Supporting information

A thermo-responsive supermolecule gel and its luminescence enhancement induced by rare earth Y³⁺

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Materials

O-Phenylendiamine (\geq 98%) was purchased from Tianjin Guangfu Fine Chemical Research Institute, Hexanedioic acid (\geq 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.. Ethyl chloroacetate and hydrazine hydrate (80%) were purchased from Alfa Aesar Chemical Co., Ltd.. 2,4-Dihydroxybenzaldehyde was purchased from Shanghai Bangcheng Chemical Co., Ltd.. All chemicals were used without further purification, unless otherwise noted.

Measurements

¹H NMR spectra were recorded on a Bruker 400MHz spectrometer. Elemental analyses were performed with an Elementar VarioELcube. 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. XRD (X-ray diffraction patterns) were determined with a Rigaku-Dmax 2400 diffractometer using Cu K α radiation over the 2 θ range of 4-90°. The morphologies of the as-synthesized samples were characterized with a JSM-6701F SEM using an accelerating voltage of 5kV. The measurements of steady-state luminescence were performed with a spectrofluorimeter (HITACHI F-4500, Japan). 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). All measurements were carried out at room temperature.



Synthesis of gelator L

Scheme S1. Synthesis of Gelator L

Synthesis of L1

Hexanedioic acid (8.77g , 0.06mol)) and O-Phenylendiamine (14.05g, 0.13mol) were added to a round-bottom flask with 200mL hydrochloric acid (4mol/L), then the solution was refluxed for 8h. After cooling to room temperature, the reaction mixture was slowly added ammonia until a pH value into 7. 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 L1. Yield: 11.90g (68%). Anal. calcd for $C_{18}H_{18}N_4$: C 74.46, H 6.25, N 19.30. Found: C 74.13,

H 6.15, N 19.42. ¹H NMR (400MHz, DMSO-D₆): δ (ppm) 12.24 (s, 1H, -NH-), 7.49 (s, 2H, Ar-H), 7.18-7.09 (m, 2H, Ar-H), 2.90 (t, *J*=6.0 Hz, 2H, -CH₂-), 1.89 (t, *J*=4.9 Hz, 2H, -CH₂-); ¹³C NMR (100.5 MHz, DMSO-D₆): δ (ppm) 155.32, 121.59, 28.78, 27.70. ESI-MS: m/z (L + H)⁺ 291.18.

Synthesis of L2

Ethyl chloroacetate (8.82g, 0.072mol) and potassium carbonate (13.82g, 0.1mol) were added to a 100mL DMF of L1 (10g, 0.034mol), then the solution was refluxed for 12h. The reaction mixture was evaporated under reduced pressure, and then was added to water. The solid separated was collected by filtration. The crude product was washed with ethyl acetate to give L2. Yield: 14.10 g.

Synthesis of L3

The solution of L2 9g in DMF (50mL) was mixed with 2.5g hydrazine hydrate (80%). The solution was refluxed for 9h, 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 mixed solvent of DMF/H₂O to give L3. Yield: 7.0 g. Anal. calcd for $C_{22}H_{26}N_8O_2$: C 60.81, H 6.03, N 25.79. Found: C 60.99, H 6.15, N 25.88. ¹H NMR (400MHz, DMSO-D₆): δ (ppm) 9.60 (s, 1H, -NH-), 7.57 (d, *J*=7.3 Hz, 1H, Ar-H), 7.40 (dd, *J*=23.5 Hz, 1H, Ar-H), 7.24-7.10 (m, 2H, Ar-H), 4.86 (s, 2H, -NCH₂-), 4.43 (s, 2H, -NH₂), 2.88 (d, *J*=36.0 Hz, 2H, -CH₂-), 1.95 (s, 2H, -CH₂-); ¹³C NMR (100.5 MHz, DMSO-D₆): δ (ppm) 166.23, 155.54, 142.22, 135.67, 121.52, 121.27, 118.33, 109.77, 44.31, 26.36, 26.21. ESI-MS: m/z (L + H)⁺ 435.20.

Synthesis of gelator L

The solution of L3 (6.5g, 0.015mol) in DMF (100mL) was mixed with 2,4-Dihydroxybenzaldehyde (4.83g, 0.035mol) 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: 8.04g (79.5%). To be sure, this gelator L has two rotamers. The NMR data is expressed as a fraction. Anal. calcd for $C_{36}H_{34}N_8O_6$: C 64.09, H 5.08, N 16.61. Found: C 64.22, H 5.32, N 16.77. **Major product:** ¹**H NMR (400MHz, DMSO-D₆):** δ (ppm) 11.91 (s, 1H, -NH-), 11.04 (s, 1H, -OH), 9.94 (s, 1H, -OH), 8.34 (s, 1H, -N=CH-),7.61 (d, *J*=4.2 Hz, 1H, Ar-H), 7.42 (dd, *J*=4.6, 1.9 Hz, 1H, Ar-H), 7.32 (d, *J*=4.3 Hz, 1H, Ar-H), 7.27-7.04 (m, 2H, Ar-H), 6.33 (dt, *J*=7.2, 4.3 Hz, 2H, Ar-H), 5.42 (d, *J*=1.6 Hz, 2H, NCH₂-), 2.90 (dd, *J*=10.7, 3.5 Hz, 2H, -CH₂-), 2.02-1.81 (m, 2H, -CH₂-).

Major product: ¹³C NMR (100.5MHz, DMSO-D₆): δ (ppm) 167.55, 160.91, 159.32, 155.78, 148.72, 142.62, 135.95, 131.02, 121.62, 121.34, 118.39, 111.64, 109.74, 107.86, 102.59, 44.67, 26.35, 26.20. ESI-MS: m/z (L + H)⁺ 675.20.

Minor product: ¹**H NMR (400 MHz, DMSO-D₆) of:** δ (ppm) 11.49 (s, 1H, -NH-), 9.96 (s, 1H, -OH), 9.80 (s, 1H, -OH), 8.25 (s, 1H, -N=CH-), 7.55 (dt, *J*=3.9, 1.9 Hz, 1H, Ar-H), 7.42 (dd, *J*=4.6, 1.9 Hz, 1H, Ar-H), 7.32 (d, *J*=4.3 Hz, 1H, Ar-H), 7.27-7.04 (m, 2H, Ar-H), 6.33 (dt, *J*=7.2, 4.3 Hz, 2H, Ar-H), 5.02 (d, *J*=1.9 Hz, 1H, -NCH₂-), 2.90 (dd, *J*=10.7, 3.5 Hz, 2H, -CH₂-), 2.02-1.81 (m, 2H, -CH₂-).

Minor product: ¹³C NMR (100.5MHz, DMSO-D₆): δ (ppm) 162.84, 160.60, 158.11, 155.59, 148.72, 142.24, 135.64, 128.20, 121.43, 121.09, 118.23, 110.36, 109.70, 107.80, 102.38, 43.96, 26.35, 26.20. ESI-MS: m/z (L + H)⁺ 675.20.

Tsg (gel-sol transition temperature)

Tube inversion method: the glass tubes 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 L-gel (a) and Y@gel (b) induced by temperature



Fig. S2 The change of Tsg in (a) L-gel and (b) Y@gel with respect to the gelator concentration



Fig. S3 XRD pattern of the Gelator L (a) and xerogel of the Y@gel (b)



Fig. S4 ESI-MS of L-Y³⁺



Fig. S5 Temperature-dependent ¹H NMR spectra (O-H, N-H C=NH and -CH₂- region) of gelator L with 1 equivalent Y³⁺/[D₆] DMSO (gelator L 40mg/mL)



Fig. S6 Temperature-dependent luminescence spectra of L-gel (The concentration of L in the sample is 1 wt%, DMF : water is 1:5)



Fig. S7 Multi-peak fitting luminescence spectra of the L-gel (a) and Y@gel (b) excited at 365nm (The black line is experimental curve, the red lines are fitting curves); Luminescence spectra of L-gel and Y@gel excited at 325 nm (c)



Fig. S8 The possible luminescence mechanism of L-gel and Y@gel