Electronic Supplementary Information

Unusual fluorescence and sol-gel transition properties of pyridine-based polymeric gel formed by hydrazone reaction

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Experimental Section

Materials and instruments. The building block **1** was synthesized according to the procedures of our previous work.¹ The Building block **2** was purchased from TCI. The ¹H and ¹³C NMR spectra were taken on a Bruker DRX 300, and mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. An UV-visible (UV-vis) spectrophotometer (Thermo Evolution 600) was used to obtain the absorption spectra. All fluorescence spectra were recorded in RF-5310PC spectrophotometer. The elemental analysis was performed with a Perkin Elmer 2400 series II instrument.

Fluorescence measurement. Solutions of building blocks **1**, **2** $(1 \times 10^{-5} \text{ M})$ and mixed solutions of the building blocks (0.15 M of **1** and **2**, respectively, without HCl and with 0.05 mmol of HCl) in DMSO were measured in 3 mL quartz cell and the gels were measured in 0.1 mL quartz cell. The temperature control of the gel in the fluorometer was performed with NTT-2200P accessory. The temperature dependent fluorescence measurements of the gel were repeated five times.

Preparation of the gel. Building blocks **1** (30 mg, 0.15 mmol) and **2** (20 mg, 0.15 mmol) were dissolved in DMSO (1 mL) by sonication. Then various amounts of HCl (0.10-1.00 mmol) were added to the mixture solution. Finally, the mixed solutions were maintained at room temperature to afford translucent gels.

SEM observation. The observed gel samples were freeze dried to provide the corresponding xerogels. An FE-SEM, Philips XL30 S FEG field emission SEM was used to obtain images of the freeze-dried gel samples using an accelerating voltage 5-15 kV and an emission current of $10 \mu A$.

Rheological properties. Rheological tests of the gels were carried out by using An AR-2000ex (TA Instruments Ltd) implemented with a 40 mm diameter parallel plate that was attached to a transducer. The gap in the setup for rheological testing of the gels was 1.0 mm and experiments were conducted at 25 °C. Strain sweep tests were performed with increasing amplitude oscillation up to 1000 % apparent strain on shear. Frequency sweeps were performed from 1-1,000 Hz. The recovery properties of the gels in response to applied shear force were investigated with the following 1,500 s procedure: 1% (300 s) \rightarrow 1000% (300-600 s) \rightarrow 1% (600-900 s) \rightarrow 1000% (900-1,200 s) \rightarrow 1% (1,200-1,500 s).

GPC measurements. The molecular weights of polymers were measured relative to polystyrene standards on a Tosoh HLC-8320 gel-permeation chromatography (GPC) equipped with EcoSEC software, $2 \times \text{TSKgel}$ Supremultipore HZ-M (4.6 × 150 mm) columns and RI detector. DMF was used as an eluent at a flow rate of 0.35 mL/min, and the instrument was calibrated using polystyrene standards. GPC samples were prepared by passing a DMF solution of sample through 0.45 µm PTFE filter. 10 µL of 3 mg/mL sample dissolved in DMSO was injected, and GPC analysis was done at 40 °C.



Fig. S1 Photograph of polymeric gels formed with building block **1** (30 mg, 0.15 mmol) and **2** (20 mg, 0.15 mmol) in DMSO (1 mL) in the presence of various concentrations of HCl ((a) 0.10 mmol, (b) 0.20 mmol, (c) 0.40 mmol, (d) 0.60 mmol, (e) 0.80 mmol, (f) 1.00 mmol).



Fig. S2 Photographs showing the time required for the gelation of **1** (30 mg, 0.15 mmol) and **2** (20 mg, 0.15 mmol) mixture in 0.10 mmol of HCl.



Fig. S3 Photographs showing the time required for gelation of **1** (30 mg, 0.15 mmol) and **2** (20 mg, 0.15 mmol) mixture in (A) 0.20 mmol, (B) 0.40 mmol of HCl, respectively.



Fig. S4 ¹H NMR spectra of the building blocks (A) **1** and (B) **2**. (C) The time-dependent ¹H NMR spectra of the mixture of **1** (30 mg, 0.15 mmol) and **2** (20 mg, 0.15 mmol) in the presence of DCl (0.10 mmol) in DMSO (1 mL).



Fig. S5 ¹H NMR spectra of the gels formed with (A) 0.20 mmol, (B) 0.60 mmol, (C) 1.00 mmol of DCl, respectively.

	0.10 mmol	0.20 mmol	0.40 mmol
$M_{\rm w} \ ({\rm g \ mol^{-1}})$	$8.4 imes10^3$	$7.6 imes10^3$	$5.1 imes10^3$
$M_{\rm n}~({\rm g~mol^{-1}})$	$2.9 imes10^3$	$2.4 imes10^3$	$1.4 imes10^3$
$M_{ m w}\!/M_{ m n}$	2.9	3.1	3.6

Table S1 Molecular weights of polymeric gels formed with 0.10 mmol, 0.20 mmol, 0.40 mmol, respectively, measured by GPC.



Fig. S6 Fluorescence spectra of (A) **1**, **2** in DMSO (1×10^{-5} M), and (B) those of **1**, **2** in DMSO (1×10^{-5} M) in the presence of 0.10 mmol HCl.



Fig. S7 UV-vis absorption spectra of 1, 2 dissolved in DMSO, respectively (1×10^{-5} M).



Fig. S8 UV-vis absorption spectrum of gel formed in 0.10 mmol of HCl (dispersed in DMSO with the concentration of 1×10^{-5} M) and obtained spectra from curve-fitting of the absorption spectrum.



Fig. S9 UV-vis absorption spectrum of hydrogel prepared by solvent exchange (dispersed in water with the concentration of 1×10^{-5} M) and obtained spectra from curve-fitting of the absorption spectrum.



Fig. S10 UV-vis spectra of the gel formed with 0.10 mmol of HCl after immersion into aqueous media for (A) 1 min, (B) 2 min, (C) 3 min and (D) 4 min, respectively, and their curve-fitting spectra.



Fig. S11 (A) Photographs of (a) the gel formed in DMSO and (b) thiourea-possessing hydrogel prepared by the solvent exchange in thiourea-saturated aqueous solution, which were taken under an UV lamp and (B) fluorescence spectra of them.

Quantity of HCl in the gel	Luminescence lifetime	
10 mmol	3.90 ns	
20 mmol	3.61 ns	
40 mmol	3.26 ns	
60 mmol	3.12 ns	
80 mmol	2.92 ns	
100 mmol	2.83 ns	

Table S2 Luminescence life time of the gel formed with various amounts of HCl.



Fig. S12 Photographs ((A) under normal light, (B) UV lamp) showing reversible sol-gel transition by temperature of gel formed in 0.10 mmol HCl.



Fig. S13 (A) Fluorescence spectra of the gel formed with 0.10 mmol of HCl at various temperatures while the gel was heated and (B) plot of fluorescence intensity of the gel at 469 nm.



Fig. S14 (A) Fluorescence spectra of the gel formed with 0.10 mmol of HCl at various temperatures while the heated gel was cooled in room temperature and (B) plot of fluorescence intensity of the gel at 469 nm.



Fig. S15 (A) Fluorescence spectra of the gel formed with 0.10 mmol of HCl, which were measured over time while the heated gel was cooled in room temperature and (B) plot of fluorescence intensity of the gel at 469 nm.



Fig. S16 ¹H NMR spectra of the gel formed in 0.10 mmol of HCl at (A) room temperature and (B) 140 °C, respectively.



Fig. S17 SEM images of the gel formed in (A) 0.10 mmol, (B) 0.20 mmol, (C) 0.40 mmol of HCl, respectively.



Fig. S18 Rheological properties of the gels formed with (a) 0.10 mmol, (b) 0.20 mmol, (c) 0.40 mmol of HCl, respectively. (A) Strain sweep (1-1000%), (B) frequency sweep (5-1000 rad/s) and (C) continuous step strain measurements at 1% and 1000%.



Fig. S19 Continuous step strain measurement ($\gamma = 1\%$, for 1 h) of 1 and 2 mixture in DMSO with 0.20 mmol of HCl during its gelation process.



Fig. S20 Schematic illustration showing sol-gel and aggregation mode transition of the polymeric gel with fluorescent property change.

Reference

1. S. H. Jung, T. K. Hyun, J. -Y. Kim and J. H. Jung, *RSC Adv.*, 2015, **5**, 26662.