na]⁺ 737.2116.

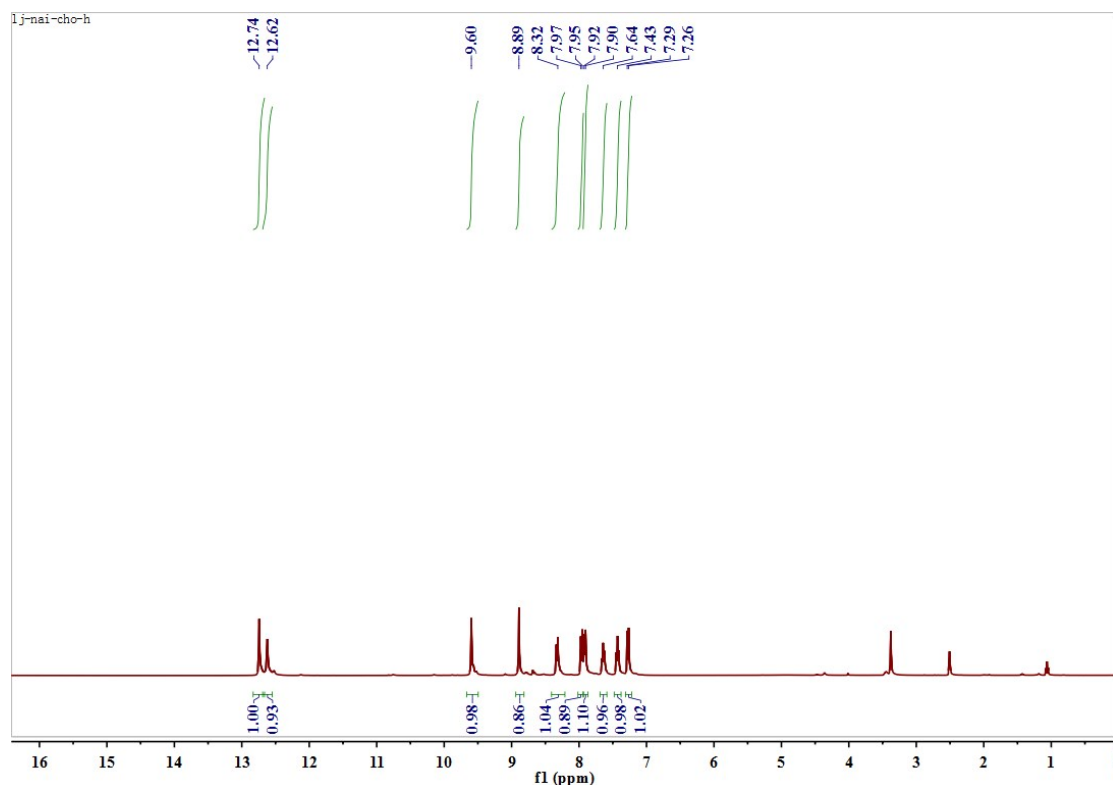


Fig. S1 ¹H NMR spectrum of gelator L

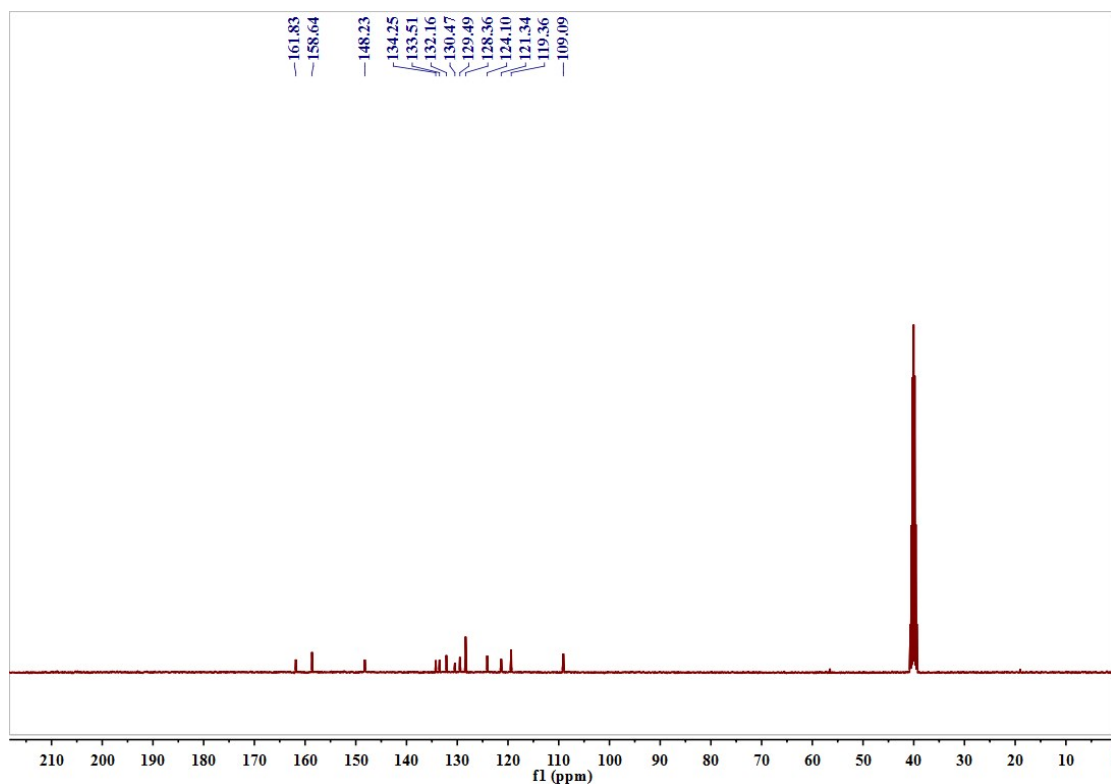


Fig. S2 ^{13}C NMR spectrum of gelator L

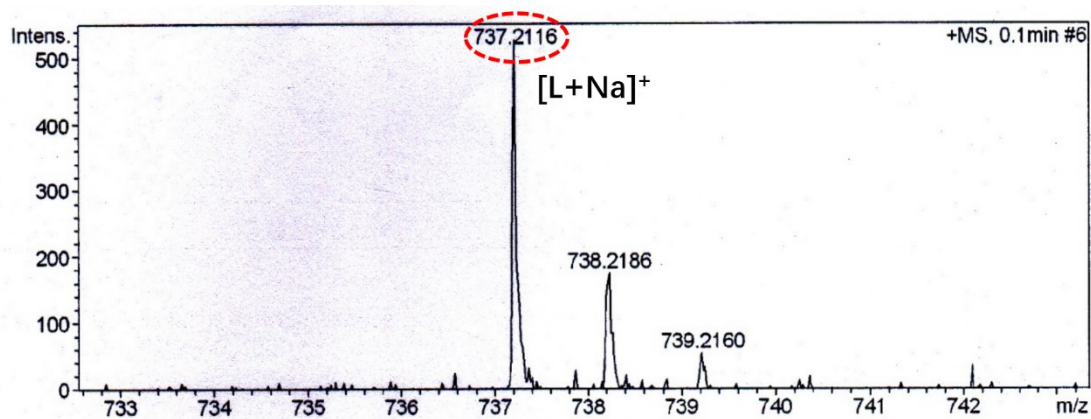


Fig. S3 ESI-MS of L

Table S1 Gel behavior of **L** in different solvents

Solvent	State ^a	T ^b gel (°C, wt %)	CGC (%)
MeOH	I	—	—
EtOH	I	—	—
n-PrOH	I	—	—
i-PrOH	I	—	—
n-BuOH	I	—	—
1,4-butanediol	I	—	—
Tetrahydrofuran	I	—	—
Pyridine	I	—	—
1,4-dioxane	I	—	—
Hexane	I	—	—
Acetone	I	—	—
Acetonitrile	I	—	—
Ethyl acetate	I	—	—
Dichloromethan	I	—	—
Chloroform	I	—	—
Carbon tetrachloride	I	—	—
Toluene	I	—	—
H ₂ O	I	—	—
DMF	G	45 °C	1.0 %
DMSO	S	—	—

^a G, gel; S, solution; I, insoluble, respectively
(wt %, w/v, 10 mg mL⁻¹ = 1.0 %)

^b T gel: The gel-sol transition temperature (°C).

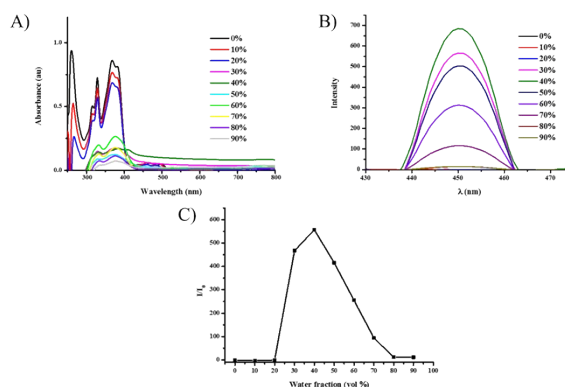


Fig. S4 (A) UV spectra of **L** in DMSO-water mixtures. (B) Fluorescence spectra of **L** in DMSO-water mixtures. (C) Plot of the relative PL intensity (I/I_0) versus the composition of the DMSO/water mixture of **L**. I_0 =emission intensity in pure DMSO solution. Concentration: 1×10^{-5} M; excitation wavelength: 450 nm.

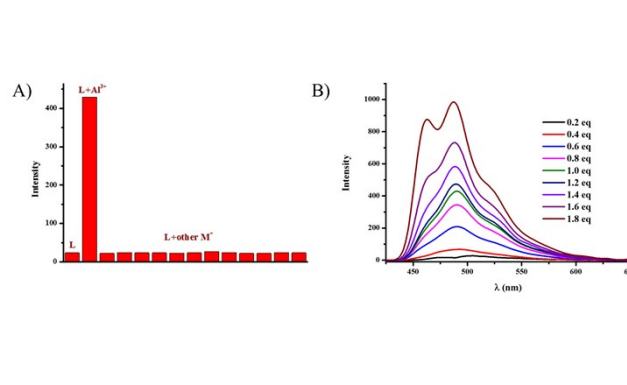
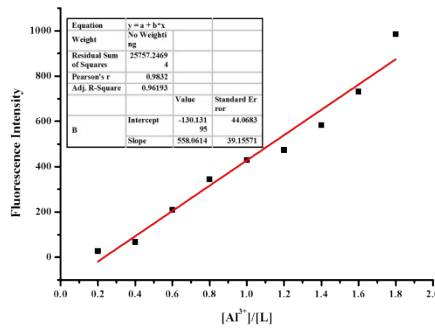


Fig. S5 (A) The metal ions selectivity of **L**, the molar ratio: M^+ / L is 1:1 (excited at 450 nm); (B) Fluorescent titration spectra ($\lambda_{ex} = 450 \text{ nm}$) of **L** ($1 \times 10^{-5} \text{ M}$) upon addition of Al^{3+} (0.2-1.8 equiv.) in DMF solution.



The result of the analysis as follows:

Linear Equation: $Y = 558.0614 \times X + 130.13195$

$R^2 = 0.96193$ $S = 5.580614 \times 10^7$

$$\delta = \sqrt{\frac{\sum (F_i - F_0)^2}{(N - 1)}} = 16.1876 \quad (N = 20) \quad K = 3$$

$LOD = K \times \delta / S = 8.702 \times 10^{-7} \text{ M}$

F_0 is fluorescence intensity of **L**, F_i is the average of fluorescence intensity F_0 .

Fig. S6. The photograph of the fluorescent spectrum linear range for Al^{3+}

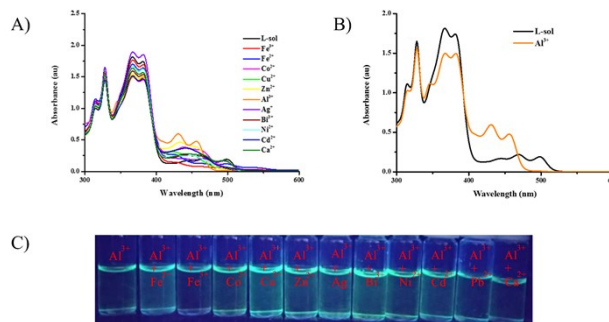


Fig. S7 (A) UV-vis absorption spectra changes of solution **L** in DMF with addition of different metal ions; (B) UV-vis absorption spectra of Al^{3+} in DMF solution; (C) The interference of other

metal ions on fluorescence of **L-Al³⁺** solution (1×10^{-5} M).

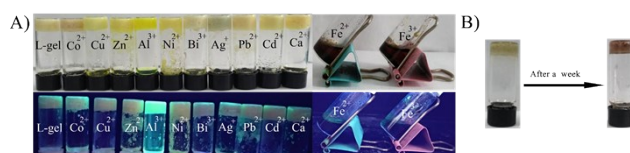


Fig. S8 (A) Fluorescence responses of **L** with addition of different metal ions; (B) The change in appearance of **Ag@gel** after a week.

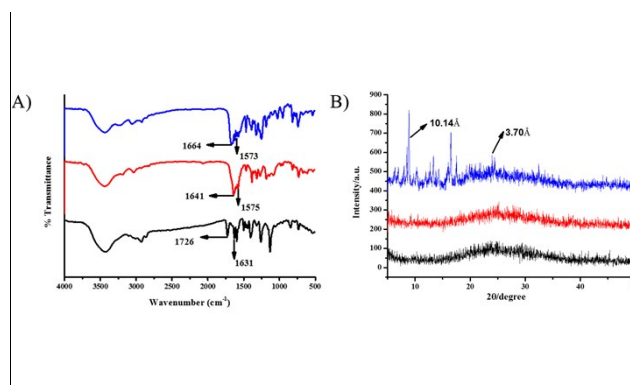


Fig. S9 The xerogel of **L-gel** (blue), **Ag@gel** (red) and **Al@gel** (black) of (A) FT-IR spectra and (B) Powder X-ray diffraction patterns.

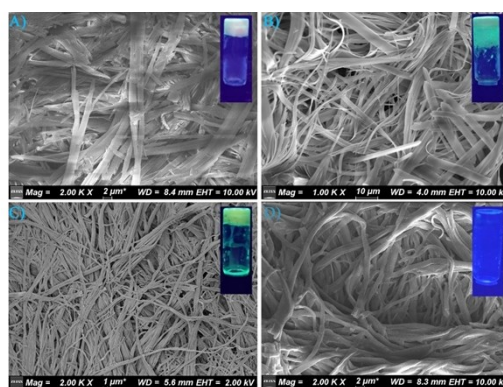


Fig.S10 FE-SEM images of (A) **L-gel** (B) The gel formed in DMSO/water mixtures (90:10, v/v) (C) **Al@gel** (D) **Ag@gel**.

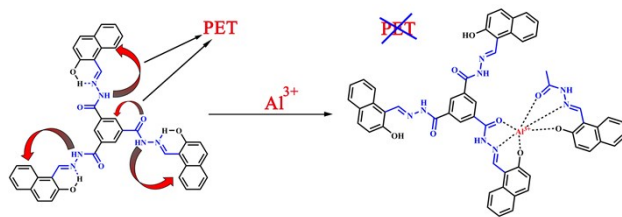


Fig. S11 A possible luminescence mechanism of the Al@gel.

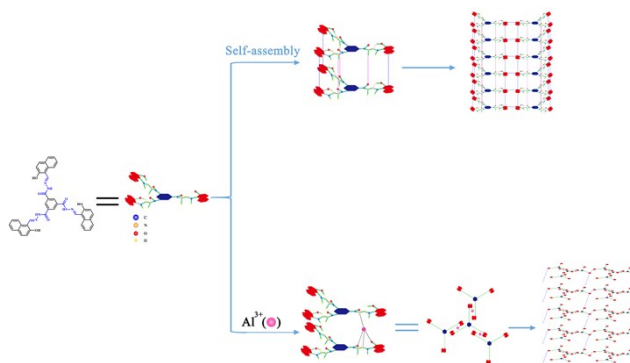


Fig. S12 A possible gelation mechanism of L-gel and Al@gel.

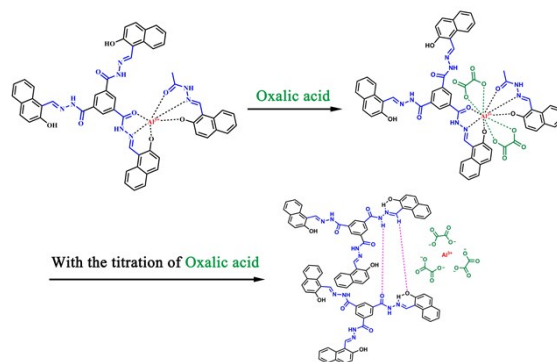


Fig.S13 A possible sensing mechanism of the oxalic acid to Al@gel.