Electronic Supplementary Information (ESI) for:

Self-Oscillating Gel Actuator Driven by Ferroin

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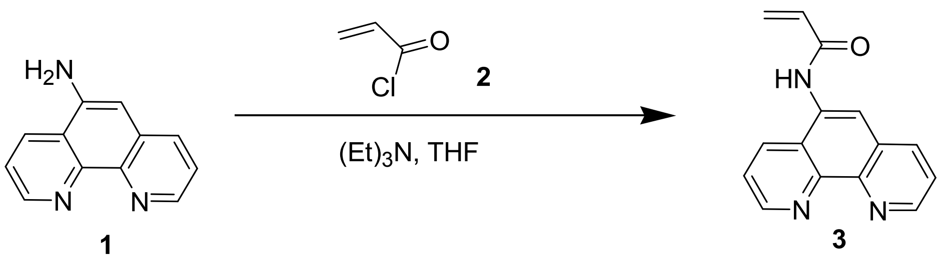
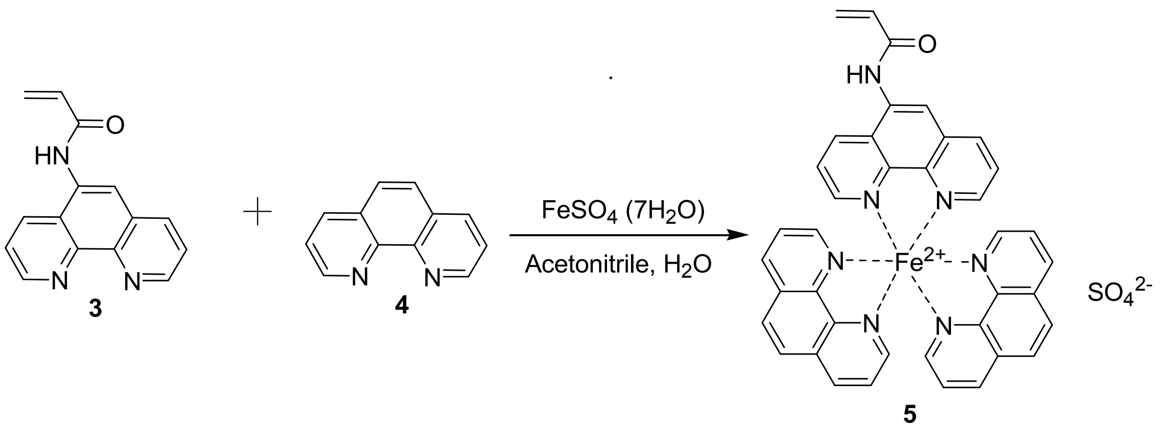
Synthetic Experimental Section for monomer and gel.

General Information. Melting points (mp) were determined with an electrothermal melting point apparatus in a sealed capillary on a Yanaco MP-S3 Micro-hot stage apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz at room temperature (20 ºC) in the Fourier transform mode. $CDCl_3$ and D_2O were used as the solvent for NMR measurement. Fourier transform infrared (FT-IR) spectra were obtained on a Thermo Nicolet Avatar 370. FT-IR measurements were performed in attenuated total refraction (ATR) mode. UV-visible absorption spectra were measured on a Shimadzu UV-3101PC spectrophotometer. High resolution mass spectrometric molecular weights (HRMS) were obtained on a Waters Micromass ZQ Mass Spectrometer equipped with an ESI interface.

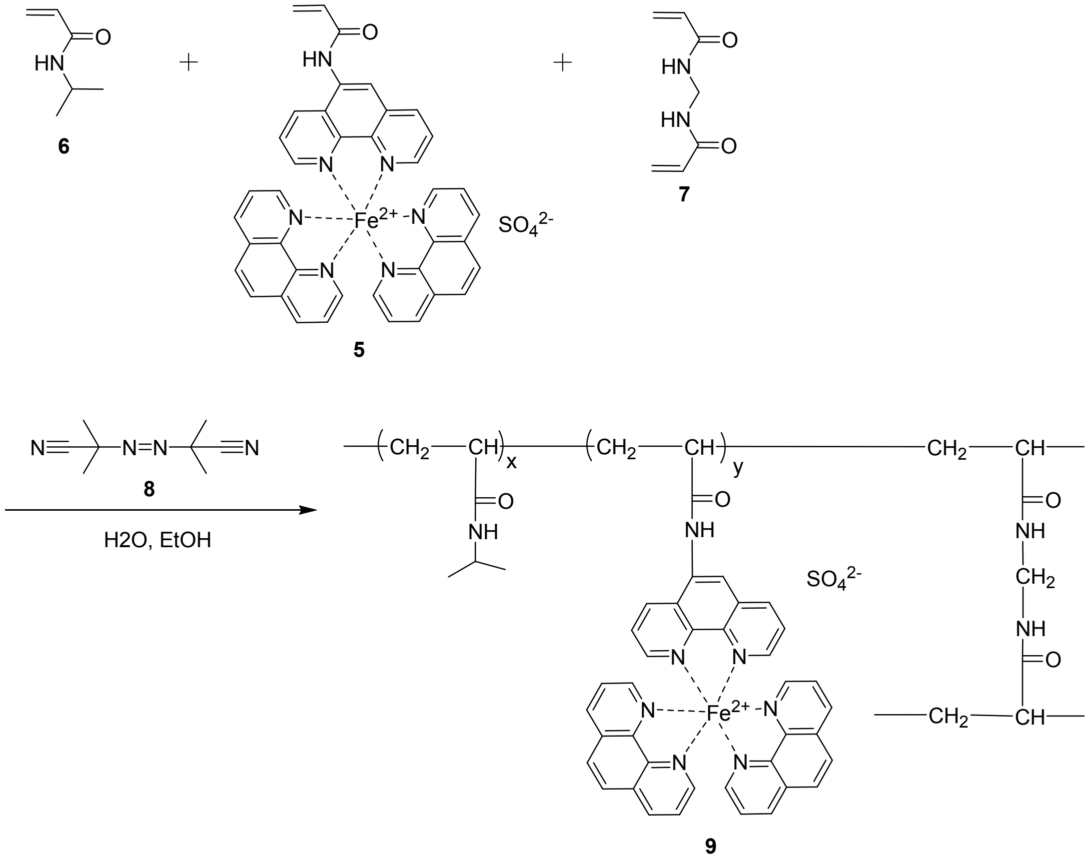
Materials. *N*-Isopropylacrylamide (NIPAAm), *N,N*'-methylenebisacrylamide (BIS) crosslinker, 2,2'-azobisisobutyronitrile (AIBN) initiator, and acryloyl chloride were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). 1,10-Phenanthroline-5-amine was purchased from Sigma-Aldrich Japan Co. Ltd. (Tokyo, Japan). Phenanthroline and ferrous sulfate heptahydrate were purchased from Wako Pure Chemical Industries Co. Ltd. (Osaka, Japan). All other solvents used were reagent grade quality and used without further purification unless otherwise noted. All column chromatography was done using Merck silica gel 60 as the solid support.



Synthesis of 5-Acrylamide-1,10-phenanthroline (3). Compound **3** has already been synthesized by several groups.[1] **3** was prepared from **1** in the reported method[1a] and purified to afford the melting point of **3**, because the melting point has not been reported in the literature so far. Phenanthroline-5-amine **1** (1.0 g, 5.1 mmol) was added to a solution of 100 mL of dry THF and 0.5 mL of triethylamine. The suspension was stirred for 1 h. Acryloyl chloride **2** (0.50 g, 5.5 mmol) in THF (10 mL) solution was added at 0 °C. The mixture was kept stirring for 5 h at room temperature and poured into 5% $NaHCO_3$ aqueous solution. The organic layer was washed with H_2O and dried over Na_2SO_4. The solvent was evaporated and purification by column chromatography on silica gel gave **3** (0.31 g, 1.2 mmol) in 24% yield as a yellow powder, mp 114-115 °C. ^1H NMR ($CDCl_3$): δ 9.25-9.08 (m, 2H, phen-*H*), 8.32 (m, 2H, phen-*H*), 8.21 (m, 1H, phen-*H*), 7.92 (s, 1H, N*H*), 7.63 (m, 1H, phen-*H*), 6.55 (d, $J = 5.25\ Hz$, 2H, CH=CH_2), 5.99-5.81(m, 1H, C*H*=CH_2). ATR-IR: υ_{max}/cm^{-1}: 3258 (N-H, amide), 1656 (C=O, amide I), 1622 (N-H, amide II), 1525 (C=C). UV-vis (λ_{max}, MeOH, nm): 270, 231. The spectra of ^1H NMR and mass are identical with the reported data.[1a, 1b]



Synthesis of Iron (5-acrylamide-1,10-phenanthroline)bis(1,10-phenanthroline)sulfate (5). Compound **3** (0.10 g, 0.40 mmol) and phenanthroline **4** (0.14 g, 0.78 mmol) were dissolved in a solution of 50 mL of CH_3CN and 30 mL H_2O. The mixture was cooled to 2 °C and ferrous sulfate heptahydrate (0.17 g, 0.40 mmol) in 8 mL of H_2O was added. The mixture was kept stirring for 30 min at 2 °C. The solvent was evapotared in vacuo, the residue was washed with acetone and ethanol to give **5** (0.23 g, 0.30 mmol) in 75% yield as a red powder, mp > 300 °C. ^1H NMR (D_2O): δ 8.55-8.45 (m, 6H, phen-*H*), 8.20-8.10 (m, 5H, phen-*H*), 7.65-7.60 (m, 6H, phen-*H*), 7.50-7.45 (m, 6H phen-*H*), 6.56 (t, 1H, J = 8.14 Hz, C*H*=CH$_2$), 6.37 (d, J = 8.14 Hz, 1H, CH=CH_2), 6.93 (d, J = 8.15 Hz, 1H, CH=CH_2). ^{13}C NMR (D_2O): δ 168.53 (NH-*C*=O), 156.01, 155.45, 150.23, 149.72, 149.64, 148.76, 137.72, 137.13, 133.15, 132.49, [130.29, 130.25 (each *C*H=*C*H$_2$)], 129.78, 129.60, 129.44, 127.83, 127.31, 125.65, 125.31, 123.91. HRMS (ESI-quadrupole) m/z: $[M - SO_4^{2-}]^{2+}$ Calcd for $C_{39}H_{27}FeN_7O$ 332.5813; Found 332.5811. ATR-IR: υ_{max}/cm^{-1}: 1673 (C=O, amide I), 1626 (N-H, amide II), 1547 (C=C), 1089. UV-vis (λ_{max}, H_2O, nm): 222, 265, 511. As for the NMR spectra of **5**, the chemical shifts of two phenanthroline ligands **4** in the complex **5** were almost the same.



Synthesis of ferroin cross-linked gel (9) and brief characterization. The hydrogel **9** was prepared in similar procedure by Yoshida.[2] NIPAAm **6** (0.31 g, 2.7 mmol), BIS crosslinker **7** (5.6 mg, 0.036 mmol), and AIBN initiator **8** (13 mg, 0.080 mmol) were dissolved in 1 mL of ethanol, and ferroin monomer **5** (14 mg, 0.018 mmol) was dissolved in 1 mL of distilled water. These solutions were mixed (mixture ratio of the solvents was 1:1, v/v). The gelation was carried out for 5 h at 75 °C. After gelation, the gel stuff was rinsed thoroughly with ethanol several times. 20 percent of ferroin monomer **5** was unreacted, which was estimated from the ferroin concentration of the reaction flask and the first rinsed ethanol harnessing UV-visible spectra.[3] The incorporated amount of ferroin into the chain was approximately 0.52%. Next, the gel was immersed in a solution of ethanol/distilled water (1:1, v/v) mixtures for removing unreacted compounds for 5 days. Then the gel was immersed in distilled water for additional 5 days.

Characterization and measurement section for ferroin cross-linked gel (9).

Equilibrium swelling ratio measurement.[2, 4] For the measurement of the temperature dependence of the swelling ratios, the gel was cut into two cuboids (approximately 22 mm × 3 mm × 3 mm). Each sample was immersed in cerium sulfate solution. Two kinds of cerium sulfate solutions (one solution contained 1.0 mM $Ce(SO_4)_2$ and 0.30 M HNO_3, and the other contained 1.0 mM $Ce_2(SO_4)_3$ and 0.30 M HNO_3) were caused the gels into oxidized Ru(III) state and reduced Ru(II) state, respectively. The gel samples were equilibrated in the solution at a temperature ranging from 5 to 40 °C. The length of the cuboid gel samples were measured. The relative length is defined as the ratio of characteristic length to that at the shrunken state over the phase transition temperature.

Self-oscillation by the BZ reaction measurement and detail. The bulk gel was cut into a miniature cube (each side length is about 1 mm); the cutting was then immersed into 10 mL of an aqueous solution containing malonic acid (63 mM), and HNO_3 (0.3 M) for 3 h at 20 °C. To commence the BZ reaction, sodium bromate was added to adjust the concentration to 84 mM in the BZ reaction mixture.

Swelling-deswelling ratio of ferroin cross-linked gel (9). The length of recorded gel image was stored at regular time intervals (15 s). The stored line images were sequentially lined up as a function of time on the computer. This image-processing procedure constructs a spatio-temporal diagram expressing both the redox changes in the gel and the displacement of the gel edge. From the diagram obtained, the swelling-deswelling profiles as a function of time were expressed as a track of the moving gel edge, and the time dependent change in the oxidized fraction of ferroin at a fixed position of the gel was expressed as 8-bit gray-scale changes by using the image processing software (imageJ 1.47 as a free software from National Institutes of Health, US).

CCD Recording of ferroin cross-linked gel (9). The gel oscillation was recorded by a digital video recorder through a CCD camera (SWIFTCAM 5, Swift Co.

Ltd.) attached to a microscope (LZ-LED-T, Kenis Co. Ltd.). Images of the gel were sampled every 15 s, and changes a movie file.

Self-oscillating region given by the initial concentrations of the BZ substrates. Table 1 indicates the interval of oscillation and the swelling-deswelling ratio of ferroin cross-linked gel **9** in the presence of different concentrations of sodium bromate ($NaBrO_3$), nitric acid and malonic acid, at a fixed temperature of 20 °C.

Table 1 The self-oscillating region of ferroin cross-linked gel **9**.[a)]

Run	$[NaBrO_3]$ (mM)	$[HNO_3]$ (M)	[Malonic acid] (mM)	Interval (min)	Swelling-deswelling ratio (%)
1	83	0.30	63	7	7
2	83	0.15	63	16	3
3	83	0.60	63	5	6
4	83	0.30	126	-[b)]	-[b)]
5	166	0.30	63	10	3

a) Temperature: 20 °C.

b) No oscillation was observed.

ESI movie 1. The oscillating behavior of the ferroin cross-linked gel **9** at 20 °C in Figure 3. File name "**CCD Ferroin Gel**" attached.

References of ESI section.

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