Supporting information

Emissive intelligent supramolecular gel for highly selective sensing of Al^{3+} and writable soft material

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Materials

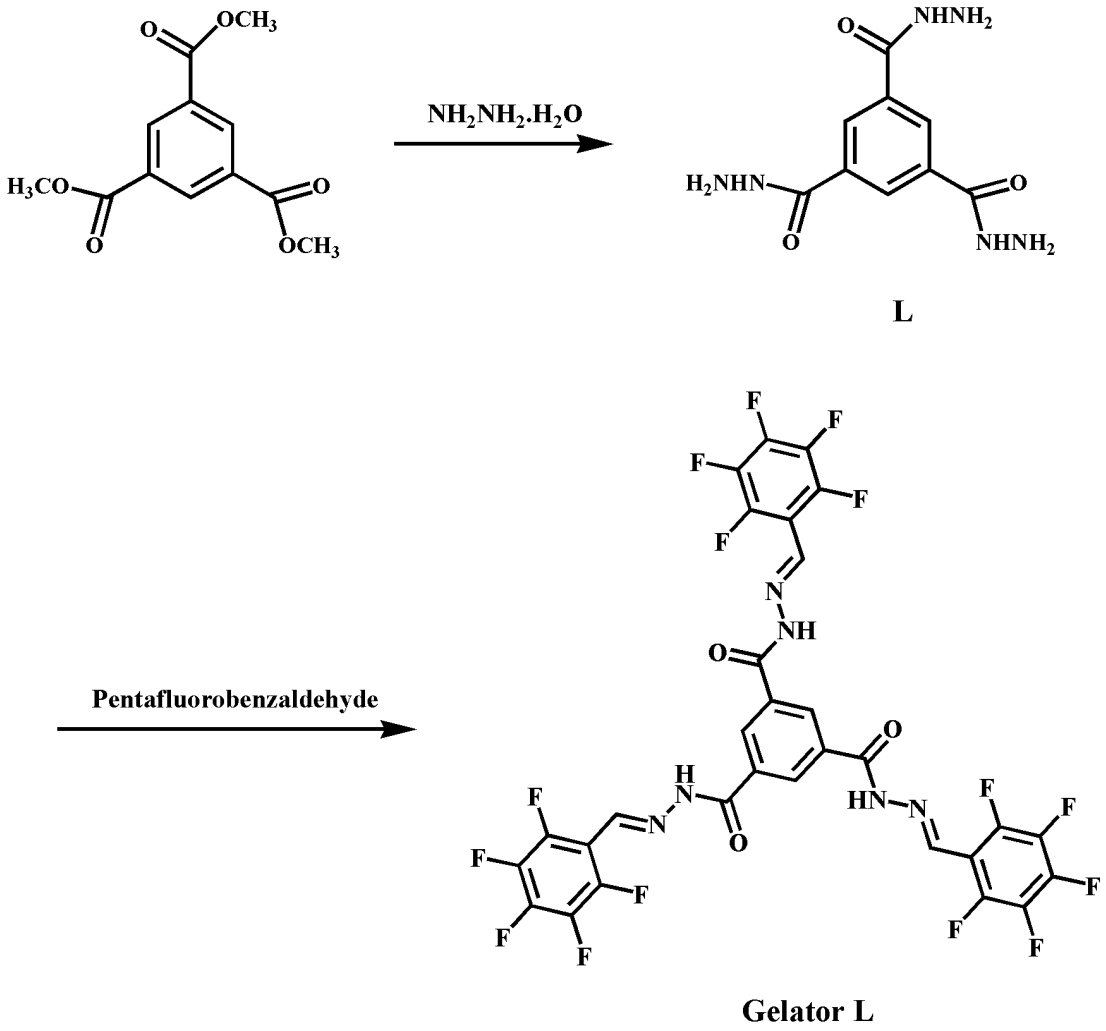
1,3,5-Benzenetricarboxylic acid trimethyl ester was purchased from Shanghai Sinofluoro Scientific Co., Ltd.. Hydrazine hydrate (80%) were purchased from Alfa Aesar Chemical Co., Ltd.. Pentafluorobenzaldehyde was purchased from Shanghai Bangcheng Chemical Co., Ltd.. All chemicals were used without further purification, unless otherwise noted.

Measurements

^{1}H NMR spectra were recorded on a Bruker 400MHz spectrometer. Elemental analyses were performed with an Elementar VarioELcube. XRD (X-ray diffraction patterns) were determined with a Rigaku-Dmax 2400 diffractometer using Cu Kα radiation over the 2θ range of 5-80 °. FT-IR (Fourier transform infrared) spectra were conducted within the 4000–500cm^{-1} wavenumber range using a Nicolet 360 FT-IR spectrometer with the KBr pellet technique. The morphologies of the as-synthesized samples were characterized with a JSM-6701F SEM using an accelerating voltage of

5kV. Fluorescence micrographs of the samples were imaged by fluorescent optical microscopy (Olympus BX53) by exciting the gel samples with an unfocused UV radiation (330−385nm). The measurements of steady-state luminescence were performed with a spectrofluorimeter (HITACHI F-4500, Japan). All measurements were carried out at room temperature.

Synthesis of gelator L



Scheme S1. Synthesis of Gelator L

Synthesis of L

1,3,5-Benzenetricarboxylic acid trimethyl ester (10.00g, 0.04mol) and Hydrazine hydrate (80%, 9.18g, 0.125mol) were added to a round-bottom flask with 300mLEthanol, then the solution was refluxed for 8h. After cooling to room temperature. Excess solvents was removed from the clear filtrate by distillation. The residue was washed three times with water. Further purification was done by recrystallization from ethanol to give L. Yield: 15.50g (77.18%).

Synthesis of gelator L

The solution of L (5.00g, 0.02mol) in DMF (150mL) was mixed with Pentafluorobenzaldehyde (11.67g, 0.06mol) and refluxed for 10h. Then the mixture was added to excess water. The solid separated was collected by filtration. The crude product was washed with ethanol three times to give gelator L. Yield:14.56g (87.34%). Anal. calcd for $C_{22}H_{18}N_4O_4$: C 45.82, H 1.15, N 10.69. Found: C 45.81, H 1.16, N 10.69. ^{1}H NMR (400MHz, DMSO-D_6): δ (ppm) 12.84-12.20 (m, 3H, -NH-), 8.91-8.66 (m, 3H, -N=CH), 8.61 (d, J = 12.1 Hz, 3H, Ar-H). ^{13}C NMR (100.5MHz, DMSO-D_6): δ (ppm) 145.76, 145.70, 143.24, 143.17, 139.20, 138.43, 136.62, 135.97, 109.39. ^{19}F NMR (376 MHz, DMSO-D_6): δ(ppm) -139.76 to -143.98 (s, 2F), -151.34 to -154.82 (s, 1F), -160.12 to -166.20 (m, 2F). ESI-MS: m/z $(L + H)^+$ 787.05.

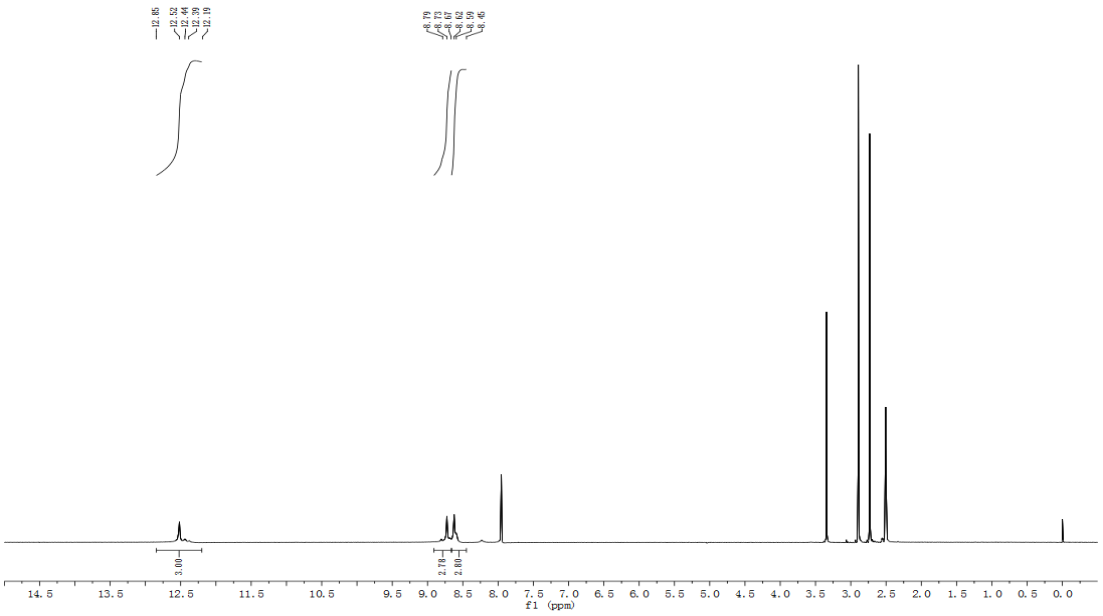


Fig. S1. ^{1}H NMR Spectrum of gelator L

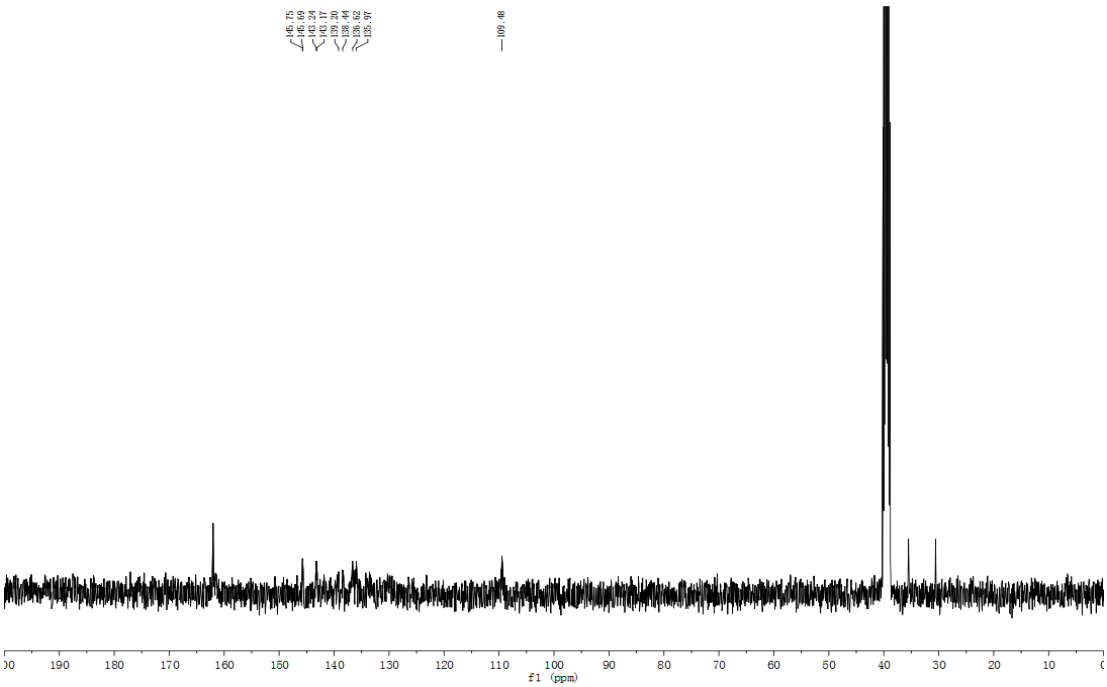


Fig. S2. ^{13}C NMR Spectrum of gelator L

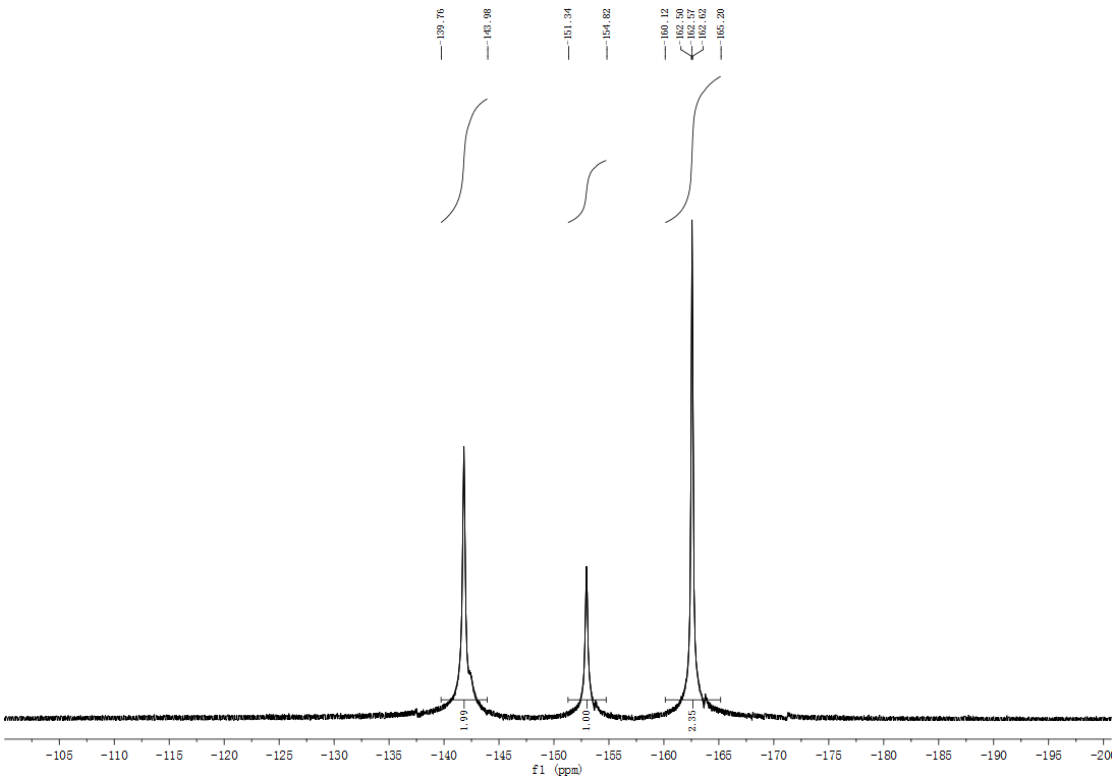


Fig. S3. ^{19}F NMR Spectrum of gelator L

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Fig. S4 Sol–gel phase transitions of L-gel and Al@gel induced by temperature

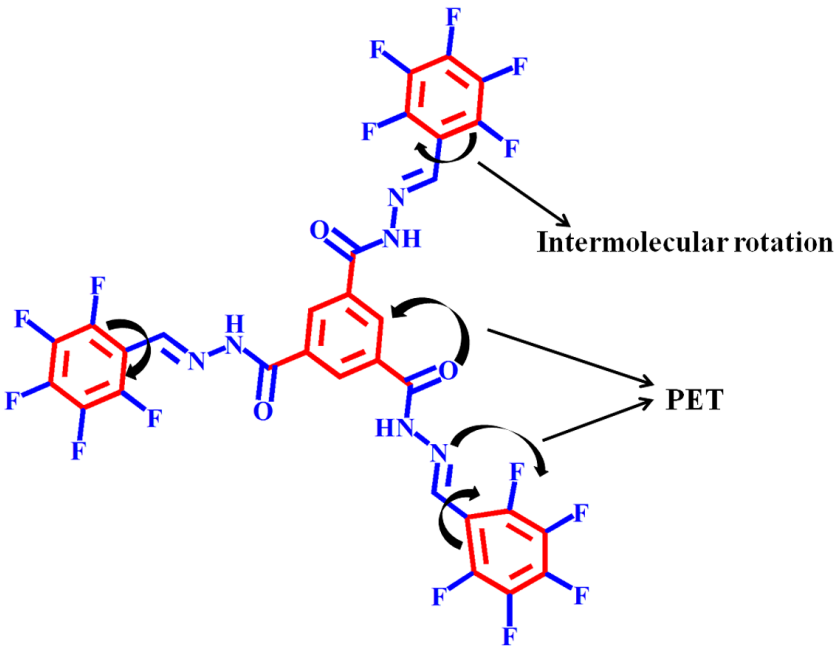

Fig. S5 The possible luminescence mechanism of the free ligand (**weaker**)

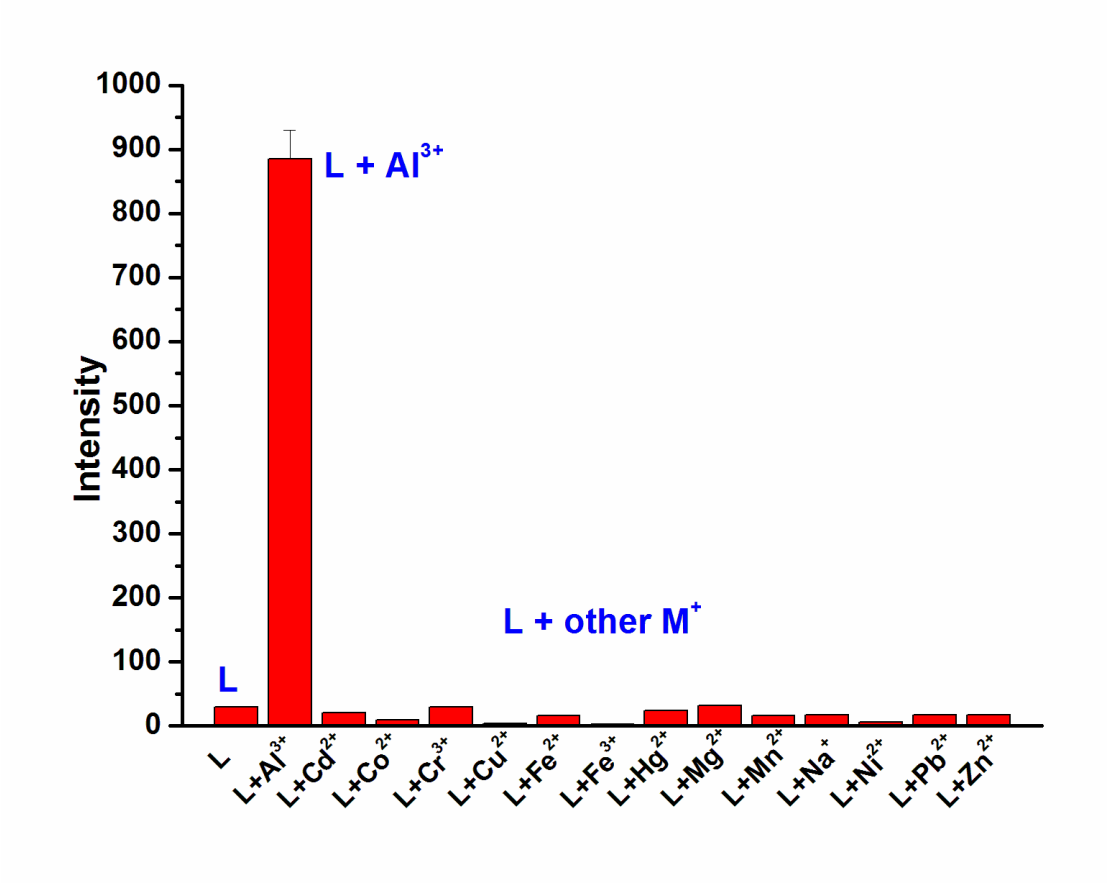

Fig. S6 The metal ion selectivity of L, the molar ratio: M^+/L is 1:1 (excited at 380nm)

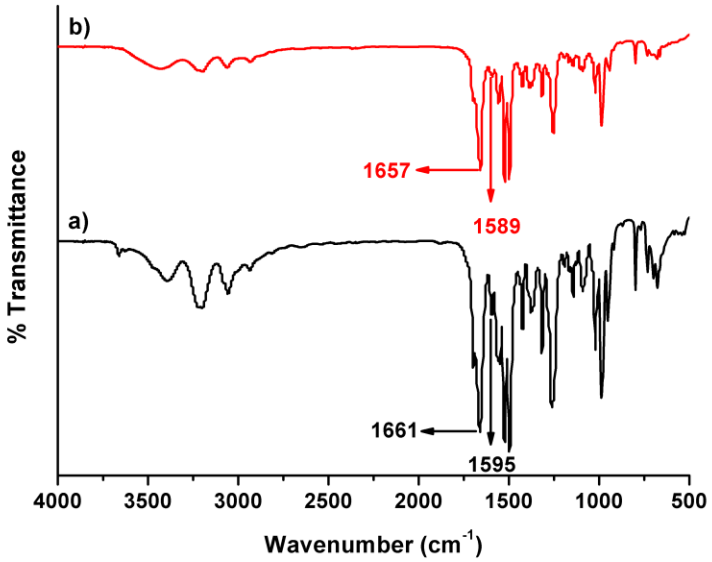

Fig. S7 FT-IR spectra of the gelator L (a) and L-Al^{3+} (b)

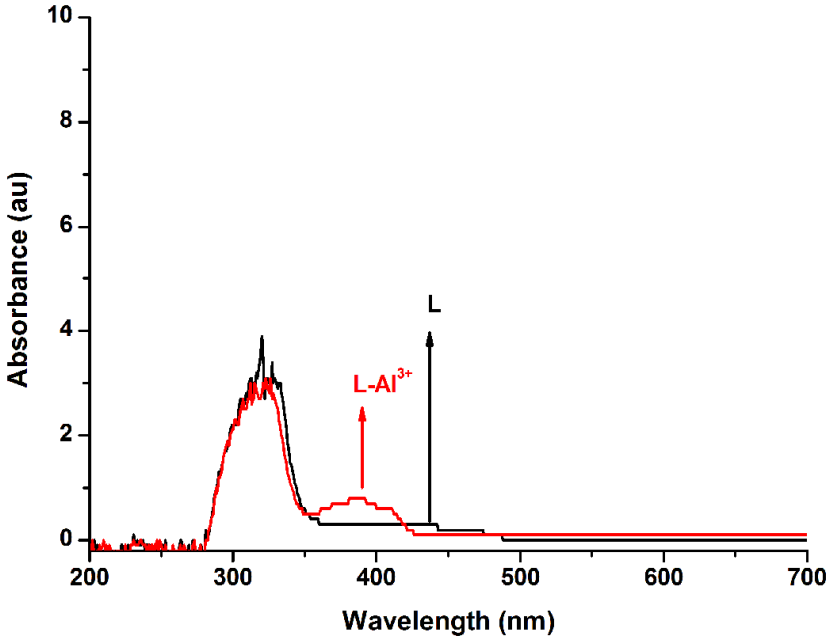

Fig. S8 UV-vis of L and L-Al^{3+} (1×10^{-6} mol L^{-1}) in DMF

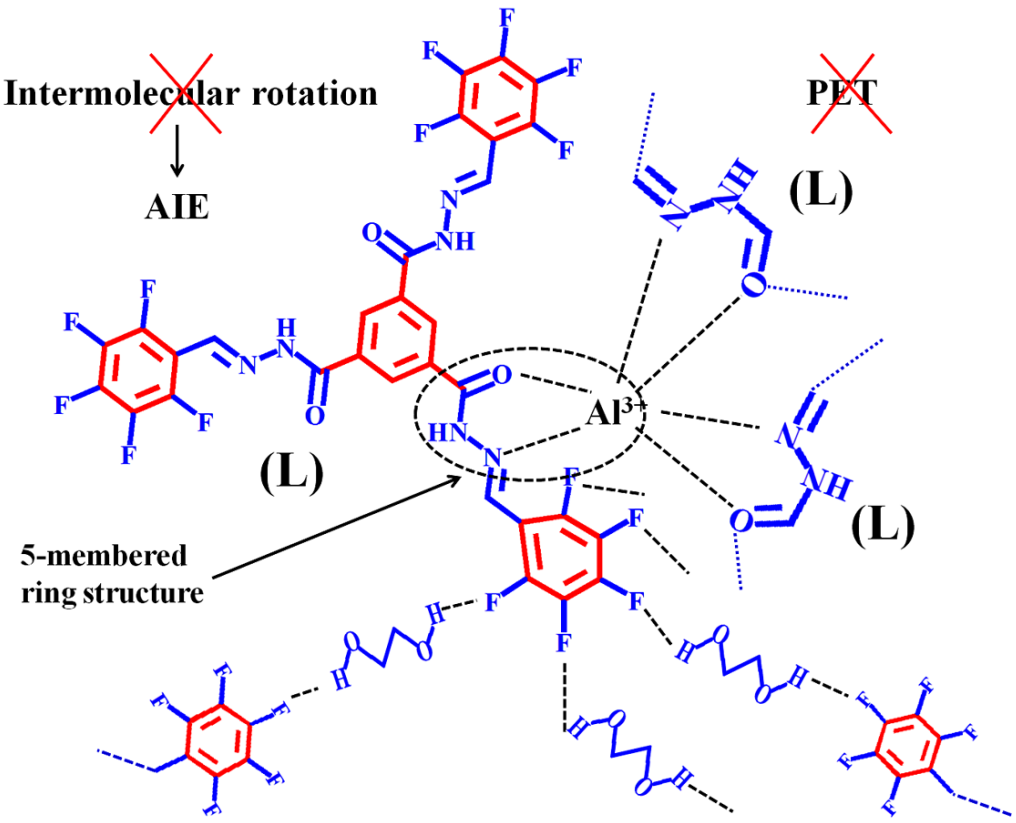

Fig. S9 The possible luminescence mechanism of the Al@gel (**Enhanced**)

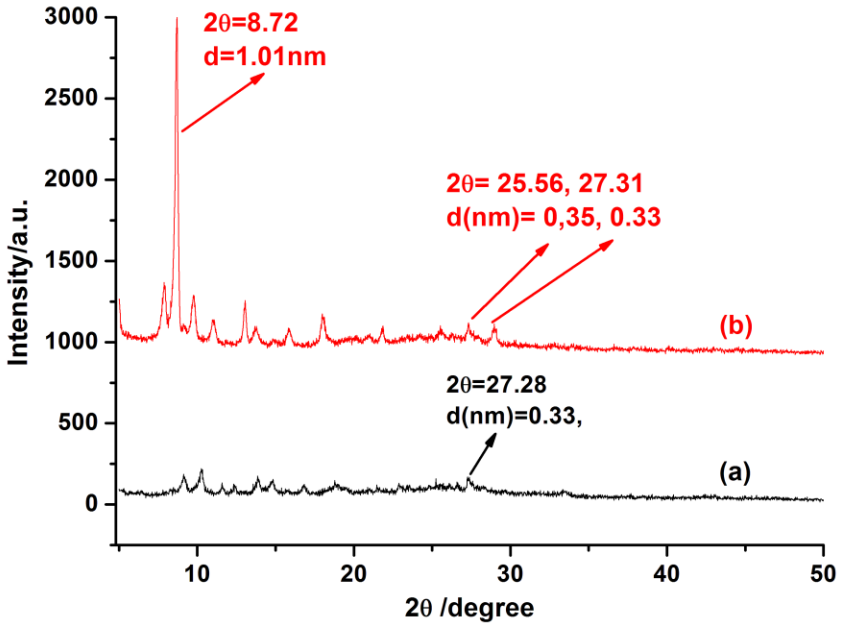

Fig. S10 XRD pattern of the Gelator L (a) and xerogel of the Al@gel (b)

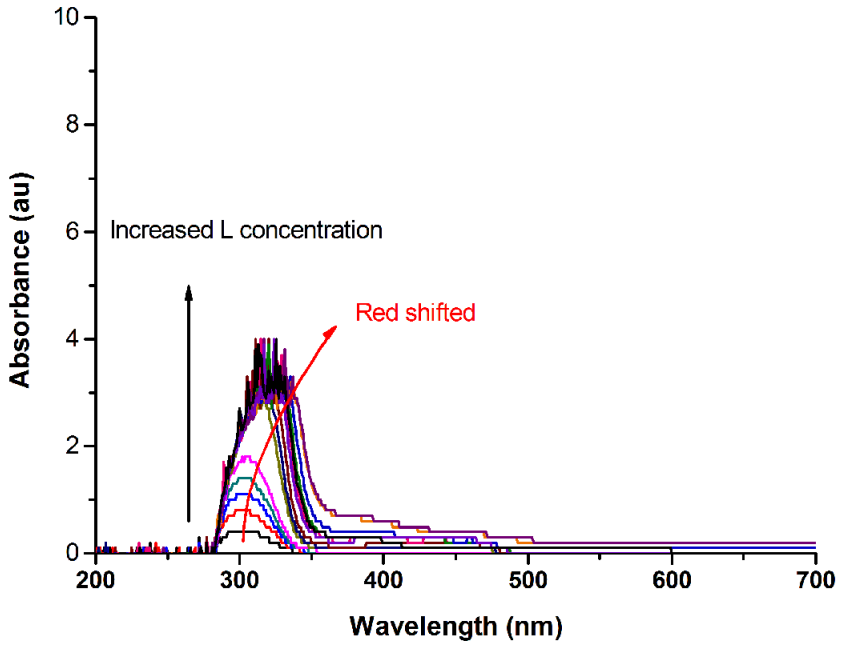

Fig. S11 Concentration-dependent UV-Vis spectrum of L, L concentrations in DMF, 1×10^{-7}mol/L, 2×10^{-7}mol/L, 4×10^{-7}mol/L, 8×10^{-7}mol/L, 1.6×10^{-6}mol/L, 3.2×10^{-6}mol/L, 6.4×10^{-6}mol/L, $1,3\times10^{-5}$ mol/L, $2,6\times10^{-5}$ mol/L, 5.2×10^{-5} mol/L, 1×10^{-4} mol/L, 2×10^{-4} mol/L, 4×10^{-4} mol/L, 8×10^{-4} mol/L, 1.6×10^{-3} mol/L, respectively.

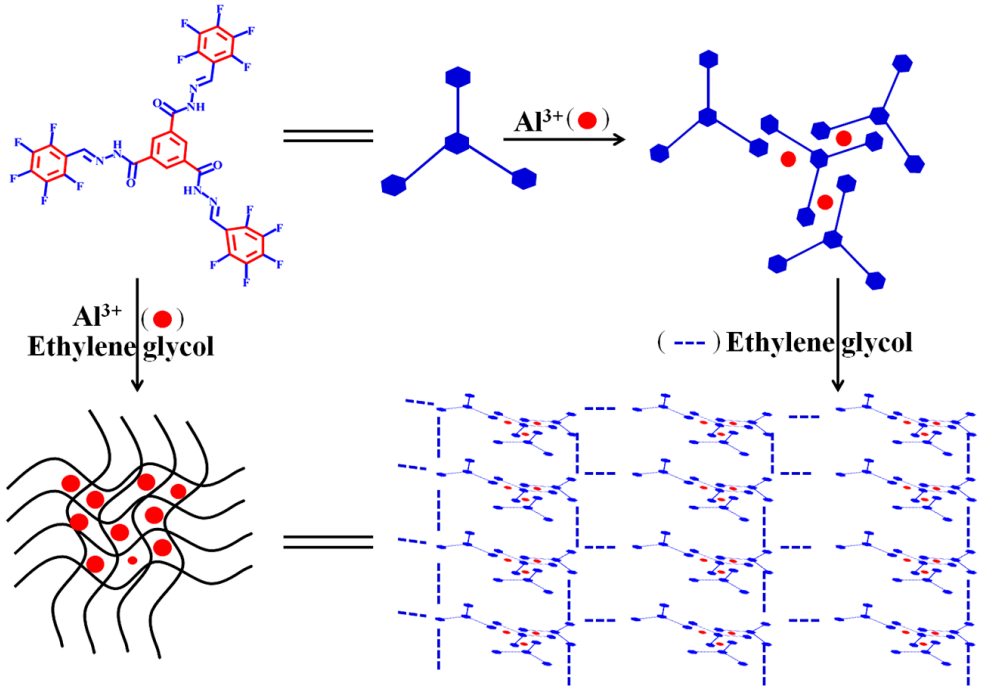

Fig. S12 Possible gelation mechanisms of Al@gel