

Electronic Supplementary Information

Control of mechanical strength of bipyridine-based polymeric gel from linear nanofibre to the helix with chiral dopant

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Experimental Section

Characterization. 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. A UV–visible (UV–vis) spectrophotometer (Thermo Evolution 600) was used to obtain the absorption spectra. IR spectra were obtained for KBr pellets, in the range 400–4000 cm⁻¹, with a Shimadzu FTIR 8400S instrument. The elemental analysis was performed with a Perkin Elmer 2400 series II instrument.

Preparation of gel. For **gel-3S** and **gel-3R** with Fe²⁺ (1.0 wt%), Building block **1** (4 mg, 15 μmol) was dissolved in DMSO (0.4 mL) by heating. Building block **2** (2 mg, 15 μmol), **3R** or

3S (0-0.5 equiv.) and $\text{Fe}(\text{BF}_2)_4 \cdot 6\text{H}_2\text{O}$ (0.33 equiv.) were added to solution of building block **1**. Then amount of HCl (10-50 μmol) was added the mixture solution. Finally, the mixed solution was maintained at room temperature.

SEM observation. 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 μA . The observed gel samples were freeze dried to provide the corresponding xerogels.

AFM observation. Atomic force microscope (AFM) imaging was performed by using XE-100 and a PPP-NCHR 10 M cantilever (Park systems). The AFM samples of gel were prepared by spin-coating (1500 rpm) onto freshly cleaved Muscovite Mica, and images were recorded with the AFM operating in noncontact mode in air at RT with resolution of 512×512 pixels, using moderate scan rates (0.5 Hz).

Circular dichroism studies. The CD spectra were recorded on a Jasco J-815 CD spectrophotometer. CD spectra were determined over the range of 250-550 nm using a quartz cell with 0.1 mm path length. Scans were taken at a rate of 100 nm/min with a sampling interval of 1.0 nm and response time of 1s. The scans were acquired for the gel directly at room temperature in DMSO.

Rheological properties. Rheological test of 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: 0.1% (300 s)→100% (300-600 s)→0.1% (600-900 s)→100% (900-1,200 s)→0.1% (1,200-1,500 s).

NMR studies. The homogenous solution [**1+2+3S** (**1**, **2**: 37.5 mM and **3S**: 0.3 equiv.) 22 μmol , 600 μL in DMSO- d_6] was transferred by a micro pipet to an NMR tube. The DCI (10 μmol , 30 μmol and 50 μmol) was added, respectively. Time-dependent ^1H NMR spectrum was measured with average 100 scans at ambient temperature.

Synthesis of 2

2,2'-bipyridine-5,5'-dicarboxylic acid (1 g, 4.1 mmol) was suspended in absolute ethanol (15 mL). Concentrated sulfuric acid (2 mL) was slowly added to the suspension and the resulting mixture was refluxed for 18 h. The solution was cooled to room temperature and poured onto cold water (4 °C, 400 mL) to obtain the precipitation of a white solid, which was filtered, washed with water and lyophilized (1.15 g, 93.5 % yield). mp. 145 °C; IR (KBr pellet): 1721, 1269, 1112 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ ppm 9.20 (dd, $J = 2.15, 0.8$ Hz, 2H), 8.57 (dd, $J = 8.3, 0.8$ Hz, 2H), 8.46 (dd, $J = 8.3, 2.15$ Hz, 2H), 4.0 (q, $J = 7.1$ Hz, 4H), 1.37 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (75 MHz DMSO- d_6) δ ppm 164.9, 157.8, 150.5, 138.8, 126.8, 121.7, 61.8, 14.5; ESI-MS (m/z): Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$ [$\text{M}+\text{H}$] $^+$ 301.11, Found 301.28; Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.95; H, 5.32; N, 9.35.

Synthesis of 1

A mixture of building block **2** (1.15 g, 3.8 mmol) and hydrazine hydrate (0.41 mL, 8.4 mmol) in a solution of ethanol (20 mL) and toluene (5 mL) was heated at 120 °C for 30 h. The precipitate was filtered, washed with CH_2Cl_2 to remove unreacted starting material, and dried in vacuo to give (0.88 g, 85.1 % yield) the pure solid. mp. 365 °C; IR (KBr pellet): 3318, 3192, 3027, 1658, 1621, 1591, 1561 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ ppm 10.09 (s, 2H), 9.09 (d, $J = 1.53$ Hz, 2H), 8.50 (d, $J = 8.28$ Hz, 2H), 8.34 (dd, $J = 8.29, 2.22$ Hz, 2H), 4.66 (s, 4H); ^{13}C NMR (75 MHz DMSO- d_6) δ ppm 164.3, 156.6, 148.4, 136.7, 121.0; ESI-MS: Calculated for $\text{C}_{12}\text{H}_{12}\text{N}_6\text{O}_2$ [$\text{M}+\text{H}$] $^+$ 272.10, Found 272.28; Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_6\text{O}_2$: C, 52.94; H, 4.44; N, 30.87. Found: C, 52.90; H, 4.47; N, 30.81.

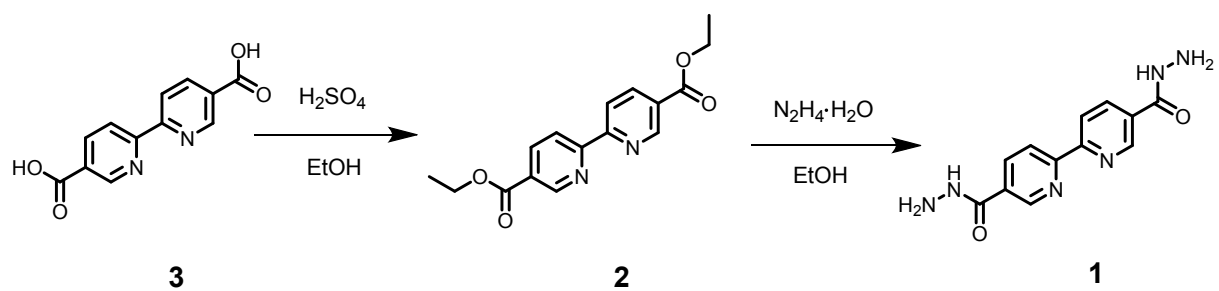


Fig. S1 Schematic of synthetic methods for building block 1.

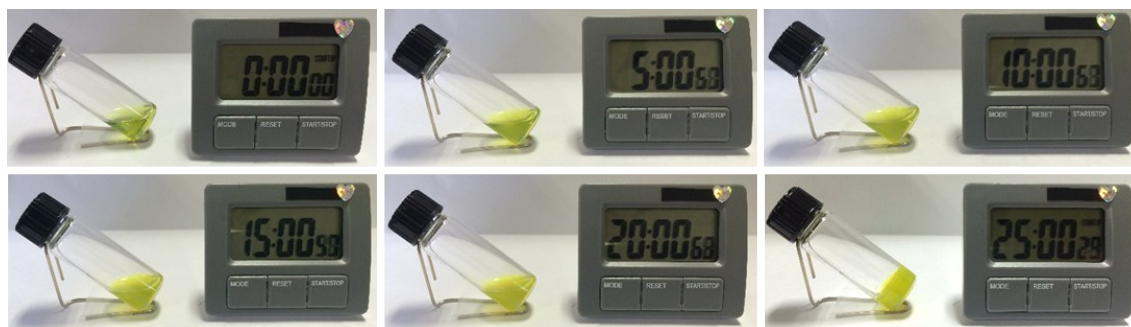


Fig. S2 The photograph for gel formation of **gel-3S** (1.0 wt%, **1** and **2**: 37.5 mM, **3S**: 0.3 equiv. and Fe^{2+} : 0.33 equiv.) in the presence of HCl (10 μmol) by increasing hydrazone reaction times.

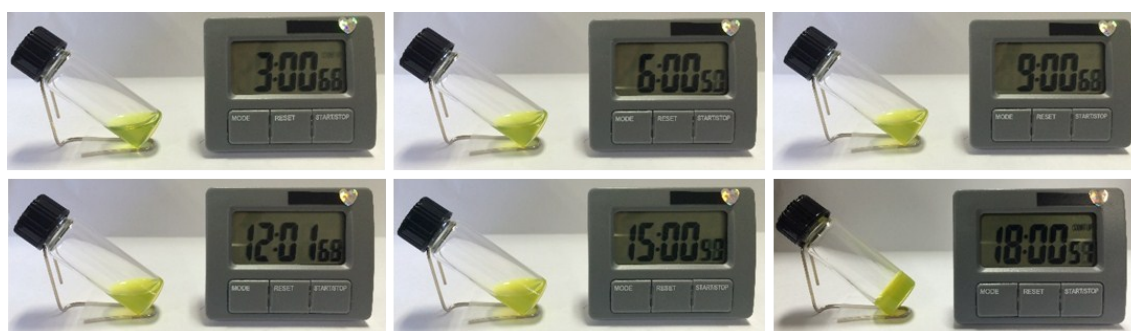


Fig. S3 The photograph for gel formation of **gel-3S** (1.0 wt%, **1** and **2**: 37.5 mM, **3S**: 0.3 equiv. and Fe^{2+} : 0.33 equiv.) in the presence of HCl (30 μmol) by increasing hydrazone reaction times.

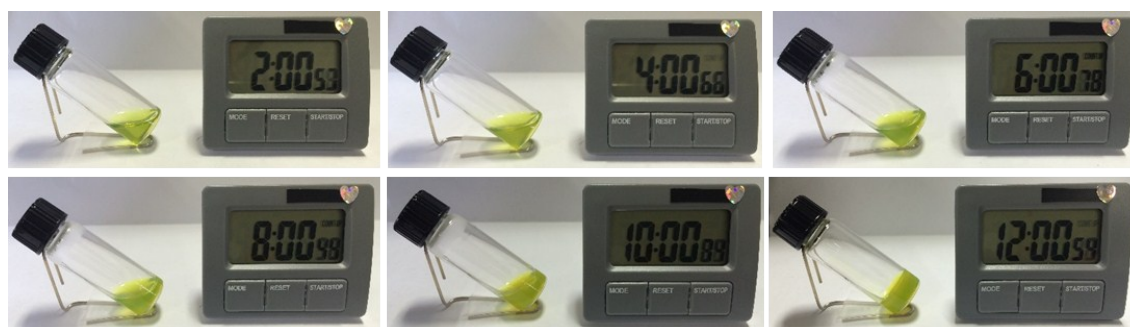


Fig. S4 The photograph for gel formation of **gel-3S** (1.0 wt%, **1** and **2**: 37.5 mM, **3S**: 0.3 equiv. and Fe^{2+} : 0.33 equiv.) in the presence of HCl (50 μmol) by increasing hydrazone reaction times.

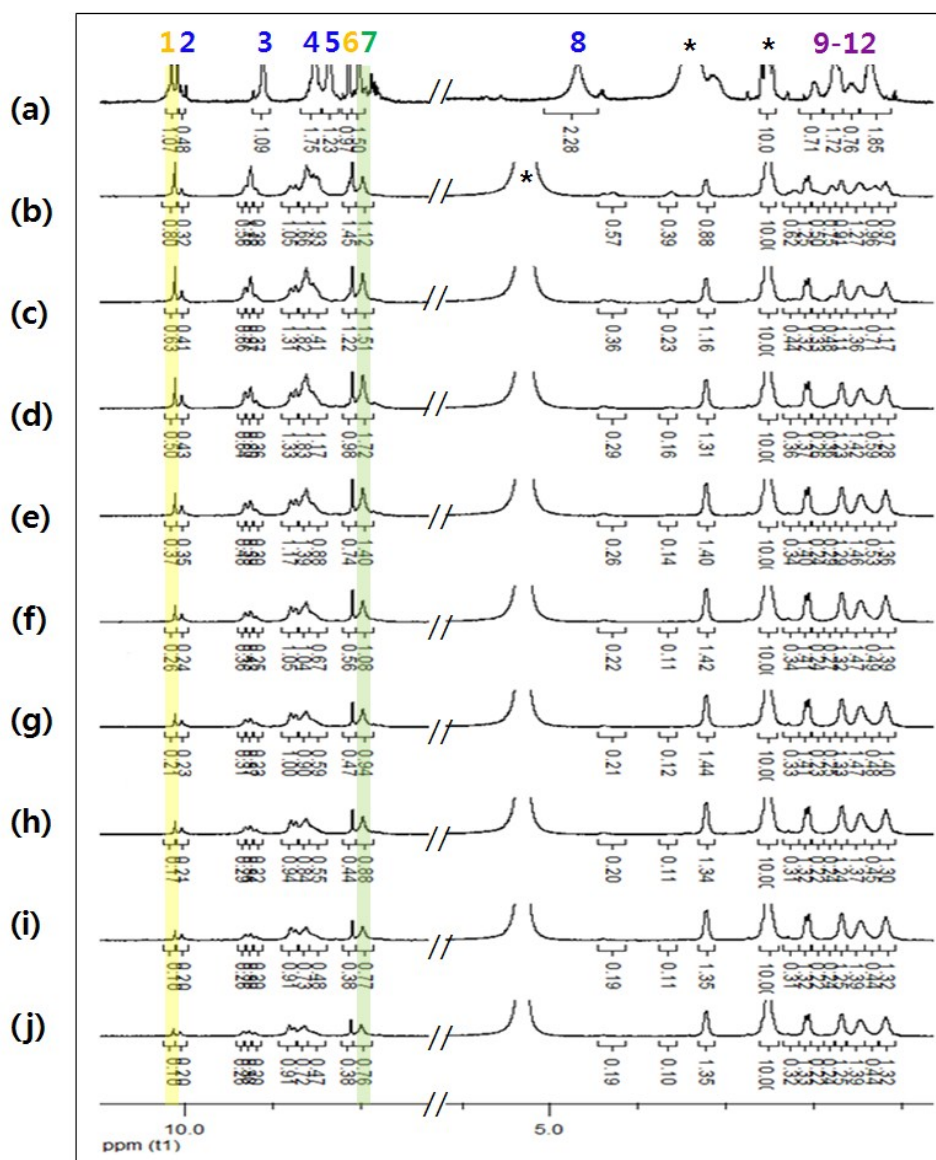
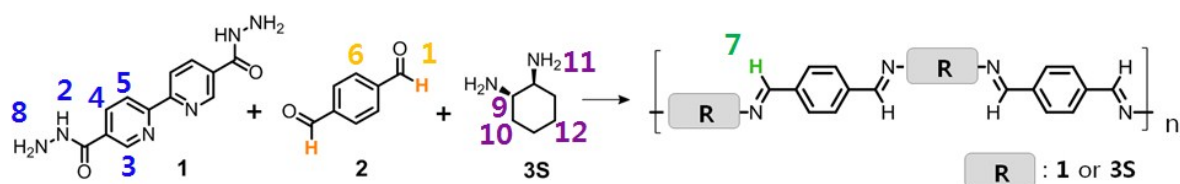


Fig. S5 NMR spectra of **gel-3S** (1.0 wt%, 37.5 mM) (a) before and after adding DCI (10 μmol), (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 45 min, (g) 60 min (h) 80 min (i) 100 min and (j) 120 min in $\text{DMSO-}d_6$.

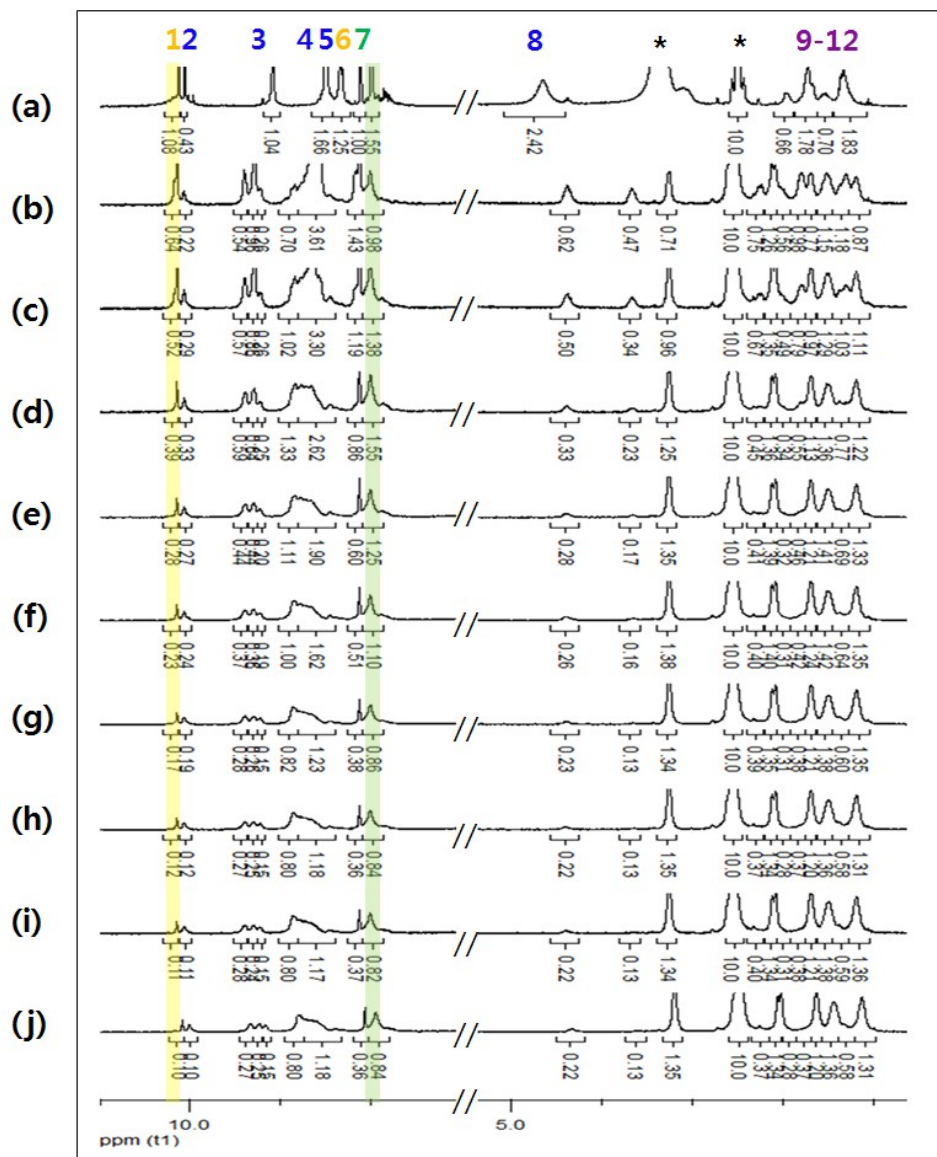
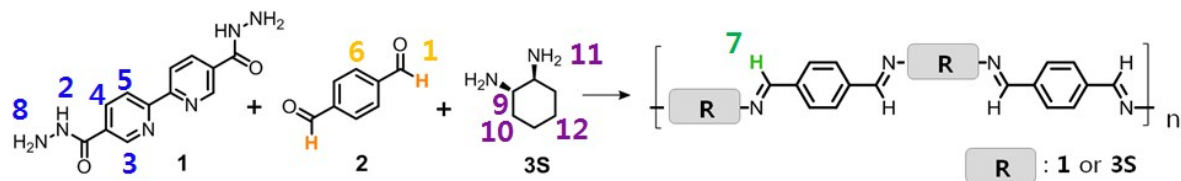


Fig. S6 NMR spectra of gel-3S (1.0 wt%, 37.5 mM) (a) before and after adding DCl (30 μmol), (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 45 min, (g) 60 min (h) 80 min (i) 100 min and (j) 120 min in $\text{DMSO-}d_6$.

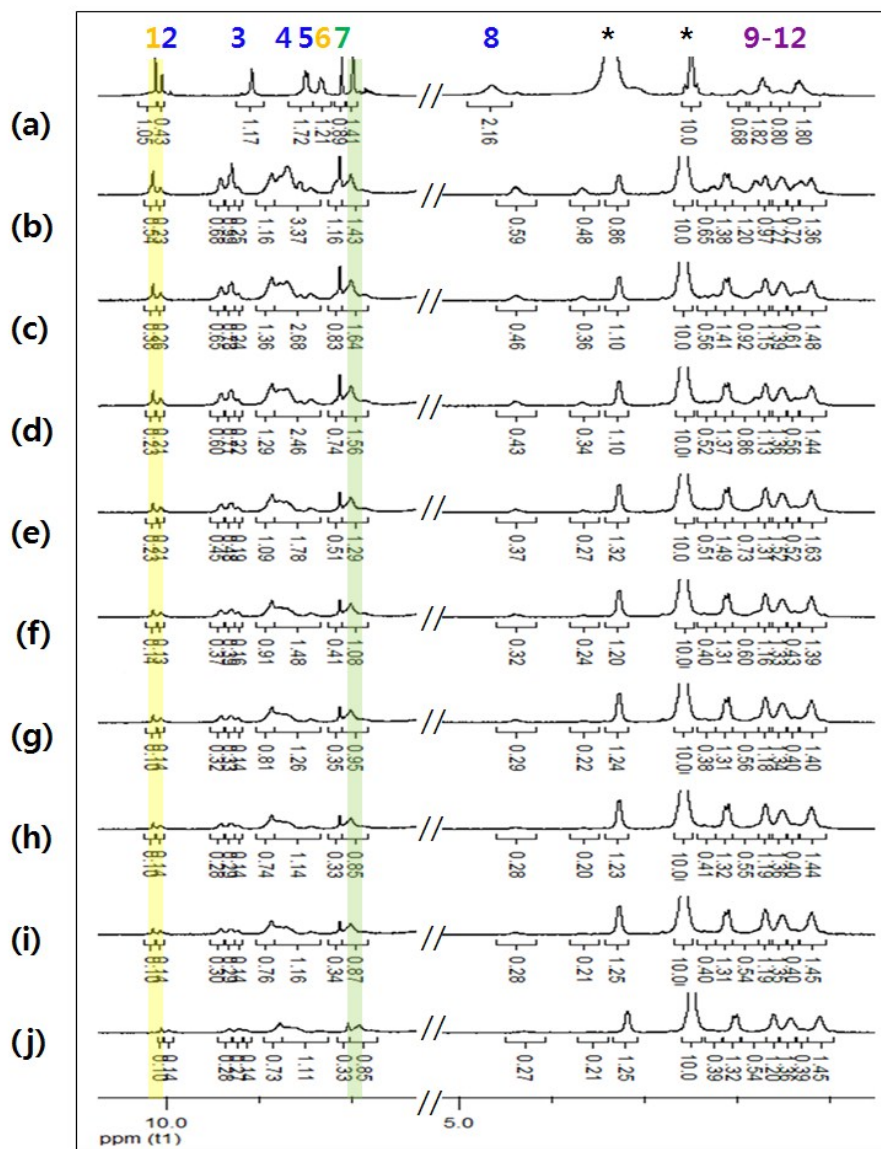
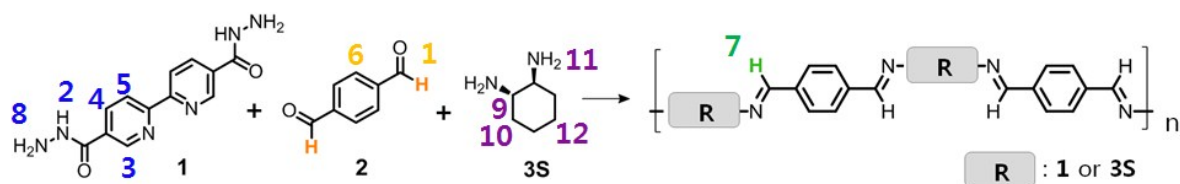


Fig. S7 NMR spectra of **gel-3S** (1.0 wt%, 37.5 mM) (a) before and after adding DCl (50 μ mol), (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 45 min, (g) 60 min (h) 80 min (i) 100 min and (j) 120 min in DMSO- d_6 .

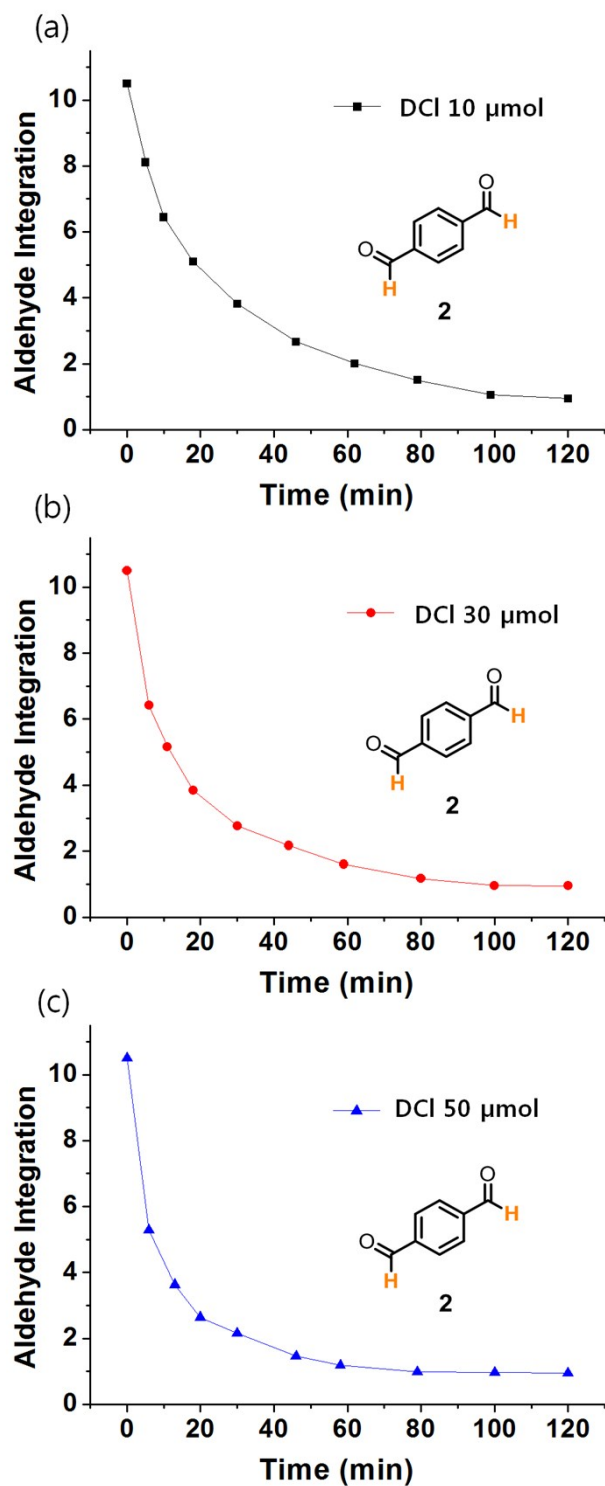


Fig. S8 The change in the amount of reactant (**2**) after product (hydrazone) formation as a function of time showing a plateau after equilibrium hydrazone reaction has been reached. The equilibrium hydrazone reaction can be seen to occur at different time points for **gel-3S** in the presence of (a) DCI (10 μmol), (b) DCI (30 μmol) and (c) DCI (50 μmol), respectively.

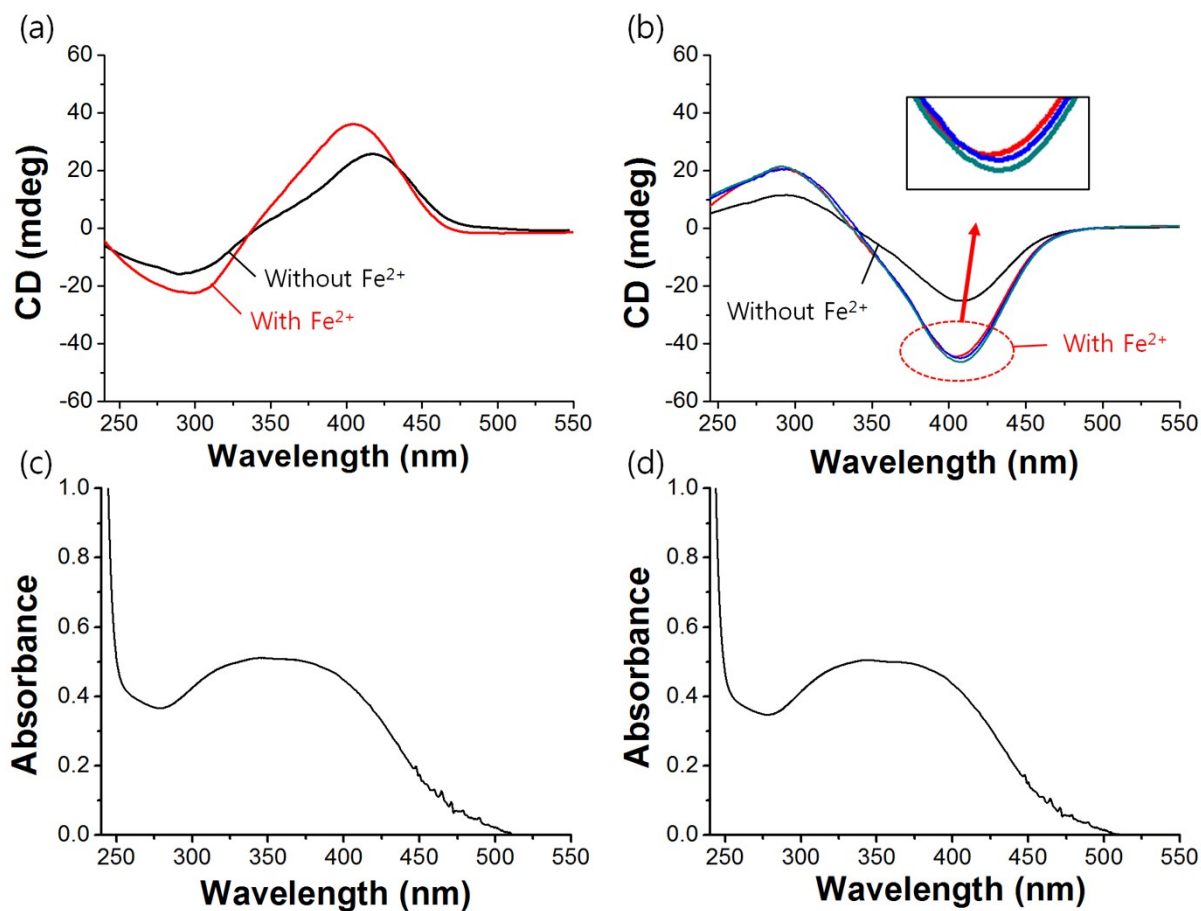


Fig. S9 CD spectra of gels (1.0 wt%) prepared by **1+2** (**1, 2**: 37.5 mM) upon addition of (a) **3R** (0.3 equiv.) without and with Fe²⁺ (0.33 equiv.). (b) CD spectra of gels (1.0 wt%) prepared by **1+2** (**1, 2**: 37.5 mM) upon addition of **3S** (0.3 equiv.) without and with Fe²⁺ (0.33 equiv., red line; 0.66 equiv., blue line; 0.99 equiv., green line) in the presence of HCl (10 μ mol). UV-vis spectra of (c) gel-**3R** with Fe²⁺ and (d) gel-**3S** with Fe²⁺.

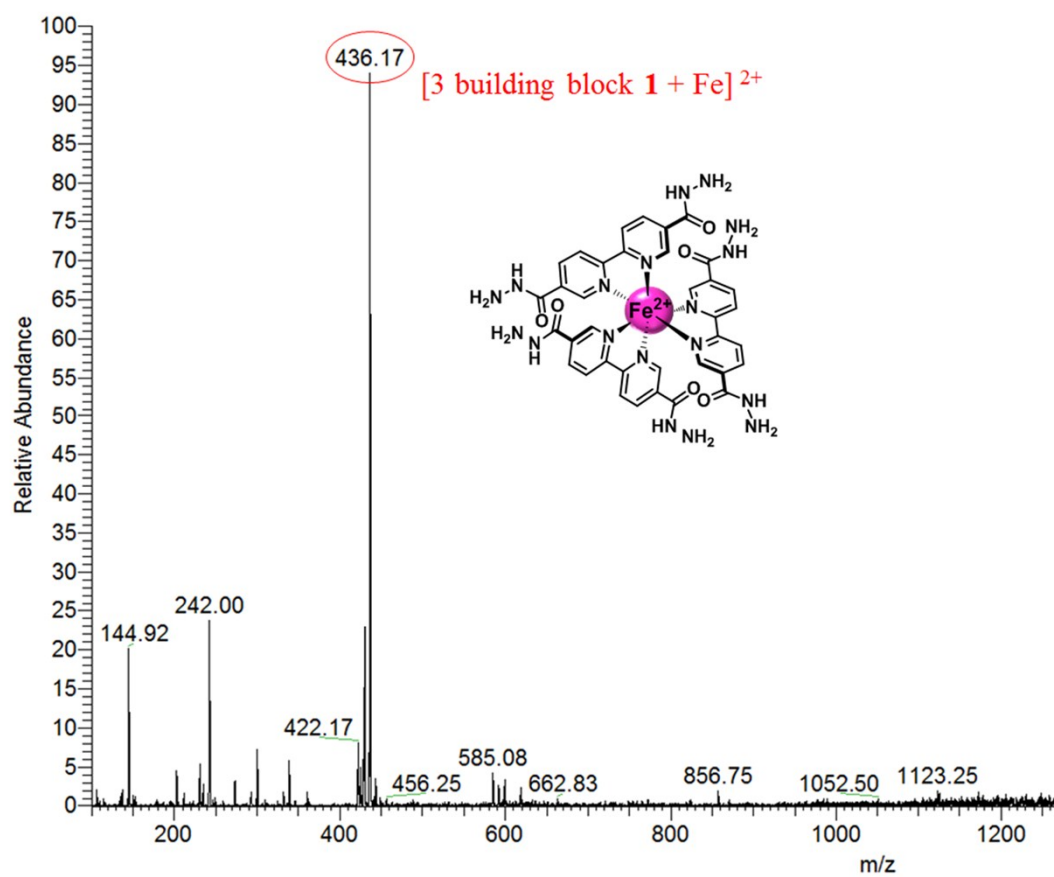


Fig. S10 ESI-mass spectrum of building block 1 with Fe^{2+} (0.33 equiv.).

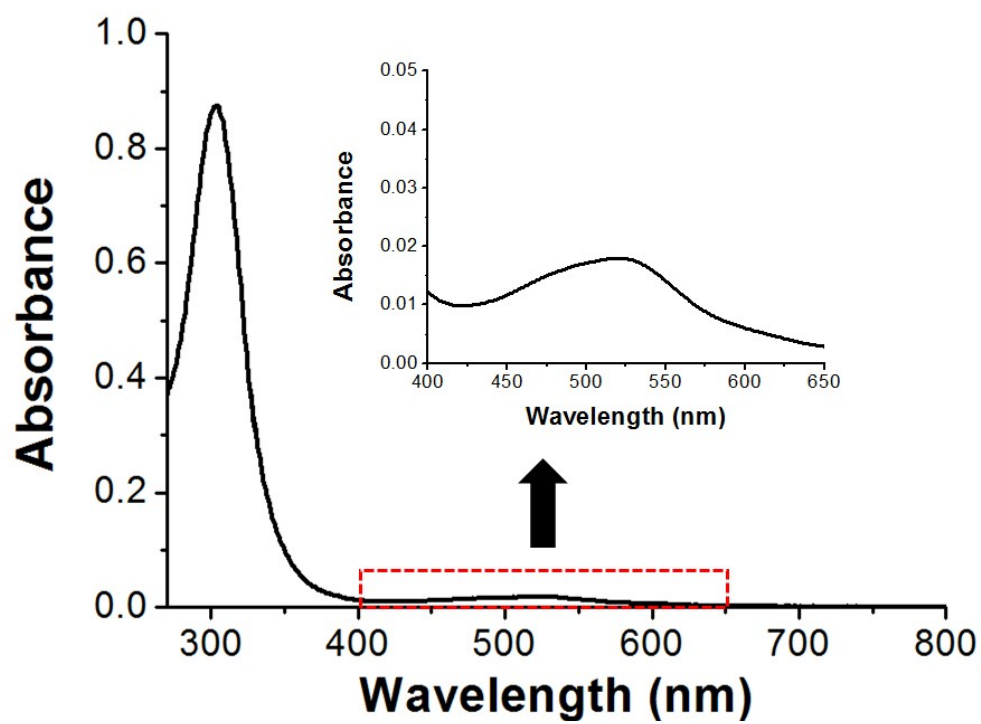


Fig. S11 UV-vis spectrum of **1** (0.07 mM) complex with Fe²⁺ (0.33 equiv.) in DMSO.

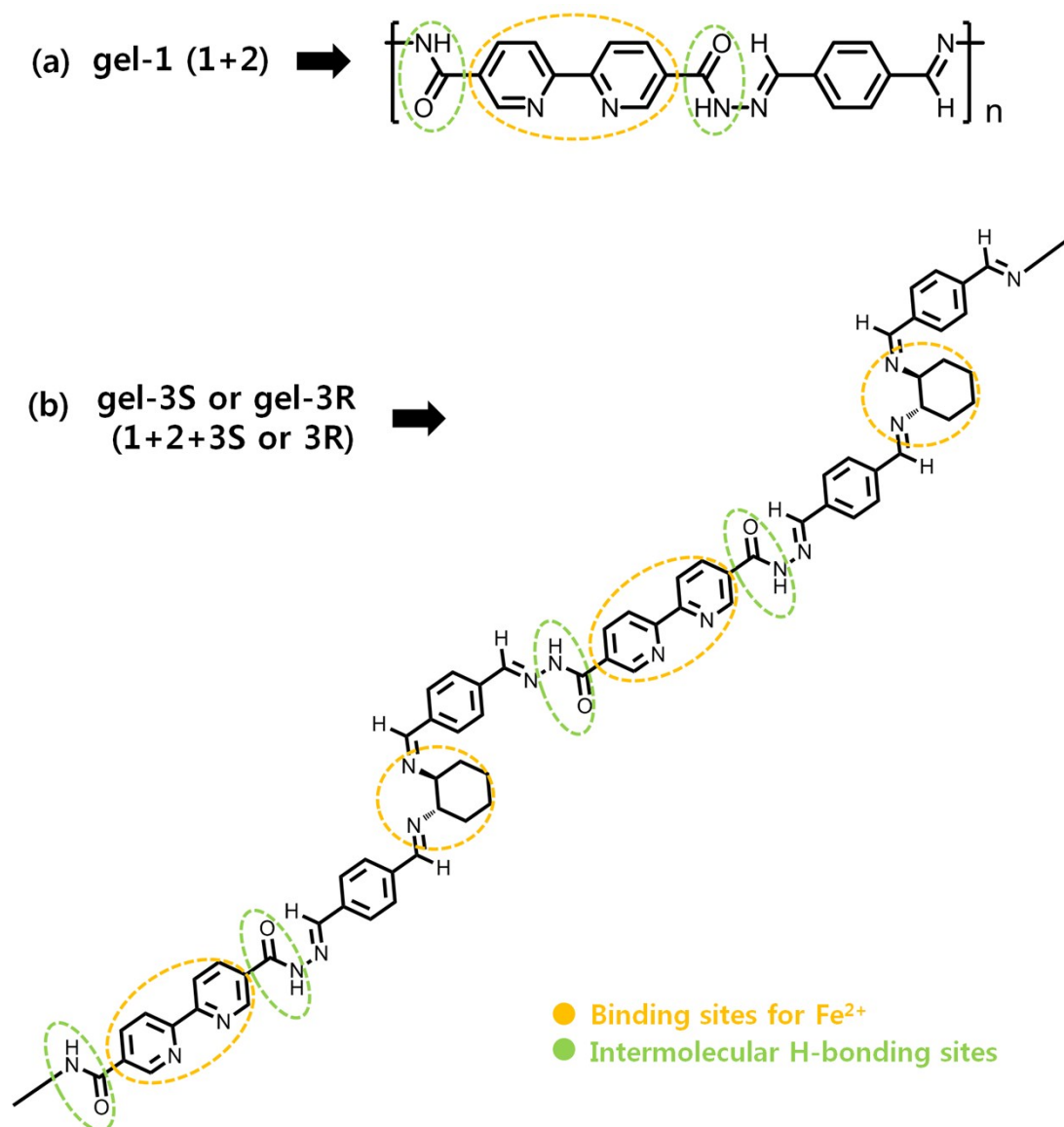


Fig. S12 Proposed polymer structures of (a) **gel-1** and (b) **gel-3S** or **gel-3R** formed by hydrazone reaction. The **gel-3S** or **gel-3R** formed helical structures with and without Fe²⁺. The **gel-3S** and **gel-3R** were random copolymers.

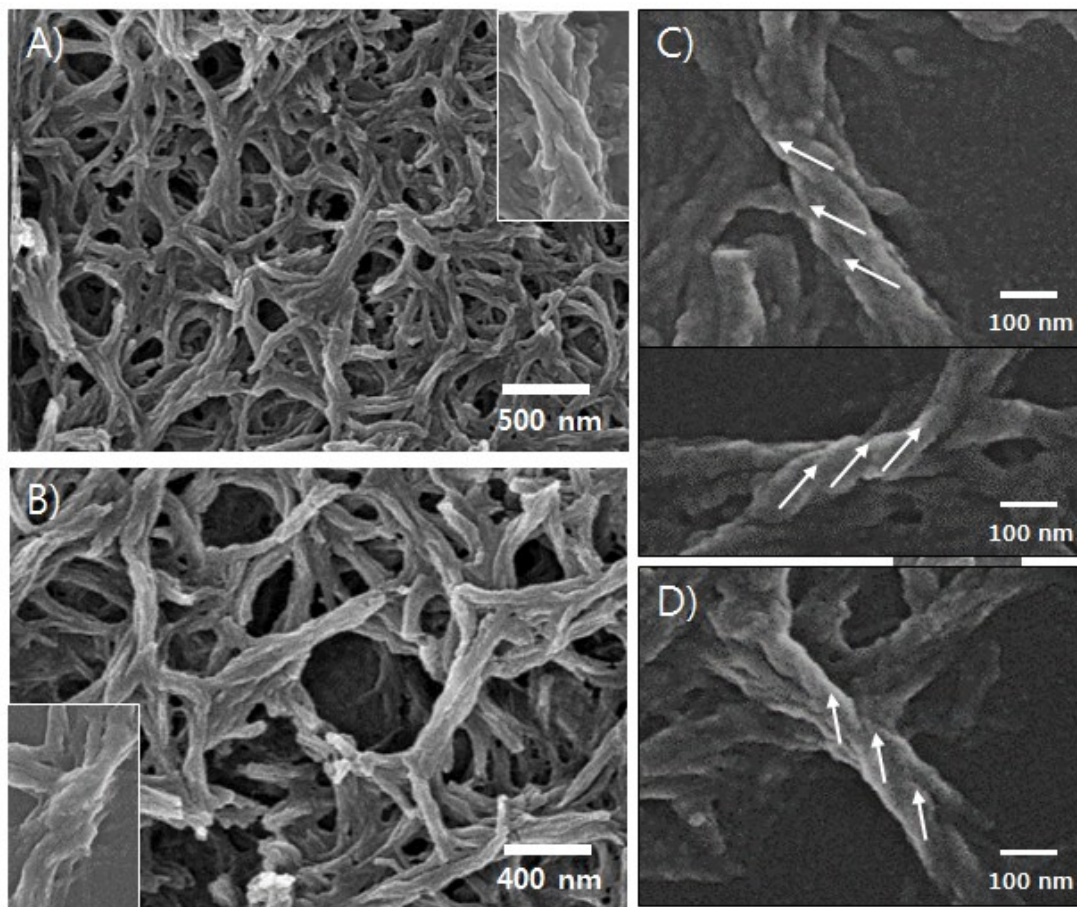


Fig. S13 FE-SEM images of (A) **gel-3R** without Fe^{2+} and (B) **gel-3S** without Fe^{2+} . FE-SEM images of (C) **gel-3R** with Fe^{2+} and (D) **gel-3S** with Fe^{2+} .

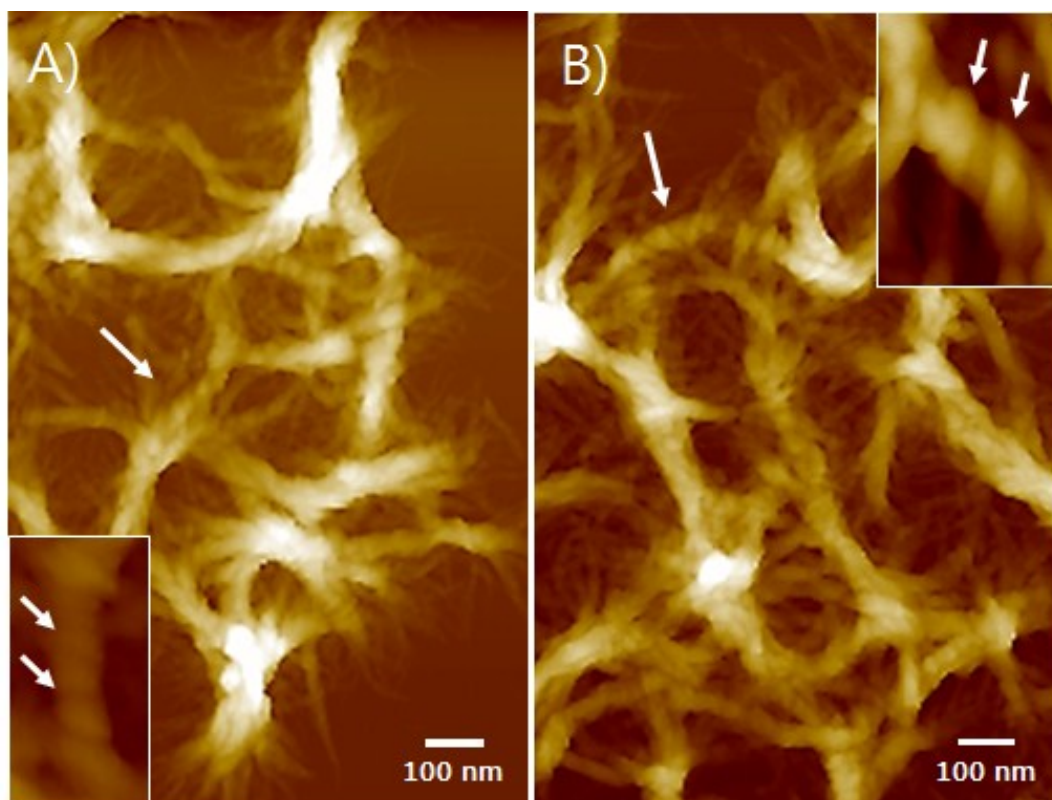


Fig. S14 AFM images of (A) **gel-3R** with Fe^{2+} and (B) **gel-3S** with Fe^{2+} (arrows indicate the helical structures).

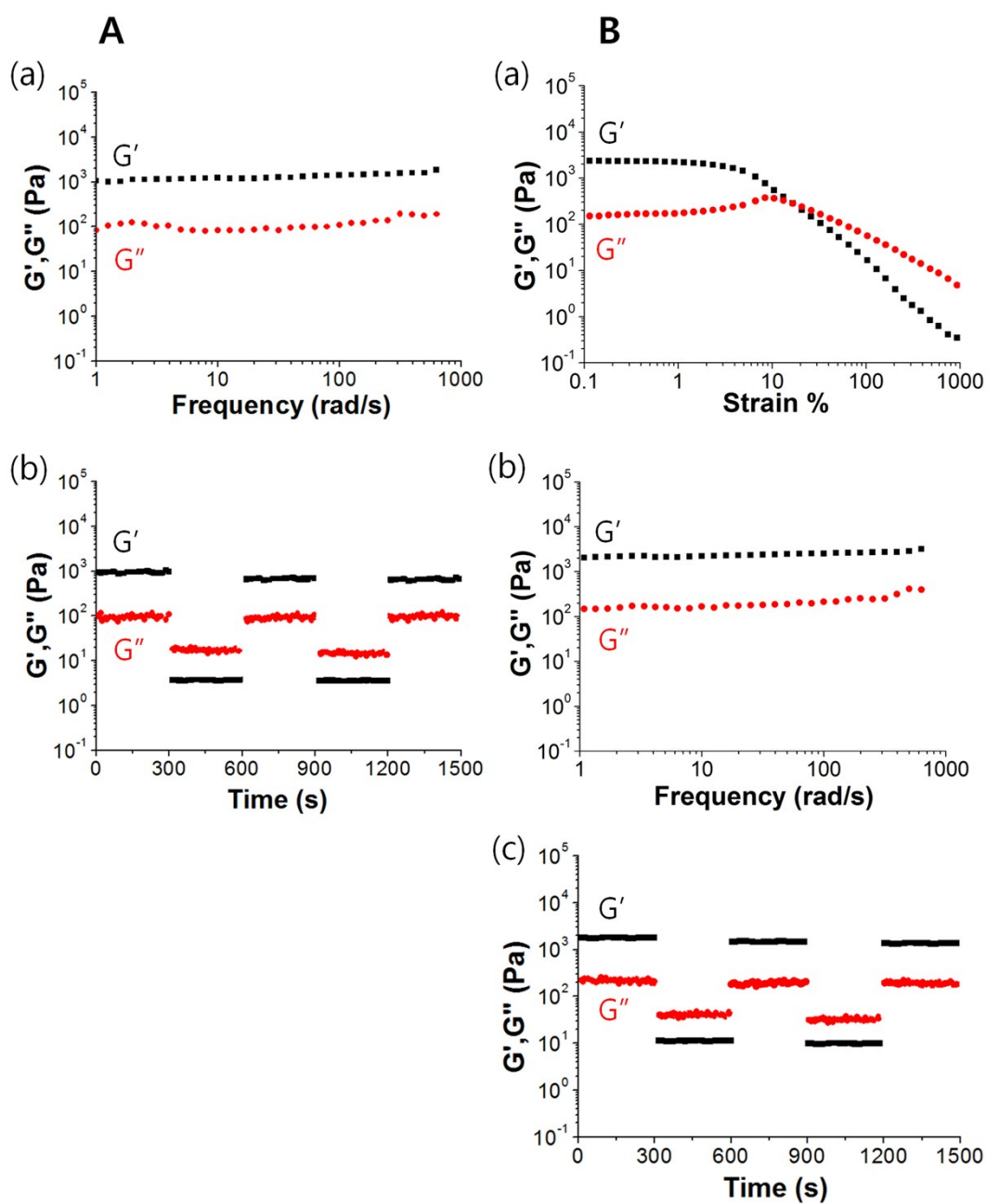


Fig. S15 Rheological properties of (A) **gel-1**; (a) frequency sweep tests at 1-1000 rad s^{-1} and strain 0.1, (b) continuous step strain test at 0.1 and 100. All experiments conducted at 25 °C, (B) **gel-1** with Fe^{2+} ; (a) strain sweep tests at 0.1-1000%, (b) frequency sweep tests at 1-1000 rad s^{-1} and strain 0.1 and (c) continuous step strain test at 0.1 and 100. All experiments conducted at 25 °C.

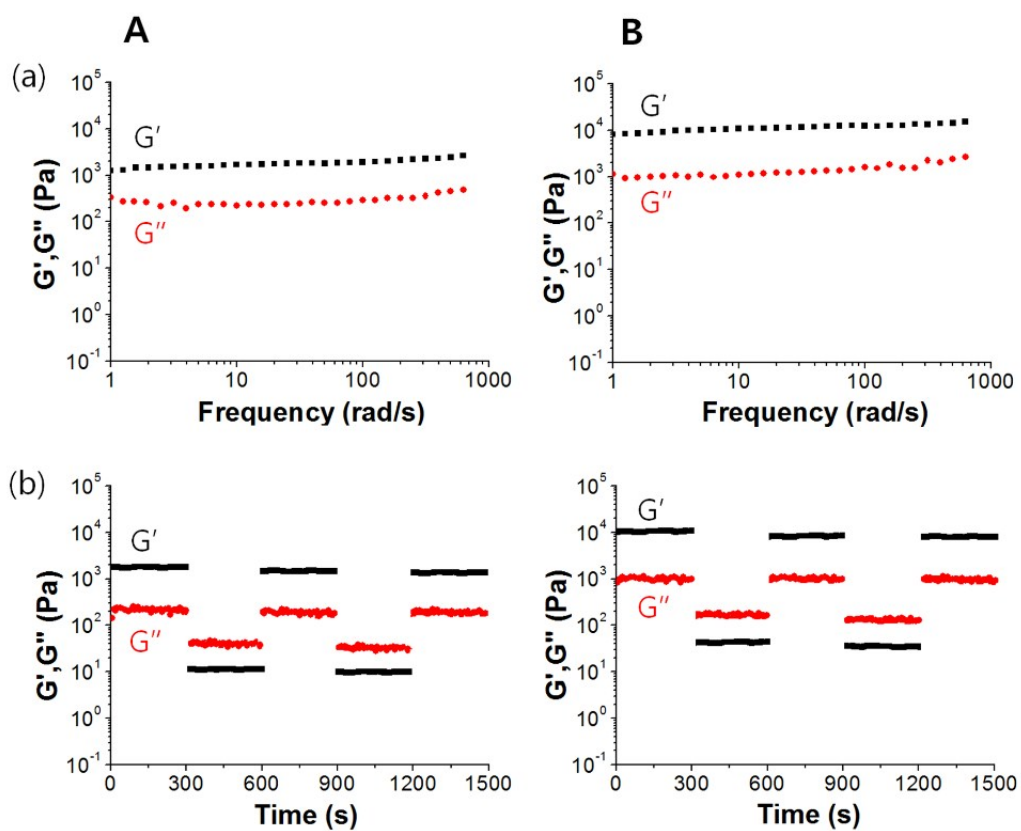


Fig. S16 Rheological properties of (A) **gel-3S** without Fe²⁺ and (B) **gel-3S** with Fe²⁺; (a) frequency sweep tests at 1-1000 rad s⁻¹ and strain 0.1 and (b) continuous step strain test at 0.1 and 100. All experiments conducted at 25 °C.

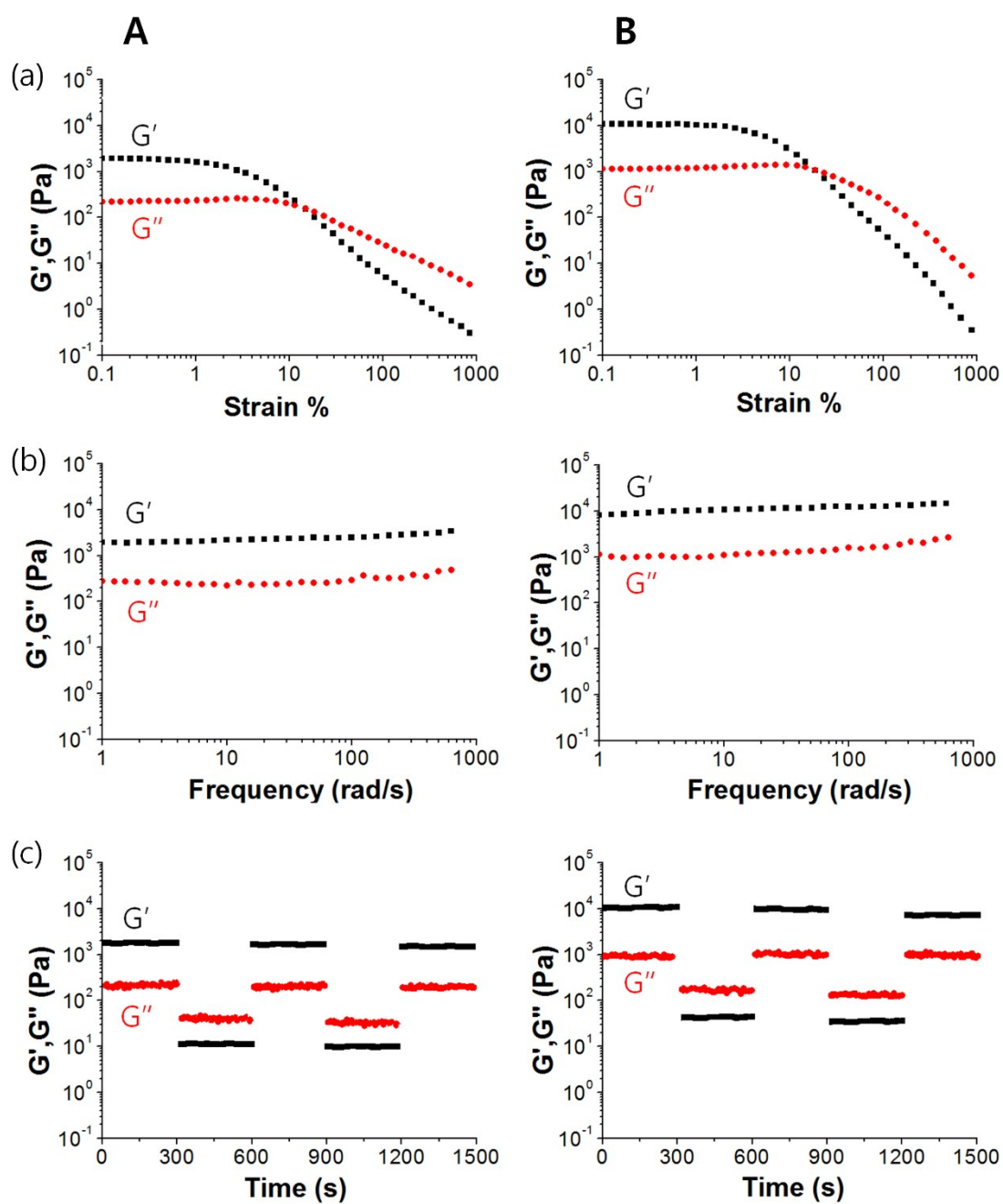


Fig. S17 Rheological properties of (A) **gel-3R** without Fe^{2+} and (B) **gel-3R** with Fe^{2+} ; (a) strain sweep tests at 0.1-1000%, (b) frequency sweep tests at 1-1000 rad s^{-1} and strain 0.1 and (c) continuous step strain test at 0.1 and 100. All experiments conducted at 25 °C.

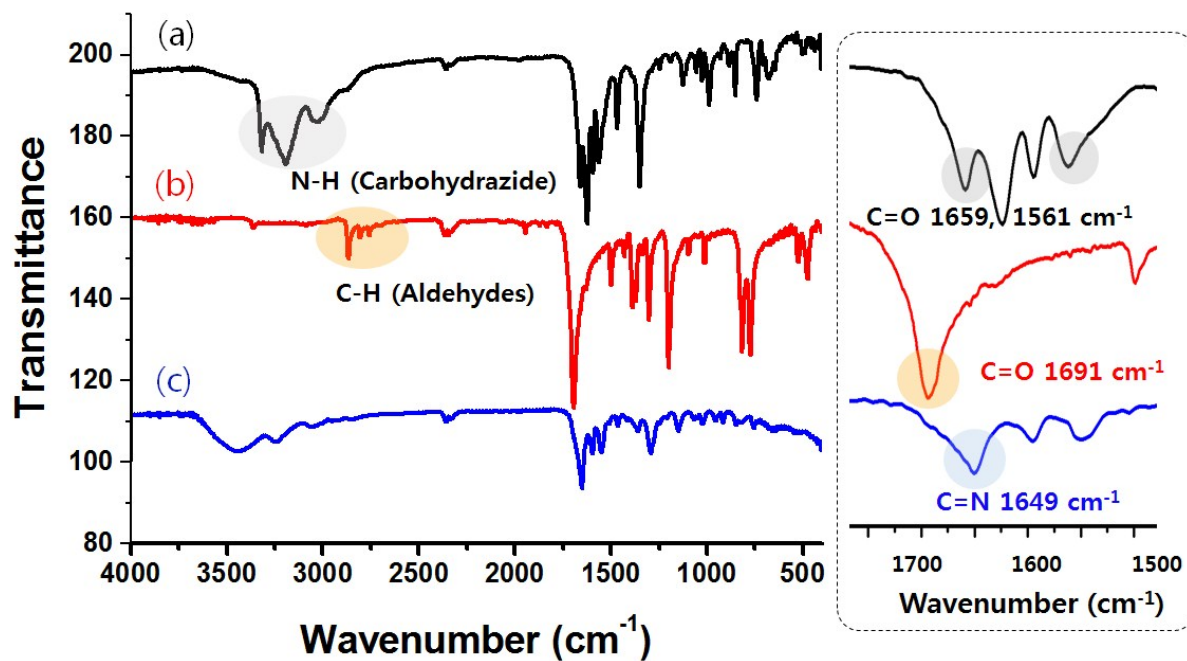


Fig. S18 FT-IR spectra of (a) building block 1, (b) 2 and (c) xerogel-1 (1+2).