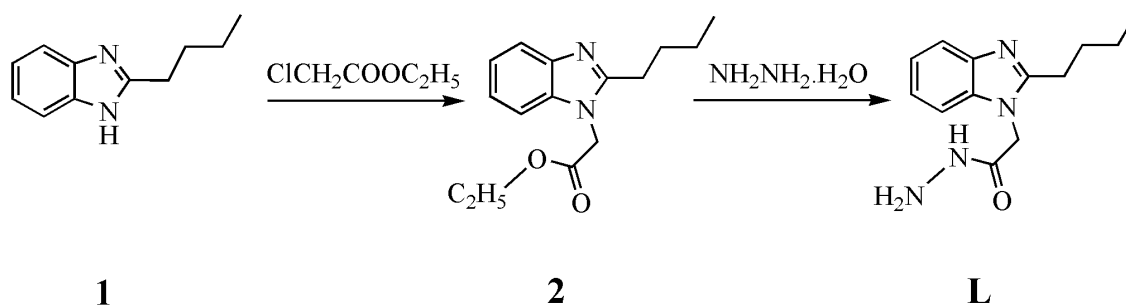


Tb³⁺-contained supramolecular hydrogels: luminescence property and reversible sol–gel transitions induced by external stimuli

Supporting Information



Scheme S1. Synthesis of Gelator L

Rare earth nitrates¹ and 2-butyl benzimidazole (**1**)^{2,3} were prepared according to the literature method.

Procedure for the preparation of 2-(2-butyl-1H-benzimidazol-1-yl) acetamide (**L**), (Scheme S1). The solution of 2-butyl benzimidazole (**1**) (0.05 mol) in acetone (30ml) was mixed with ethyl chloroacetate (0.08 mol) and potassium carbonate (0.10mol), and then refluxed for 6 h. After cooling to room temperature, the reaction mixture was filtered. From the clear filtrate, excess acetone was removed by distillation and then was added to water. The solid product separated was collected through filtration and dried. Further purification was done by recrystallization from ethyl acetate to obtain ethyl-(2-butyl-1H-benzimidazol-1-yl) acetate (**2**). Yield: 11.05 g (85%). The solution of ethyl (2-butyl-1H-benzimidazol-1-yl) acetate (**2**) (0.038mol) in ethanol (20mL) was mixed with hydrazine hydrate (99%) (2 mL, 0.04mol) and refluxed for 4 h. The solution was evaporated under

reduced pressure, and the residue was added to excess of water. The solid separated was collected by filtration. The crude product was purified by recrystallization from ethanol to give 2-(2-butyl-1H-benzimidazol-1-yl) acethydrazide (L). Yield: 8.42 g (90%). Anal. calcd for C₁₃H₁₈N₄O: C 63.39, H 7.37, N 22.75. Found: C 62.96, H 7.27, N 22.35. ¹H NMR (400MHz, CDCl₃): δ (ppm) 7.64-7.74 (d, 1H, -NH-), 7.50-7.63 (d, 1H, Ar-H), 7.14-7.35 (m, 3H, Ar-H), 4.67-4.83 (d, 2H, -CH₂-), 3.63-3.87 (d, 2H, -NH₂-), 2.51-2.74 (t, 2H, -CH₂-), 1.57-1.80 (t, 2H, -CH₂-) 1.29-1.49 (m, 2H, -CH₂-), 0.82-1.01 (t, 3H, -CH₃-); ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 166.90, 155.25, 142.50, 134.65, 123.10, 122.94, 119.52, 108.80, 45.80, 29.28, 26.92, 22.48, 13.72. ESI-MS: m/z (L + H)⁺ 247.15.

1 Q. D. Tan, W. Gou, M.A. He, *Chem. J. Chin. Univ.* 1986 **12** 1067-1069.

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

3 Y. M. Zhang, Q. Lin, T. B. Wei, X. P. Qin, Y. Li, *Chem Commun.*, 2009, 6074-6076.

FT-IR spectra of the samples were obtained from samples in KBr pellets using a Nicolet 170SX spectrometer scanning from 4000 cm^{-1} to 400 cm^{-1} at room temperature. The morphologies of the as-synthesized samples were characterized with a JSM-6701F SEM using an accelerating voltage of 5 kV. Fluorescence micrographs (FOM) of the samples were imaged by fluorescent optical microscopy (Olympus BX53) by exciting the G-gel samples with an unfocused UV radiation (330–385nm). The measurements of steady-state luminescence were performed with a spectrofluorimeter (HITACHI F-4500, Japan). The time-resolved luminescence of the gel samples were recorded on a luminescence spectrometer (FLS920, EI)

T_{sg} (gel–sol transition temperature) For the measurement, a tube inversion method was used for gelation characterization. A tube containing the gel was immersed in a temperature controlled water bath. When the gels exhibited gravitational flow upon inversion of the test tube, an average temperature of three such measurements was defined as the sol-gel transition.

Steel ball falls method: A small steel ball (250 mg, diameter 4 mm) was placed on the top of the gels in a test tube (diameter 10 mm). Then the sample was slowly heated ($2^{\circ}\text{C min}^{-1}$) in a thermostatted water bath. When the ball falls to the bottom of the test tube, the temperature is defined as the sol-gel phase transition temperature of the gels.

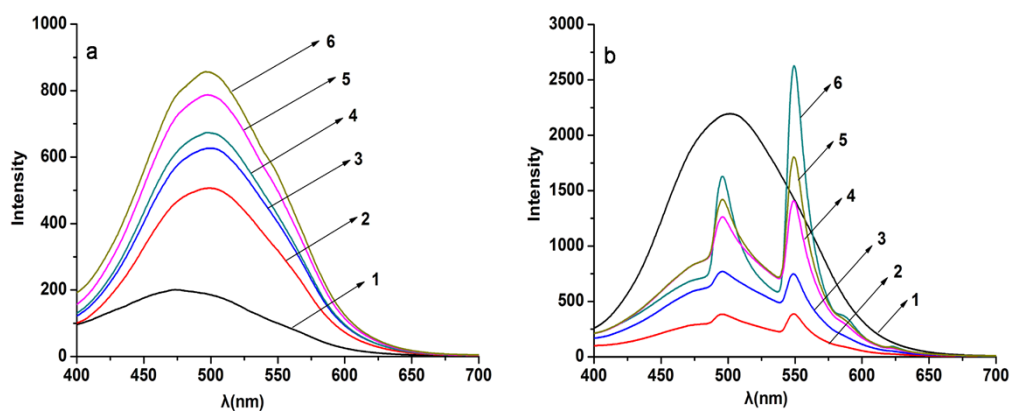


Fig. S1. Luminescence spectra of the G-gels with the varying proportion of Tb^{3+} , (1) 0 mmol; (2) 0.01 mmol; (3) 0.02 mmol; (4) 0.03 mmol; (5) 0.04 mmol; (6) 0.05 mmol. The concentrations of the L was 0.9 wt% (4mL), Slit: excitation/emission=5:5 (a). Luminescence spectra of xerogels. Slit: excitation/emission=2.5:2.5 (b).

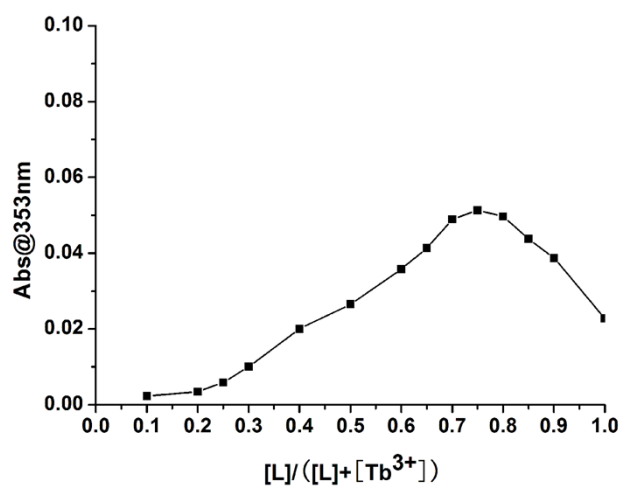


Fig. S2 Job plot of absorbance at 353 nm versus $[L]/([L]+[Tb^{3+}])$. Total concentration of (L + Tb^{3+}) was kept constant at $2.5 \times 10^{-3} \text{ mol L}^{-1}$.

L concentrations (wt%)	0.6	0.8	1.0	1.2
T _{sg} of G-gels without Tb ³⁺ (°C)	52±0.5	54±0.4	58±0.3	62±0.5
T _{sg} of G- gels with Tb ³⁺ (°C)	57±0.3	60±0.4	65±0.4	70±0.5

Note: the concentration of Tb³⁺ in L gels is 2.5×10⁻² mol L⁻¹.

Table S1. The sol–gel phase transition temperature of L gels with (without) Tb³⁺ ion

L/ Tb ³⁺ (L,0.6%)	4:1	3:1	2:1	1:1
T _{sg} (°C)	50±0.4	53±0.2	54±0.2	57±0.3

Table S2 Effect of Tb³⁺ ion concentration on the gels formed by 0.6wt% of L