Electronic Supplementary Information

A facile method to fabricate hydrogels from DMSO polymer gels via solvent exchange

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Experimental Section

Characterization. The ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker DRX 300, and mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. IR spectra were obtained for KBr pellets, in the range 400–4000 cm^{-1}, with a Shimadzu FT IR 8400S instrument. The elemental analysis was performed with a Perkin Elmer 2400 series II instrument.

Preparation of organogels. For **organogel-3S-Fe** (1.0 wt% for **1**), building block **1** (4 mg, 15 μmol) was dissolved in DMSO (0.4 mL) by heating. Building block **2** (2 mg, 15 μmol), **3S** (0.5 equiv.) and $Fe(BF_2)_4.6H_2O$ (0.33 equiv.) were added to solution of building block **1**. Then amount of HCl (10 μmol) was added to the mixture solution. Finally, the mixed solution was maintained at room temperature.

Preparation of hydrogels. For preparation of **hydrogel-1**, **hydrogel-1-Fe**, **hydrogel-3S** and **hydrogel-3S-Fe**, the corresponding organogels (1.0 wt% for **1**) previously prepared from DMSO (organogels aged for 24 h) were immersed in H_2O (10 ml) for 24 h at room temperature. After solvent exchange, the amounts of removed DMSO were evaluated by ^{1}H NMR.

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

Rheological properties. Rheological tests 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 900 s procedure: 0.1% (180 s)→100% (180-360 s)→0.1% (360-540 s)→100% (540-720 s)→0.1% (720-900 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 DCl (10 μmol) was added, respectively. Time-dependent ^{1}H NMR spectrum was measured with average 100 scans at ambient temperature.

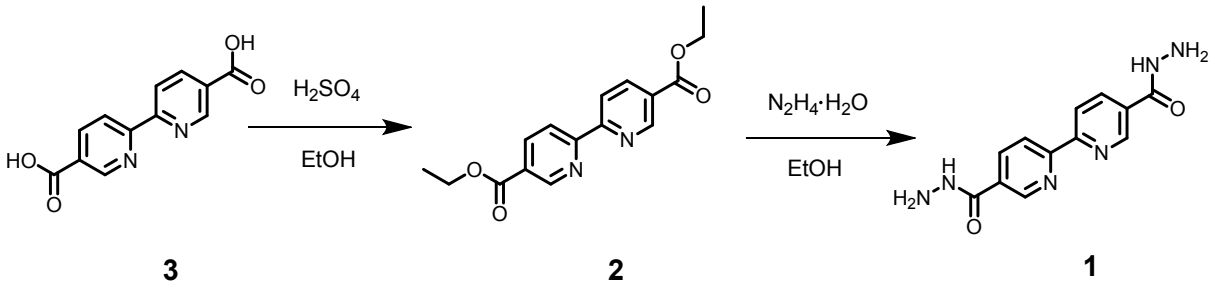
Synthesis of building block 2

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 ºC, 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. 145-147 °C; IR (KBr pellet): 1721, 1269, 1112 cm^{-1}; ^{1}H 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 $C_{16}H_{16}N_2O_4$ $[M+H]^+$ 301.11, Found 301.28; Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.95; H, 5.32; N, 9.35.

Synthesis of building block 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. >300 °C; IR (KBr pellet): 3318, 3192, 3027, 1658, 1621, 1591, 1561 cm^{-1}; ^{1}H 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 $C_{12}H_{12}N_6O_2$ $[M+H]^+$ 272.10, Found 272.28; Anal. Calcd for $C_{12}H_{12}N_6O_2$: C, 52.94; H, 4.44; N, 30.87. Found: C, 52.90; H, 4.47; N, 30.81.



3 2 1

Fig. S1 Scheme of synthetic methods for building block **1**.

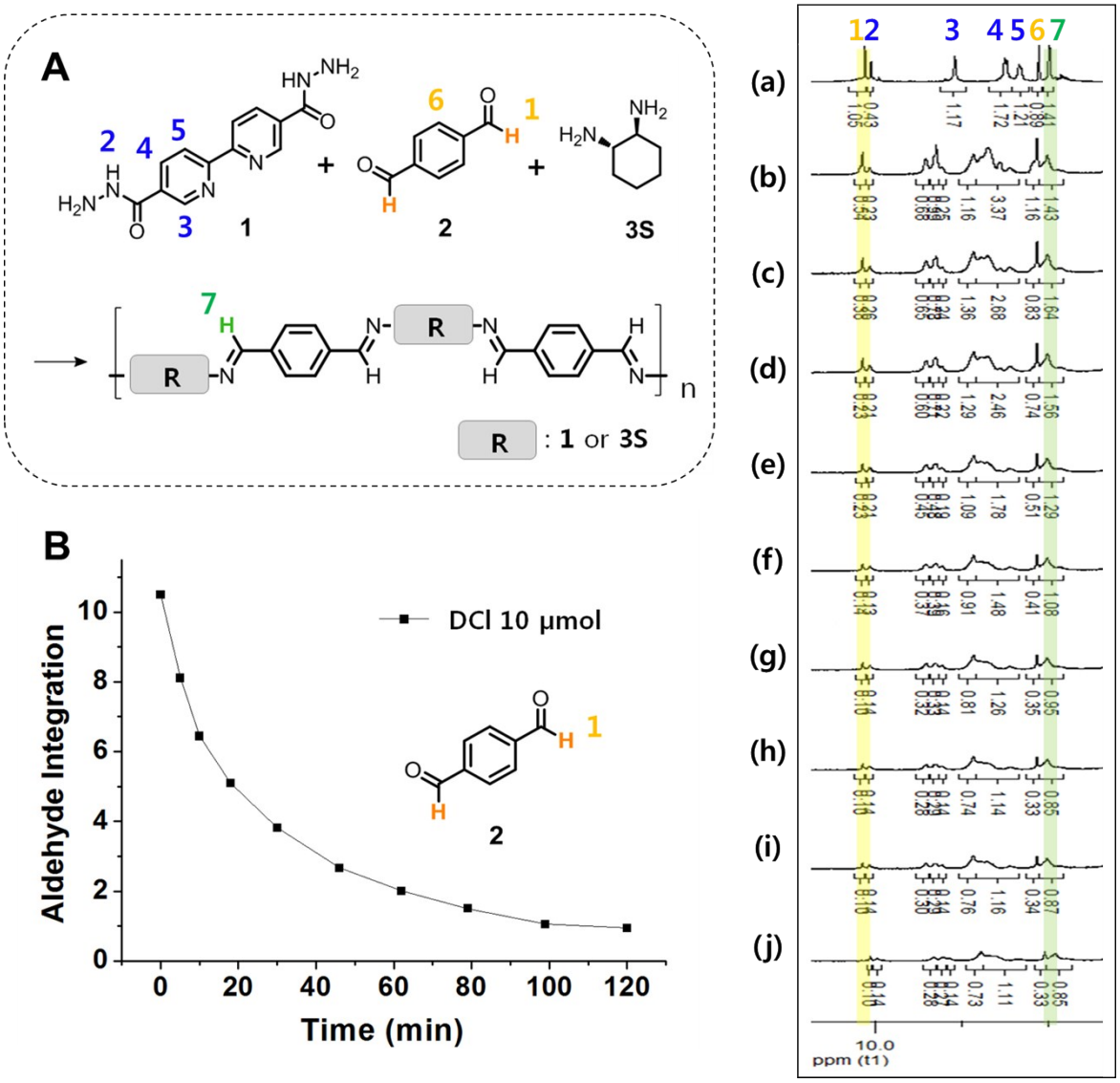


Fig. S2 (A) ^{1}H NMR spectra of **organogel-3S** (1.0 wt%, 37.5 mM) (a) before and after adding DCl (10 μmol), (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 45 min, (g) 60 min (h) 80 min (i) 100 min and (j) 120 min in DMSO-d_6. (B) The change in the amount of reactant (**2**) after product (hydrazone) formation as a function of time showing a plateau after equilibrium hydrazine reaction has been reached. The equilibrium hydrazone reaction can be seen to occur at different time points for **organogel-3S** in the presence of DCl (10 μmol).

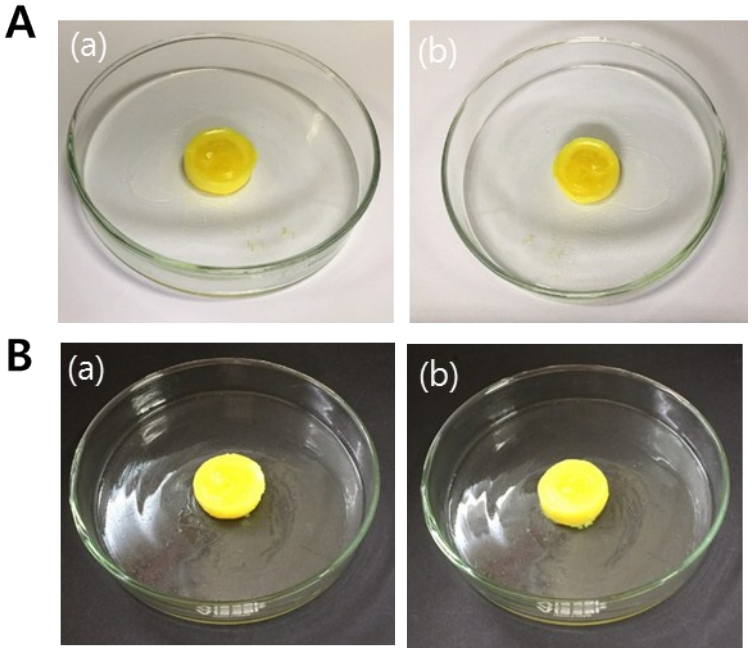


Fig. S3 (A) The photographs of (a) **organogel-3S** and (b) **organogel-3S-Fe**. (B) Photograph of (a) **hydrogel-3S** and (b) **hydrogel-3S-Fe** prepared by solvent exchange in the presence of 0 mM NaCl.

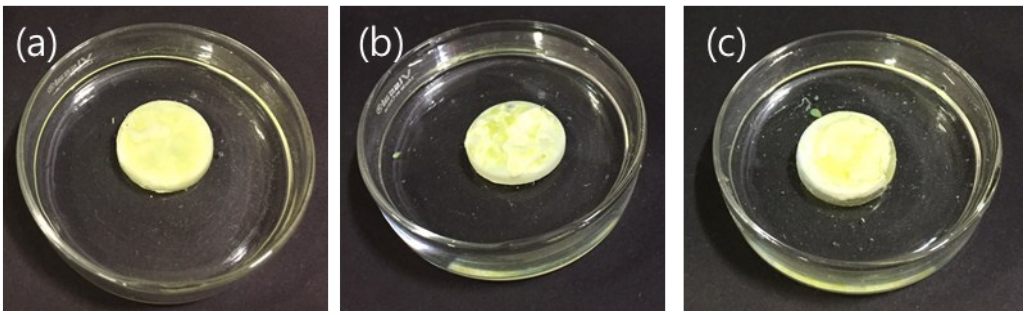


Fig. S4 The photographs of (a) **hydrogel-1**, (b) **hydrogel-3** and (c) **hydrogel-3S-Fe** prepared by solvent exchange in the presence of 50 mM NaCl.

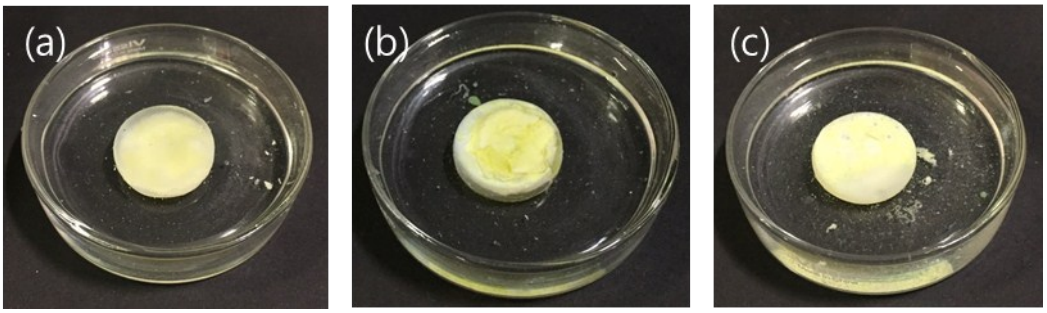


Fig. S5 The photographs of (a) **hydrogel-1**, (b) **hydrogel-3** and (c) **hydrogel-3S-Fe** prepared by solvent exchange in the presence of 100 mM NaCl.

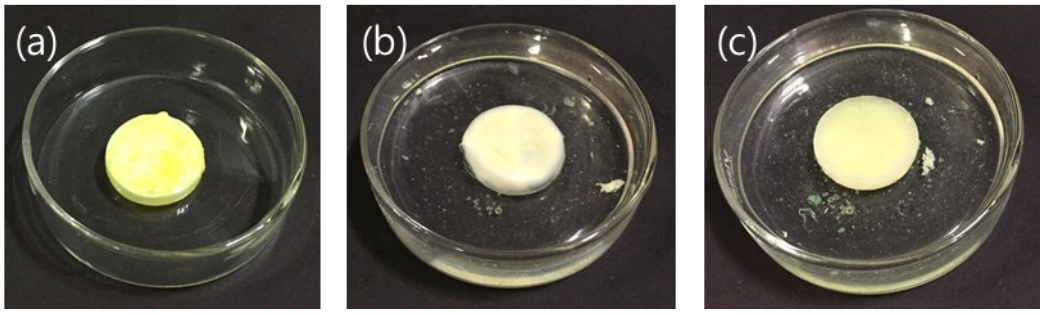


Fig. S6 The photographs of (a) **hydrogel-1**, (b) **hydrogel-3** and (c) **hydrogel-3S-Fe** prepared by solvent exchange in the presence of 200 mM NaCl.

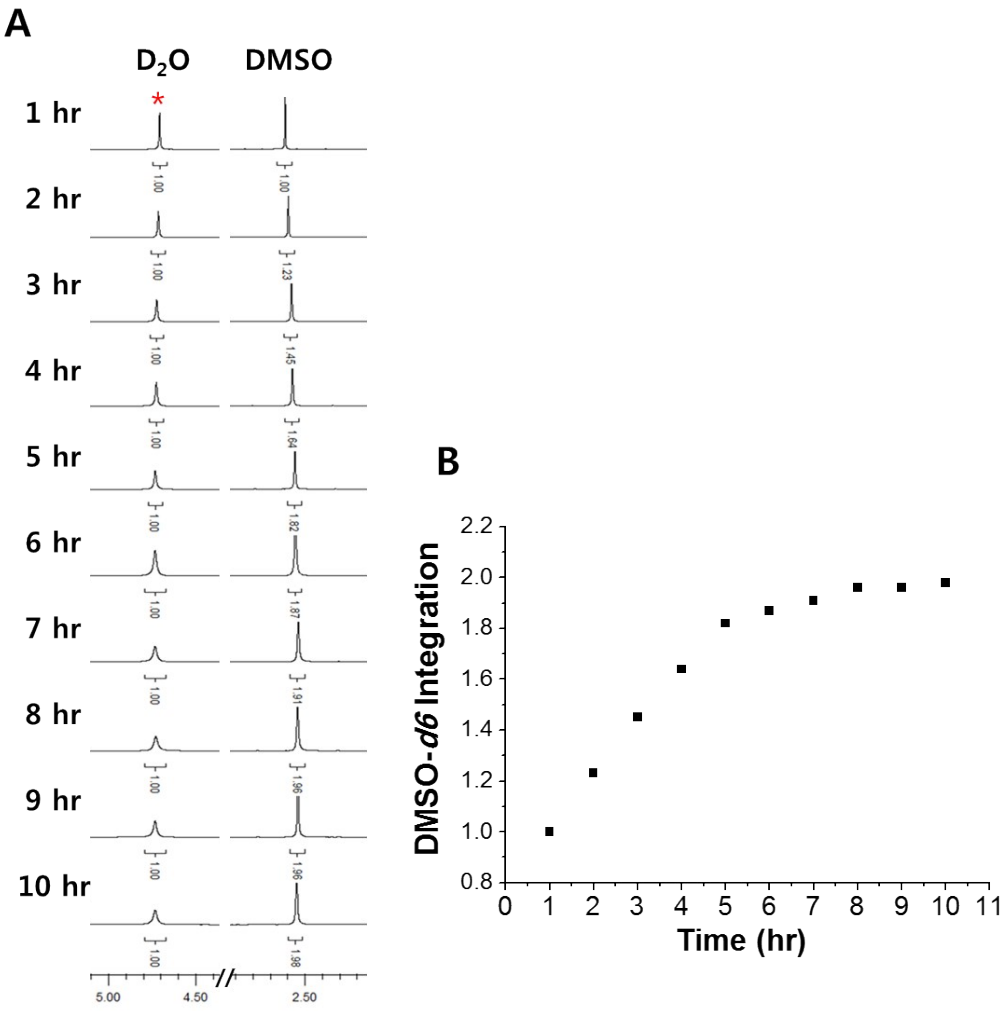


Fig. S7 (A) ^{1}H NMR spectra of DMSO released from **organogel-1** during solvent exchange. (B) Plot for intergral ratio of DMSO via solvent exchange time.

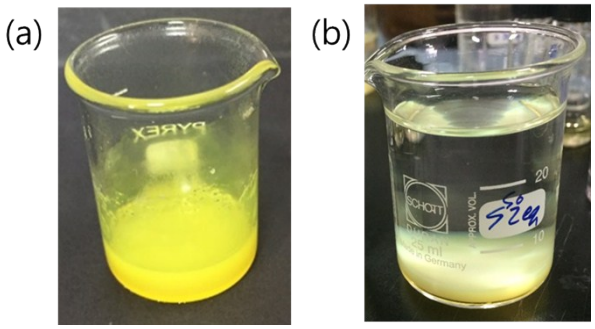


Fig. S8 Photographs of **organogel-1** (a) before and (a) after immersion in water.

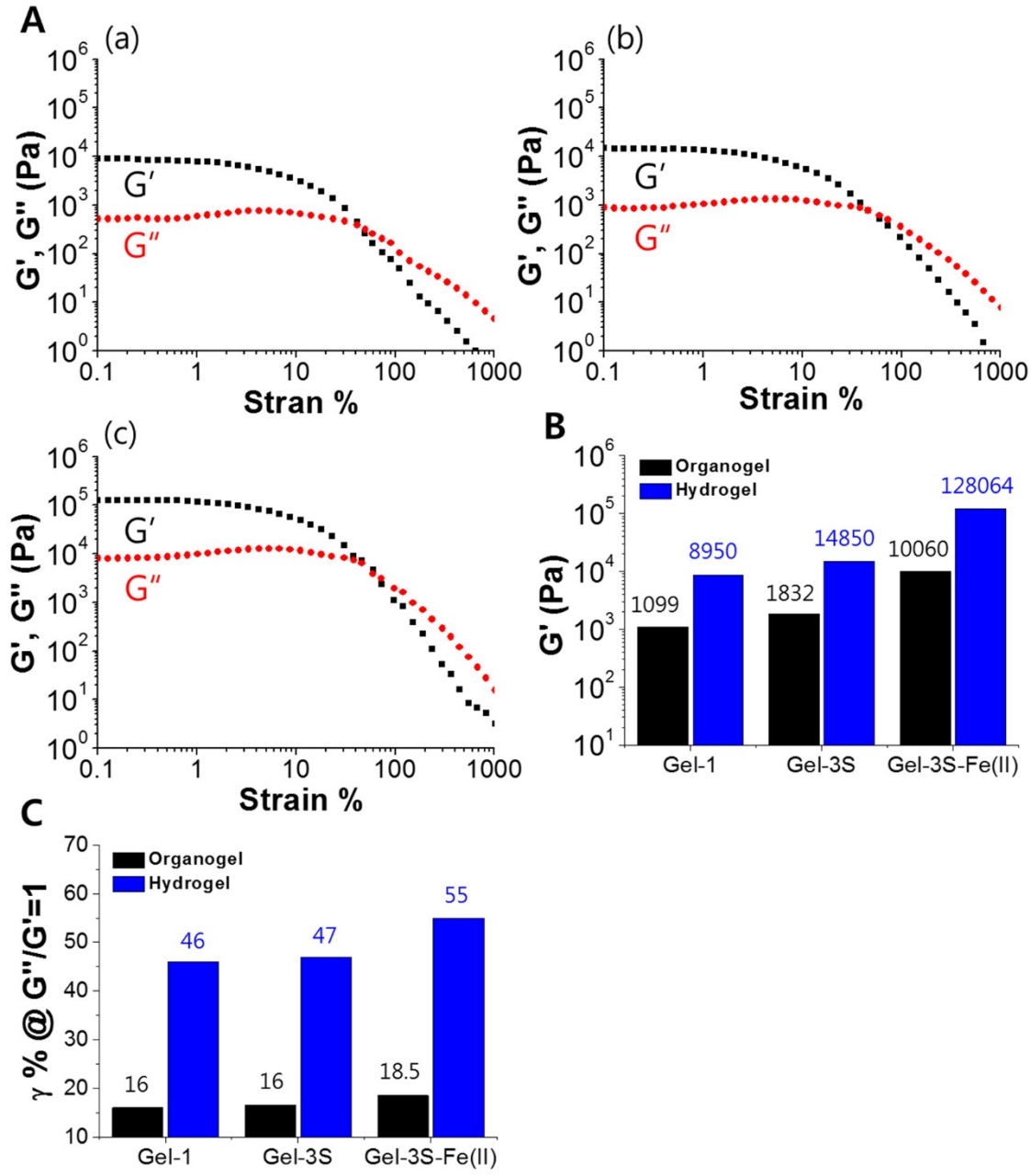


Fig. S9 (A) Rheological properties of (a) **hydrogel-1**, (b) **hydrogel-3S** and (c) **hydrogel-3S-Fe**. (B) G' values of organogels (black) and hydrogels (blue) at γ = 0.1% in A (a-c). (C) γ% of organogels (black) and hydrogels (blue) at G"/G'=1 in A (a–c).

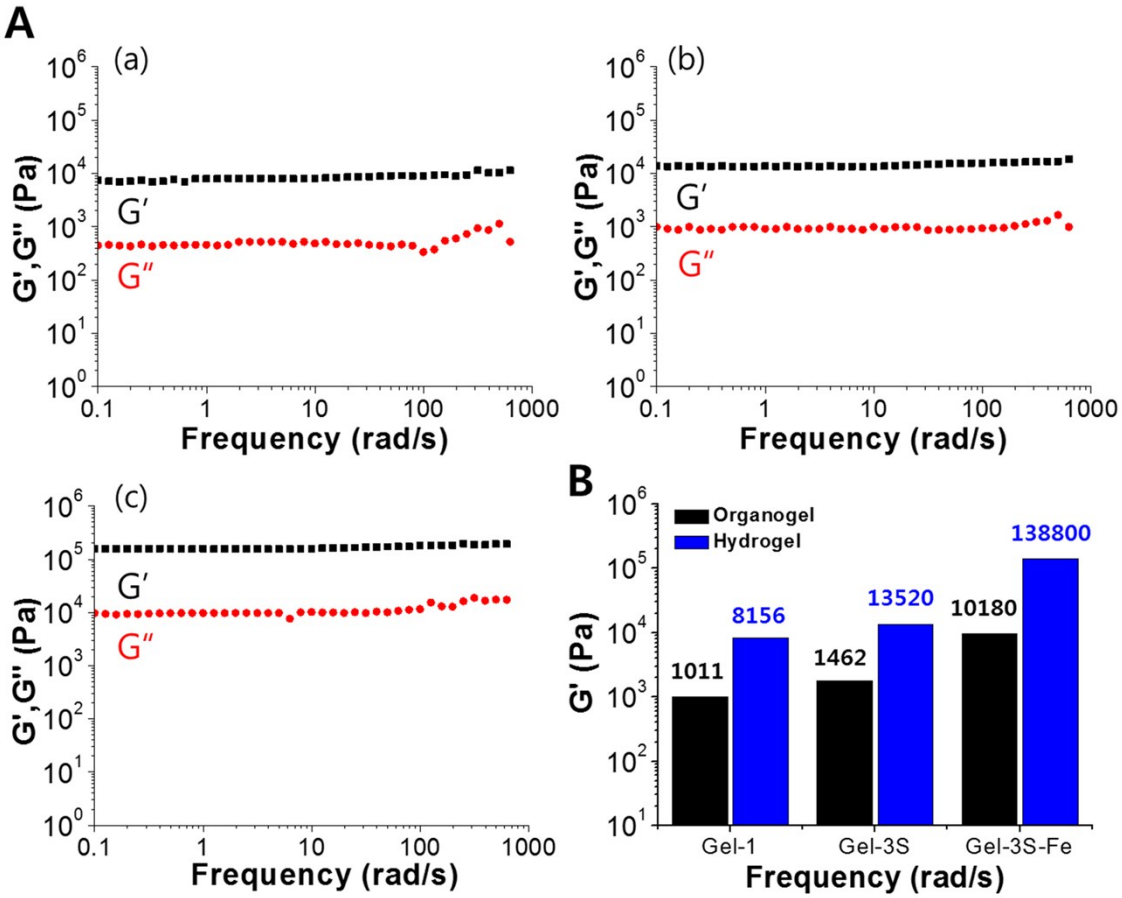


Fig. S10 (A) Rheological properties of (a**) hydrogel-1**, (b) **hydrogel-3S** and (c) **hydrogel-3S-Fe**; (A) frequency sweep tests at 0.1-1000 rad s^{-1} and strain 0.1. All experiments were conducted at 25 °C. (B) Graph of G' of organogels (black) and hydrogels (blue) at $\gamma = 0.1\%$ in A (a–c).

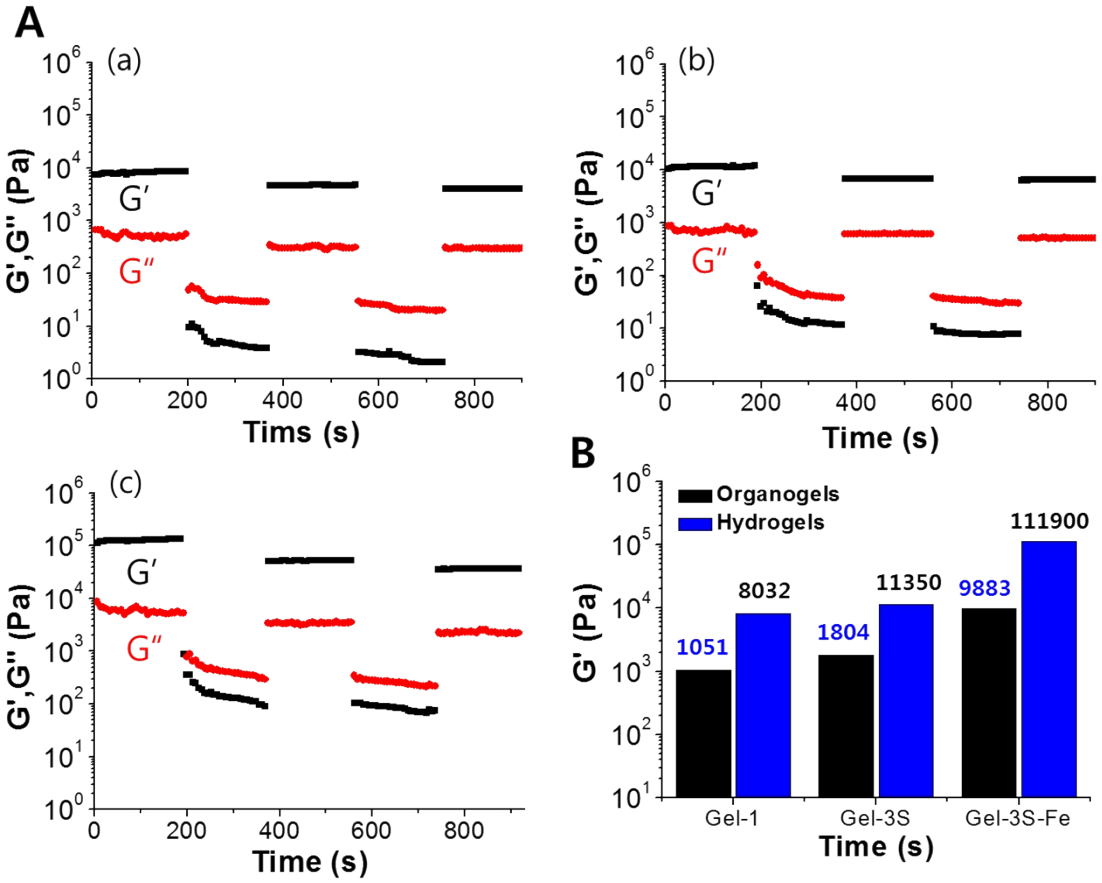


Fig. S11 Rheological properties of (a) **hydrogel-1**, (b) **hydrogel-3S** and (c) **hydrogel-3S-Fe**; (A) continuous step strain test at 0.1 and 100. All experiments were conducted at 25 °C. (B) Graph of G' of organogels (black) and hydrogels (blue) at $\gamma = 0.1\%$ in A (a–c).

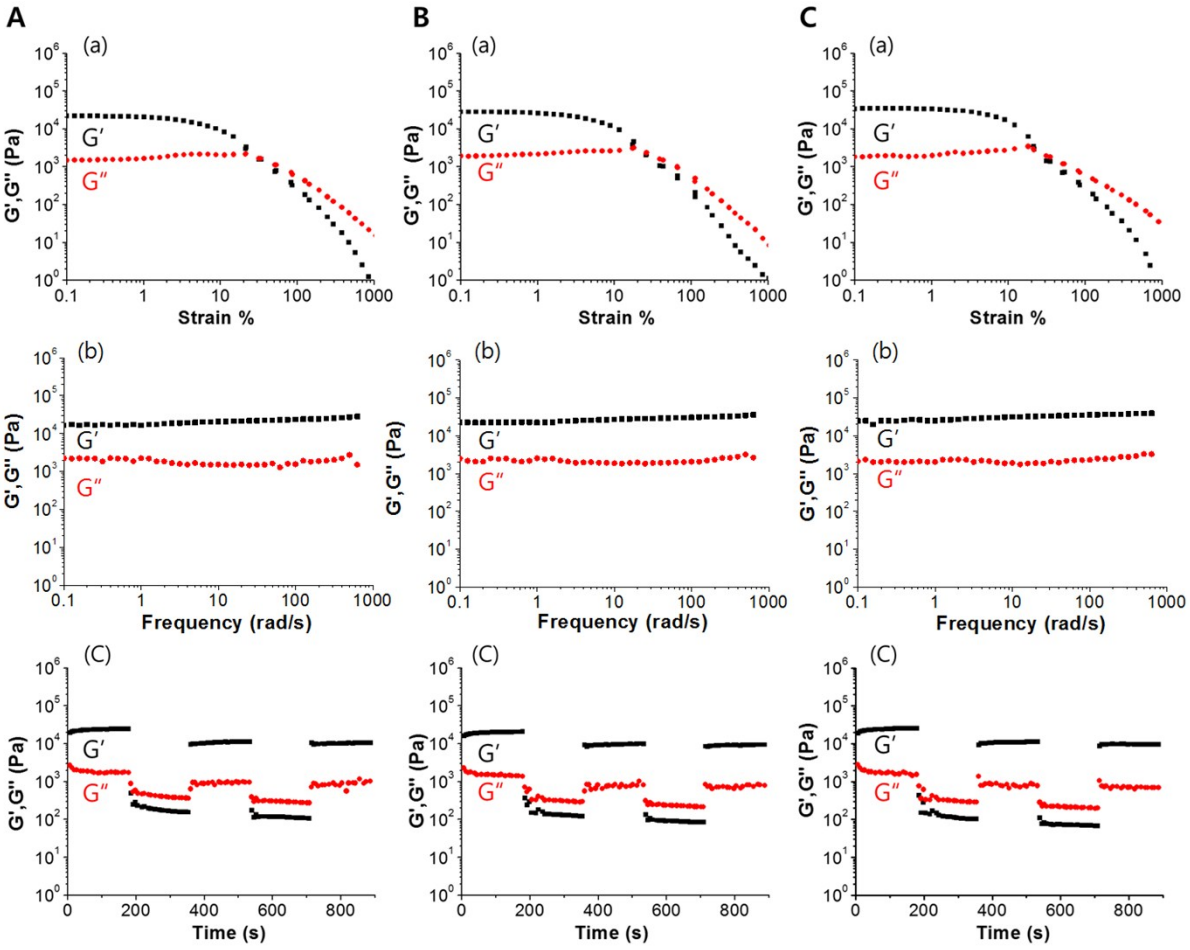


Fig. S12 Rheological properties of (A) **hydrogel-1**, (B) **hydrogel-3S** and (C) **hydrogel-3S-Fe** prepared in NaCl (100 mM); (a) strain sweep tests at 0.1-1000%, (b) frequency sweep tests at 0.1-1000 rad s^{-1} and strain 0.1 and (c) continuous step strain test at 0.1 and 100. All experiments were conducted at 25 °C.

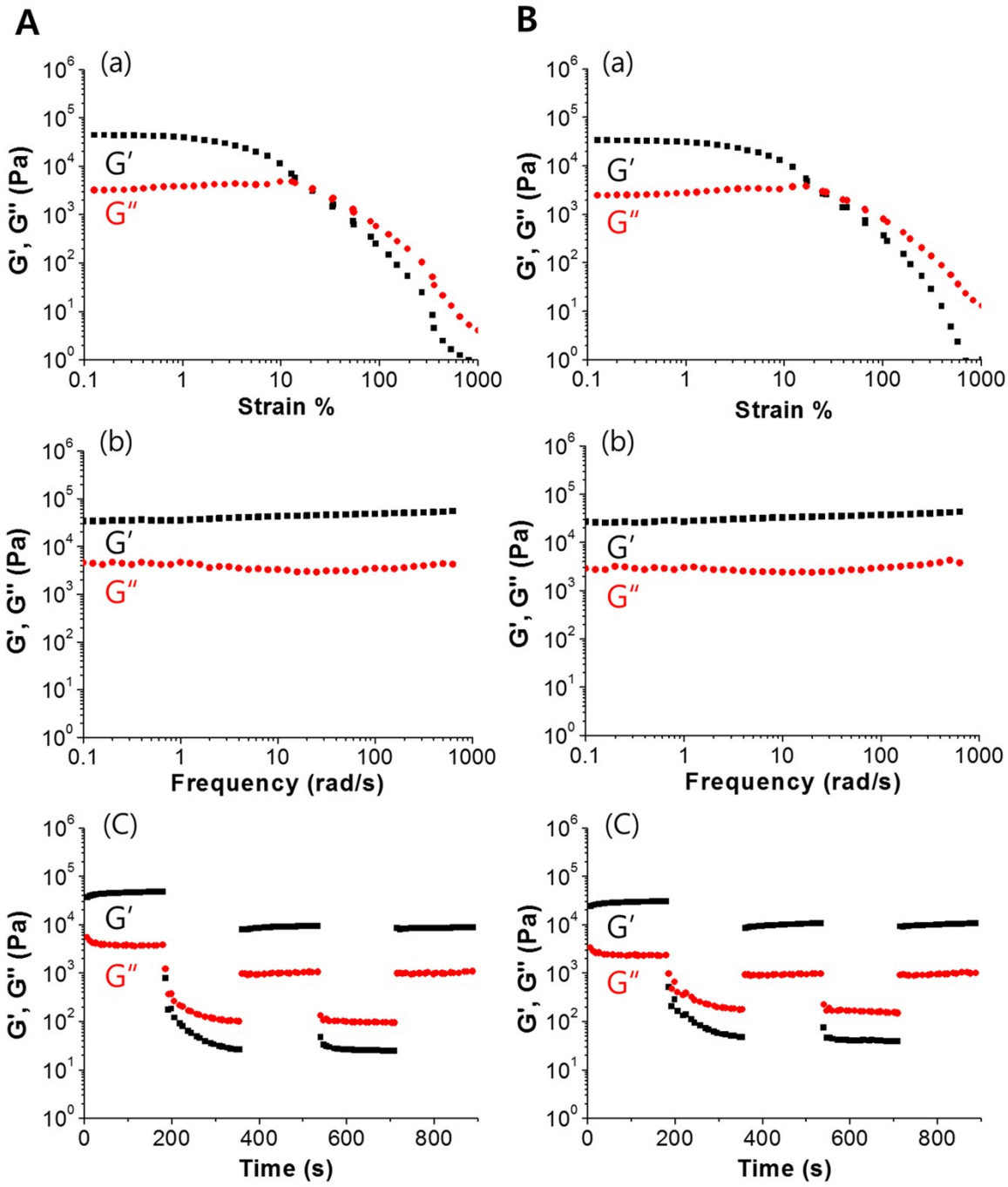


Fig. S13 Rheological properties of **hydrogel-3S-Fe** prepared in (A) NaCl 50 mM and (B) NaCl 100 mM; (a) strain sweep tests at 0.1-1000%, (b) frequency sweep tests at 0.1-1000 rad s^{-1} and strain 0.1 and (c) continuous step strain test at 0.1 and 100. All experiments were conducted at 25 °C.

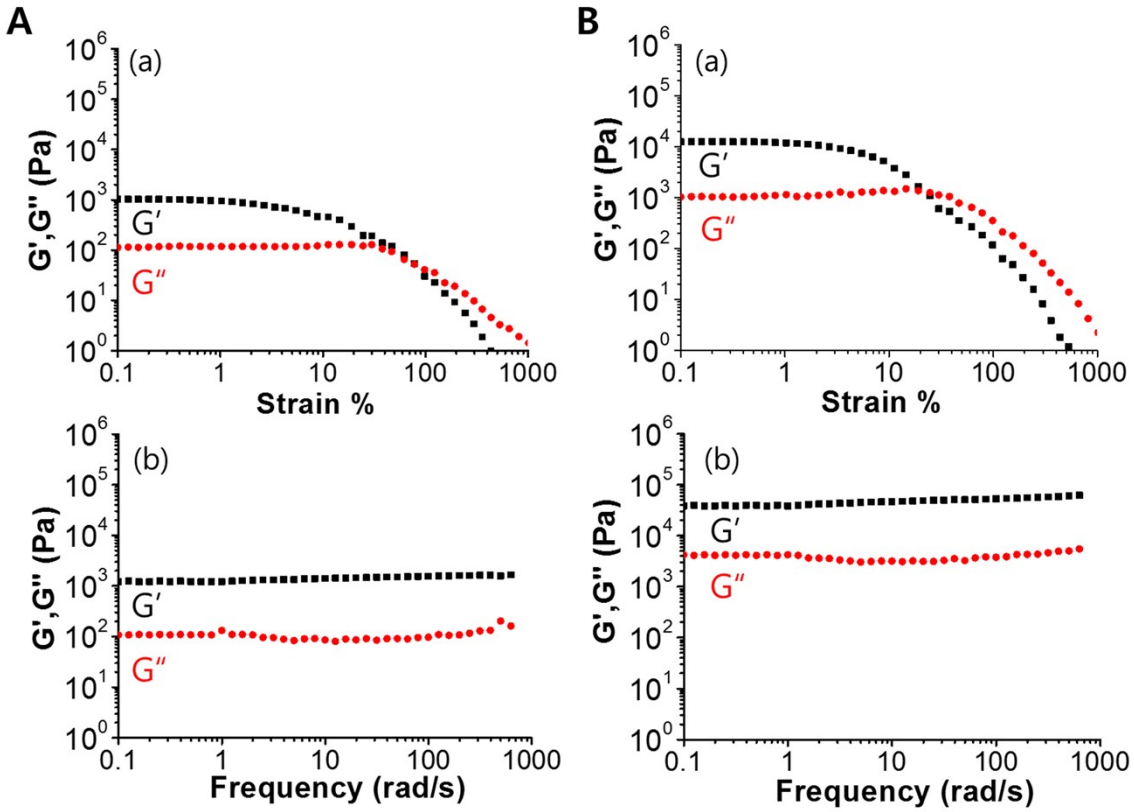


Fig. S14 Rheological properties of (A) **oroganogel-Fe** and (B) **hydrogel-Fe** prepared in H_2O; (a) strain sweep tests at 0.1-1000% and (b) frequency sweep tests at 0.1-1000 rad s^{-1} and strain 0.1.

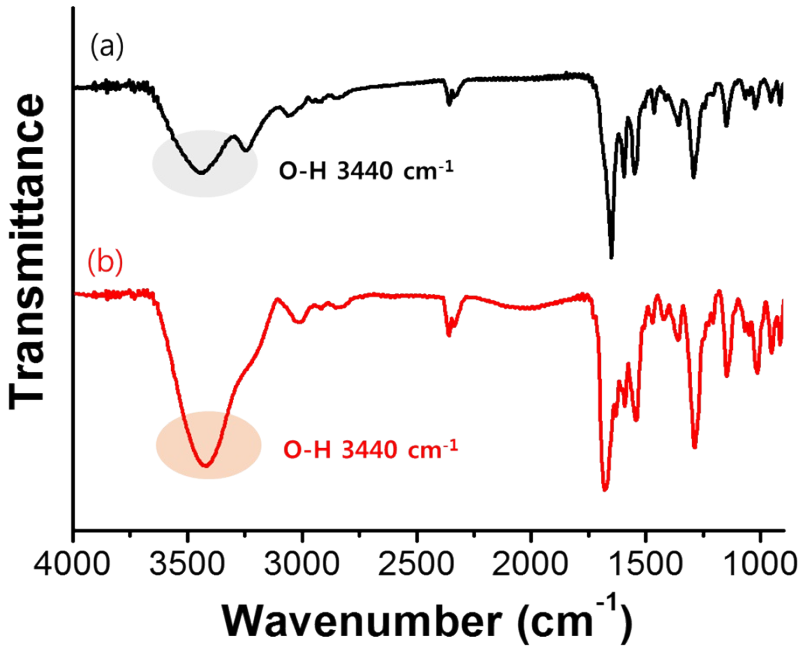


Fig. S15 FT-IR spectra of (a) **organogel-1** and (b) **hydrogel-1**.

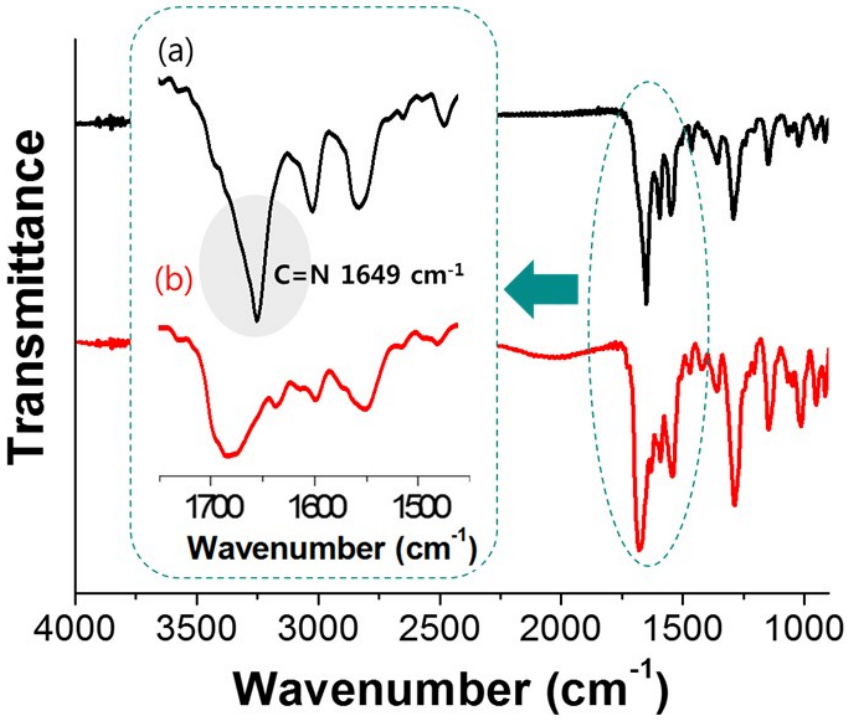


Fig. S16 FT-IR spectra of (a) **organogel-1** and (b) **hydrogel-1**.

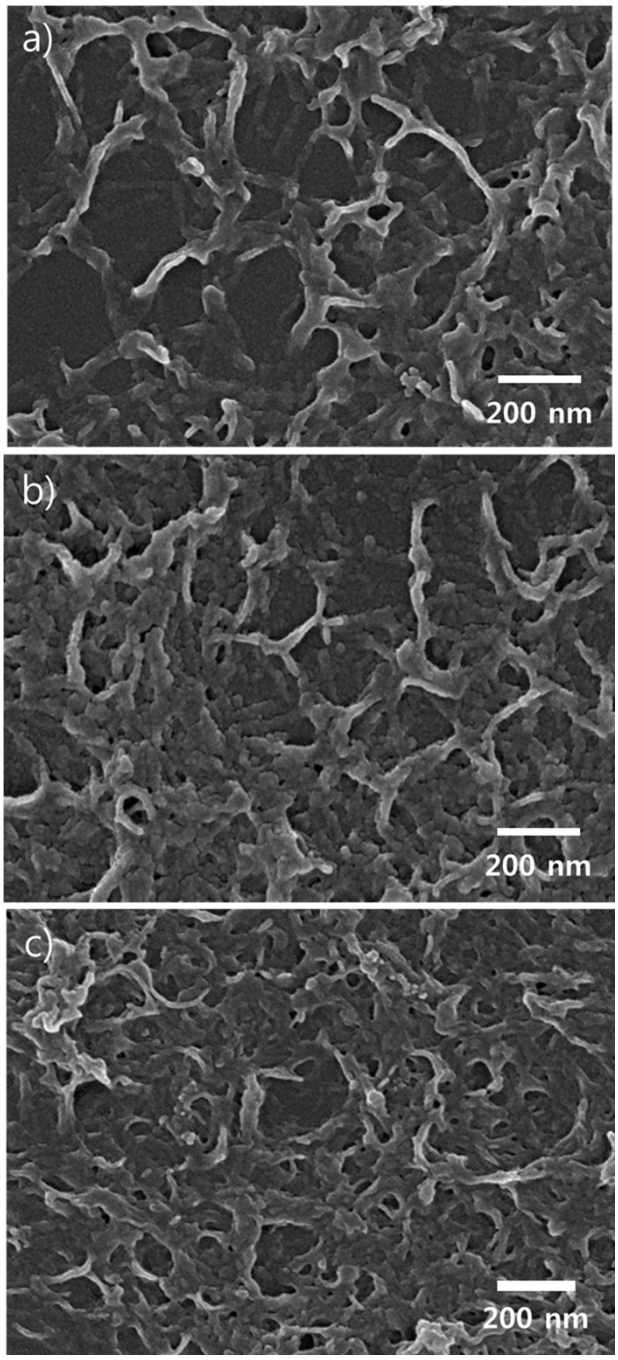


Fig. S17 SEM images of (a) **hydrogel-1**, (b) **hydrogel-3S** and (c) **hydrogel-3S-Fe** prepared with NaCl (100 mM).

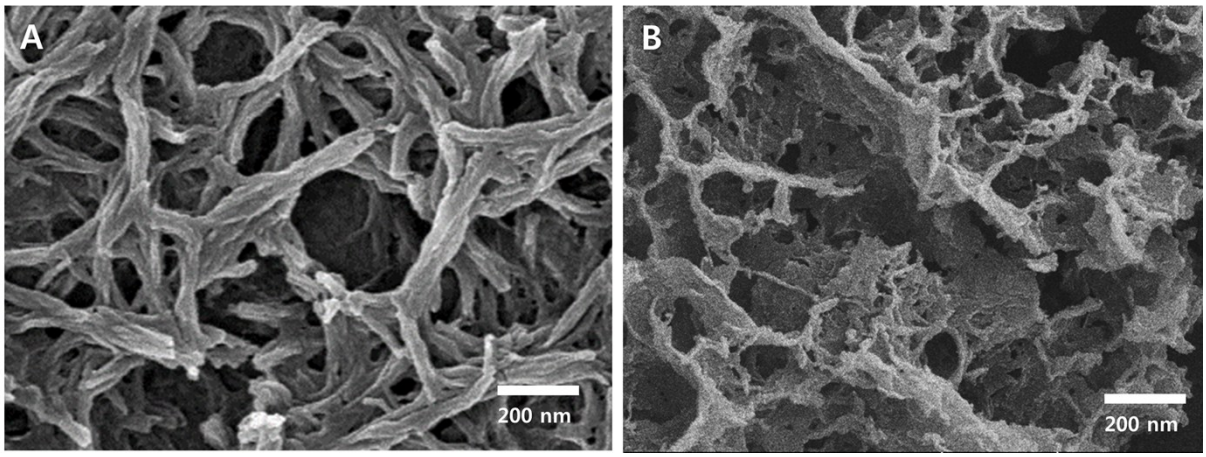


Fig. S18 SEM images of (A) **organogel-Fe** and (B) **hydrogel-Fe.**

Table S1. Hydrogels formed from organogels by solvent exchange.

Gel type	Weight (g)				
	Organogel	Hydrogels			
	DMSO	NaCl 0 mM	NaCl 50 mM	NaCl 100 mM	NaCl 200 Mm
Gel-1	4.94 g	4.69 g	4.69 g	4.59 g	4.59 g
Gel-3S	4.98 g	4.68 g	4.68 g	4.53 g	4.53 g
Gel-3S-Fe	4.96 g	4.91 g	4.90 g	4.92 g	4.91 g