Supporting information

AIE-caused luminescence of a thermal-responsive supramolecular organogel

Xinxian Ma[a,b], Jusheng Xie[a], Ning Tang[a], and Jincai Wu[a]*

[a] *Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China.*
[b] *College of Chemistry and Chemical Engineering, Ningxia Normal University, Guyuan 756000, People's Republic of China.*

Experimental

Materials

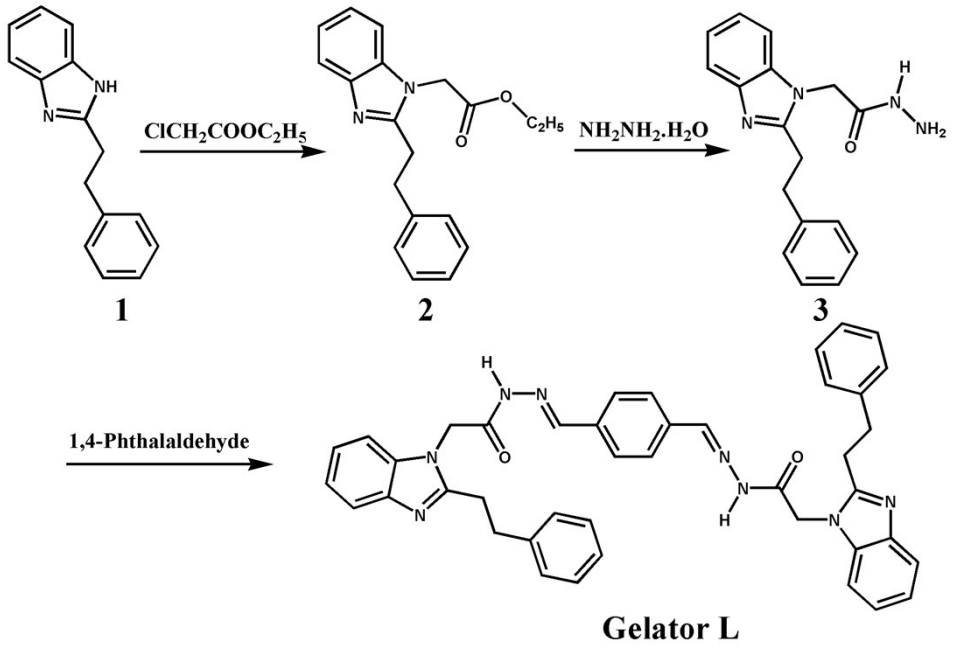
O-Phenylendiamine (≥98%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Hydrocinnamic acid (≥98%) was purchased from Shanghai Sinofluoro Scientific Co., Ltd.. Ethyl chloroacetate and hydrazine hydrate (80%) were purchased from Alfa Aesar Chemical Co., Ltd.. 1,4-Phthalaldehyde was purchased from Shanghai Sinofluoro Scientific Co., Ltd.. All chemicals were obtained from commercial suppliers and used without any further purification.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400MHz spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 6000 spectrometer. Elemental analyses were carried out on an Elemental Vario EL analyzer. Fourier transform infrared (FT-IR) spectra were conducted within the 4000–500cm^{-1} wavenumber range using a Nicolet 360 FT-IR spectrometer with the KBr pellet technique. The measurements of steady-state luminescence were performed

with a spectrofluorimeter (HITACHI F-4500, Japan). UV-vis absorption spectra were obtained with a Perkin Elmer Lambda UV-vis spectrophotometer and recorded in quartz cells with 1cm optical path length. 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). X-ray diffraction patterns (XRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu Kα radiation over the 2θ range of 4-90°. All measurements were carried out at room temperature.

Synthesis and characteristic data



Scheme S1. Synthesis of Gelator L

2-phenethyl benzimidazole (1) was synthesized as reported in the literature procedures.[1]

Synthesis of Ethyl-(2- phenethyl -1H-benzimidazole-1-yl) acetate (2)

Ethyl chloroacetate (0.12mol) and potassium carbonate (0.20mol) were added to a 80mL acetone solution of 2-phenethyl benzimidazole (**1**) (0.10mol), then the solution was refluxed for 8h. After cooling to room temperature, the reaction mixture was filtered. Excess acetone was removed from the clear filtrate by distillation, and then was added to water. The residue was washed with water, and then was dried under air. Further purification was done by recrystallization from ethyl acetate to give Ethyl- (2-phenethyl -1H-benzimidazole-1-yl) acetate (2).

Synthesis of 2-(2--phenethyl-1H-benzimidazole-1-yl)acethydrazide (3)

The solution of ethyl (2- phenethyl-1H-benzimidazole-1-yl) acetate (2) (0.08mol) in ethanol (40mL) was mixed with hydrazine hydrate (99%) (0.09mol). The solution was refluxed for 8h, then was evaporated under reduced pressure. The residue was washed with excess water. The solid separated was collected by filtration. The crude product was purified by recrystallization from ethanol to give 2-(2-phenethyl-1H-benzimidazole -1-yl) acethydrazide (**3**). Yield: 18.59 g (79%). Anal. calcd for $C_{17}H_{18}N_4O$: C 69.37, H 6.16, N 19.03. Found: C 69.44, H 6.14, N 19.33. ^{1}H NMR (400MHz, DMSO-D_6): δ (ppm) 9.55 (s, 1H, -NH-), 7.58 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.42 (d, *J* = 6.9 Hz, 1H, Ar-H), 7.32 (s, 4H, Ar-H), 7.24-7.09 (m, 3H, Ar-H), 4.81 (s, 2H, -NCH_2-), 4.37 (s, 2H, -NH_2), 3.13 (s, 4H, -CH_2-); ^{13}C NMR (100.5 MHz, DMSO-D_6): δ (ppm) 170.22, 165.95, 154.89, 142.11, 141.14, 135.51, 128.27, 128.21, 125.91, 121.49, 121.19, 118.30, 109.64, 44.20, 32.56,28.33. ESI-MS: m/z $(L + H)^+$ 295.18.

Synthesis of gelator L

The solution of 2-(2-phenethyl -1H-benzimidazole-1-yl) acethydrazide (3) (0.06mol) in N, N-Dimethylformamide (100mL) was mixed with 1,4-Phthalaldehyde (0.03mol) 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: 16.55 g (80%).

^{1}H NMR (400MHz, DMSO-D_6): δ (ppm) 12.03 (s, 0.5H, -NH-), 11.91 (s, 1.5H, -NH-), 8.30 (s, 0.5H, -N=CH-), 8.10 (s, 1.5H, -N=CH-), 7.82 (dd, *J* =6.2, 4H, Ar-H), 7.60 (s, 2H, Ar-H), 7.47 (s, 2H, Ar-H), 7.23 (d, *J* =10.2, 14H, Ar-H), 5.47 (s, 3H, -NCH_2-), 5.05 (s, 1H, -NCH_2-), 3.13 (d, *J* = 12.0 Hz, 8H, -CH_2-); ^{13}C NMR (100.5MHz, DMSO-D_6): δ (ppm) 168.88, 155.64, 144.38, 142.94, 141.73, 136.00, 128.83, 128.78, 127.96, 126.48, 122.09, 121.73, 118.96, 110.26, 44.52, 33.28, 28.94. Anal. calcd for $C_{42}H_{38}N_8O_2$: C 73.45, H 5.58, N 16.32. Found: C 73.55, H 5.62, N 16.44. ESI-MS: m/z $(L + H)^+$ 687.30.

As a note:

1) Because of this Gelator L has rotamers, so the –NH-, -N=CH-, -NCH_2- proton signals split into two groups, respectively.
2) ^{13}C NMR of the Gelator L obtained at 65 ^{o}C

Reference

1 W. O. Pool, H. J. Harwood, A. W. Ralston, *J. Am. Chem. Soc.* 1937, **59**, 178-179.

Tsg (gel−sol transition temperature)

A general method for determination of the gel−sol transition temperature-Tube inversion method: the glass tubes (volume 5mL) containing the samples were immersed in an oil bath and the heat was increased at the rate of 1°/min. After each temperature step the test tubes were inverted in order to check whether the sample flowed or not. The temperature at which solvent ran from the sample was recorded as the Tsg value, which reflects the temperature of the gel-sol transition.

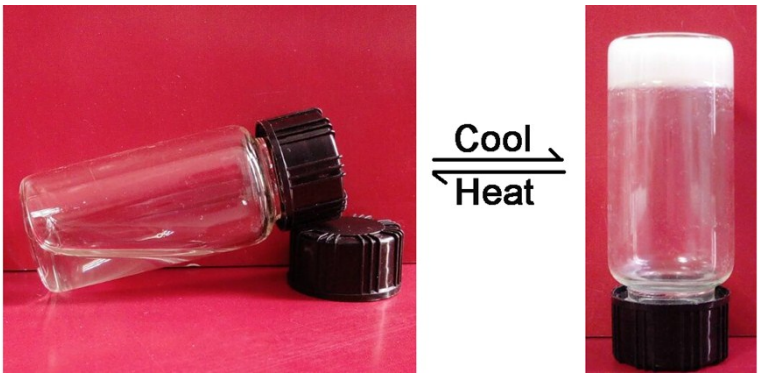


Fig.S1 Sol–gel phase transitions of the L-gel induced by temperature

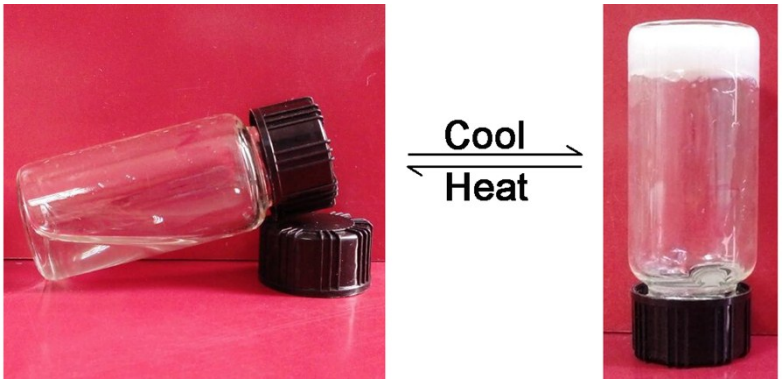


Fig. S2 Sol–gel phase transitions of the B-gel induced by temperature.

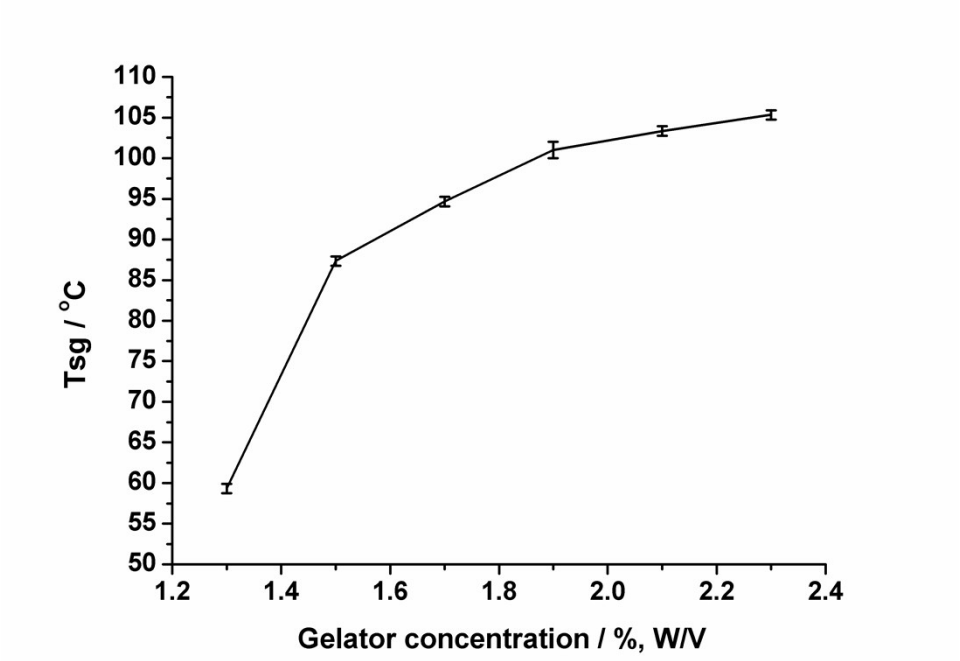


Fig. S3 The change of Tsg in L-gel with respect to the gelator L concentration.

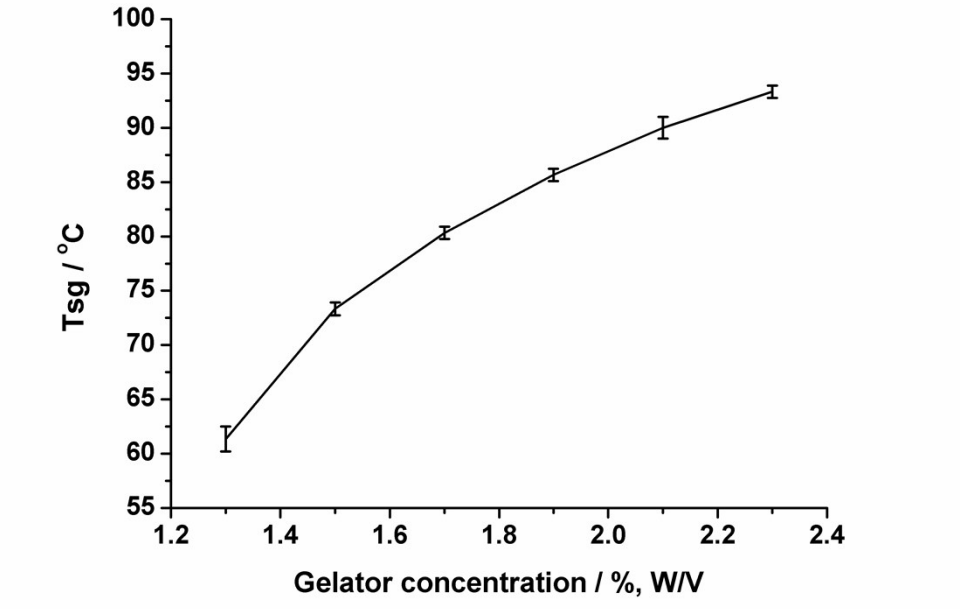


Fig. S4 The change of Tsg in B-gel with respect to the gelator L concentration

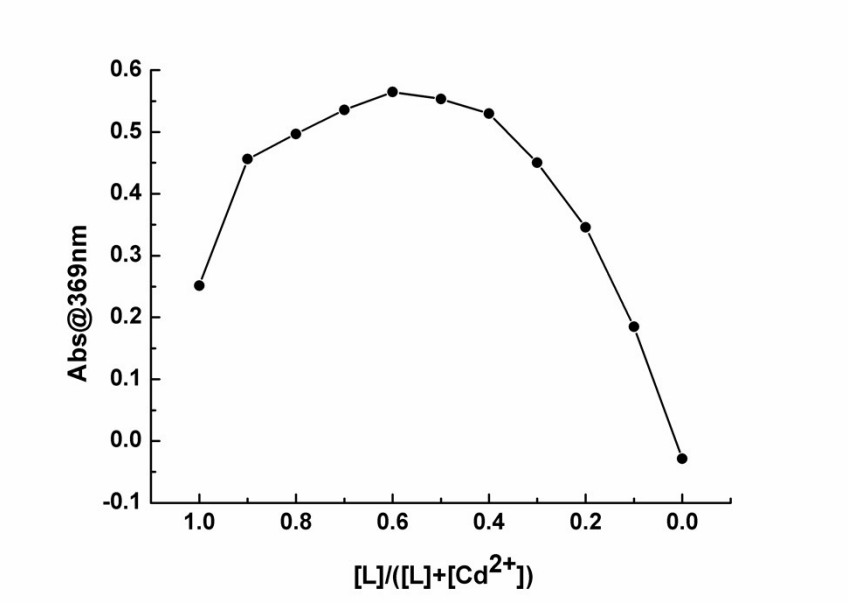


Fig. S5 Job's plots according to the method for continuous variations, indicating the 3:2 stoichiometry for L-Cd^{2+} (the total concentration of L and Cd^{2+} is 1×10^{-3} mol L^{-1}).

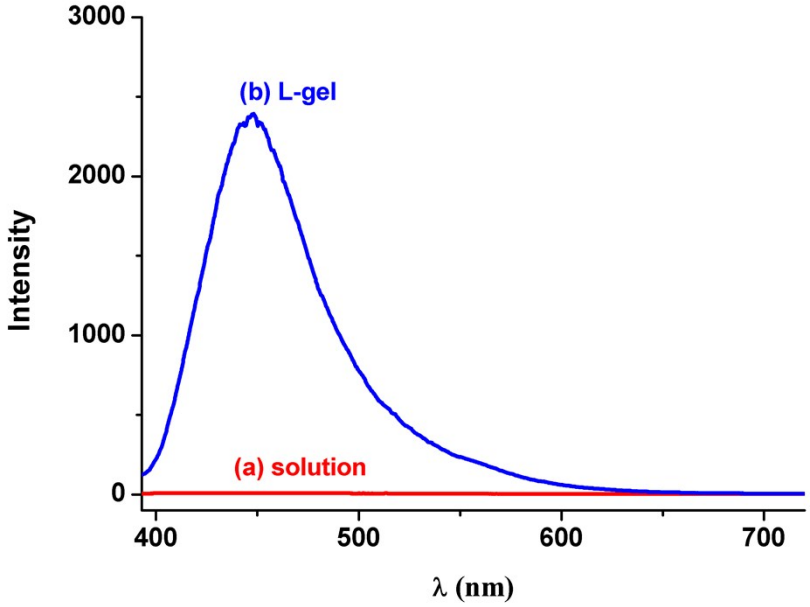


Fig. S6 Luminescence spectra of gelator L in DMSO-ethylene glycol mixtures (0.02g L in 0.5mL DMSO with 1.5mL ethylene glycol mixtures). (a) Solution state, (b) slowly formed a gel.

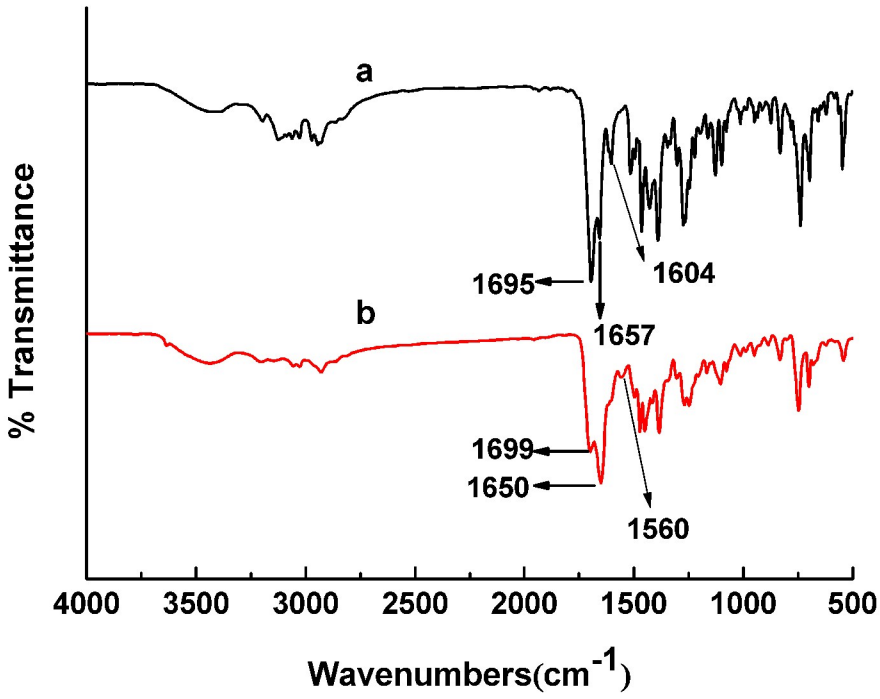


Fig.S7 FT-IR spectra of the L (a) and xerogel (b) of the B-gel

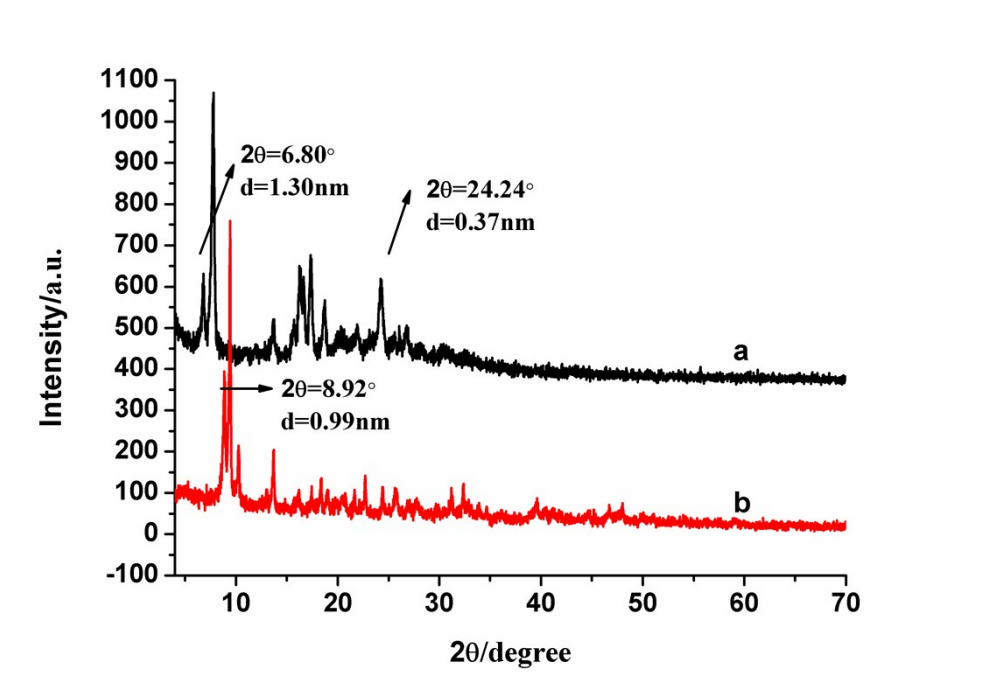


Fig. S8 XRD pattern of the L (a) and complex of the L-Cd^{2+} (b)

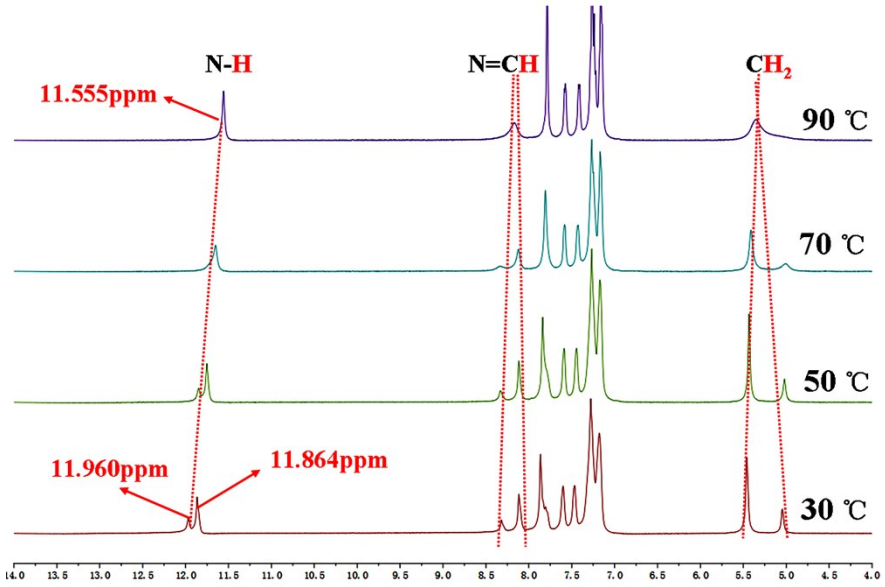


Fig. S9 Temperature-dependent ^{1}H NMR spectra (N-H region) of gelator L/[D_6] DMSO (40mg/mL)

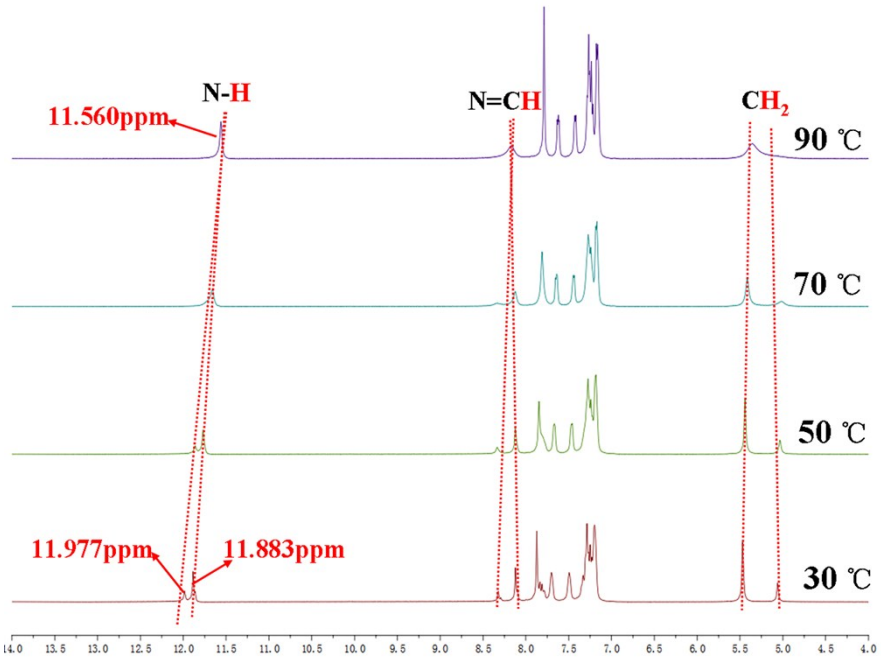
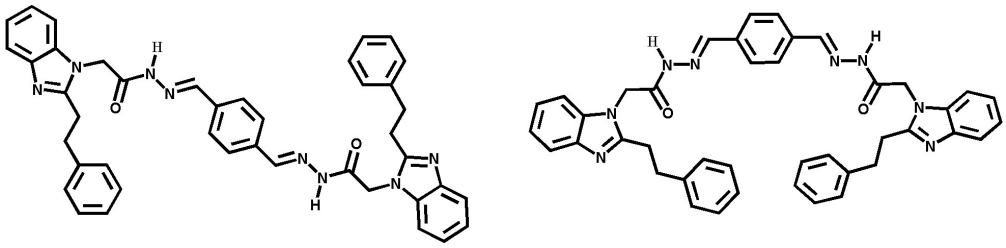


Fig. S10 Temperature-dependent ^{1}H NMR spectra (N-H region) of gelator L with 0.67 equivalent Cd^{2+}/ [D_6] DMSO (gelator L 40mg/mL)



L(a) L(b)

Fig. S11 Two rotamers of gelator L

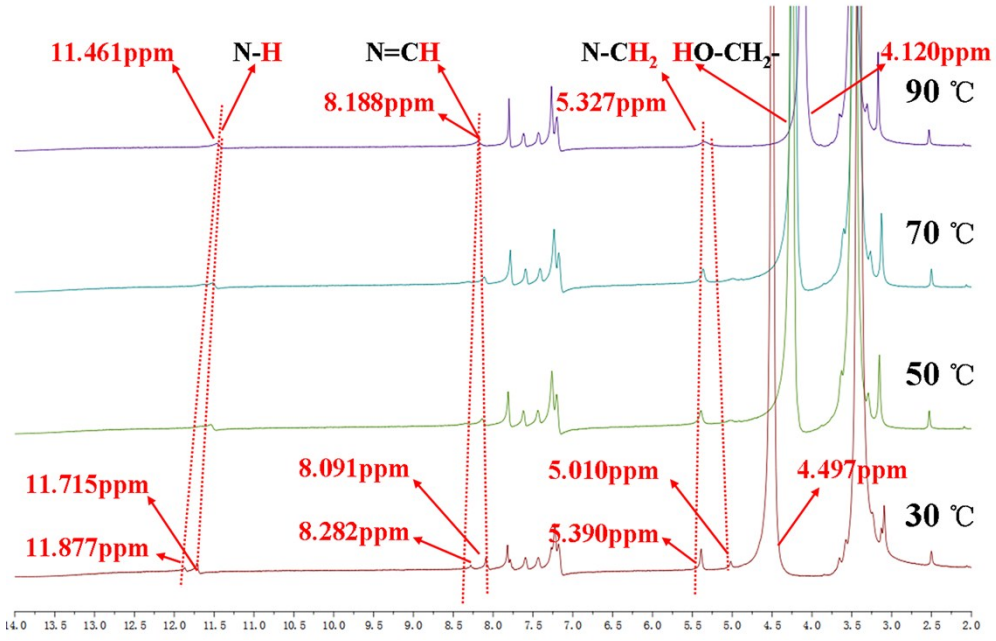


Fig. S12 Temperature-dependent ^{1}H NMR spectra (O-H and N-H region) of L-gel / [D_6] DMSO (40mg/mL)

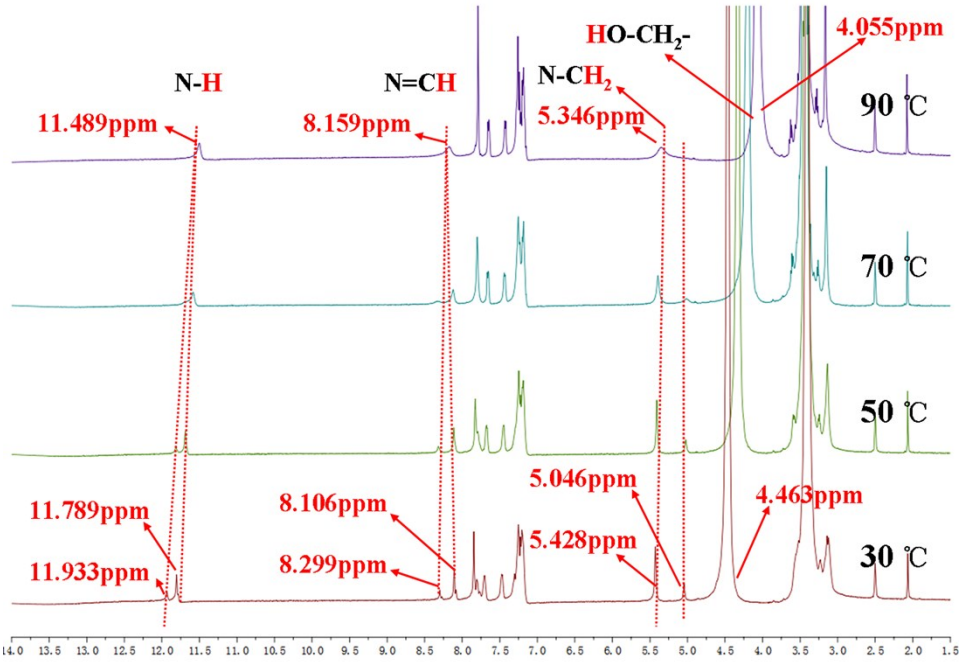


Fig. S13 Temperature-dependent ^{1}H NMR spectra (O-H and N-H region) of B-gel / [D_6] DMSO (L 40mg/mL, the mole ratio of gelator L with Cd^{2+} is 3:2)