Supporting information

# Redox-associated Phase Transition of a Marginally Stable Synthetic Polymer

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## Materials and methods

### Materials.

[(Chloromethyl)phenylethyl]trimethoxysilane (CMPETMS) was purchased from Fluorochem Ltd. (Hadfield, UK). *N*-isopropylacrylamide (NIPAAm) was generously donated by KJ chemicals Co. (Tokyo, Japan) and purified by recrystallization from a toluene/hexane mixed solvent. *N*-(3-aminopropyl)methacrylamide (NAPMAm) was purchased from Combi-Blocks (San Diego, USA) and purified by reprecipitation from methanol as a good solvent and THF as a poor solvent. Bis(2,2'-bipyridine)(1-(4'-methyl-2,2'-bipyridine-4-carbonyloxy)-2,5-pyrrolidinedione)ruthnium(II) bis(hexafluorophosphate) (Ru(bpy)$_3$-NHS) was purchased from Hangzhou Trylead Chemical Technology Co., LTD. (Hangzhou, China). All other chemical agents were purchased from FUJIFILM Wako Pure Chemical Co. (Osaka, Japan) and used as received unless otherwise noted. Indium-tin oxide (ITO) electrodes (10×20×0.5 mm, ITO layer thickness ~ 100 nm) were purchased from BAS Inc. (Tokyo, Japan). ITO-modified quartz crystal microbalance (QCM) chips (QA-A9M-ITO(M)) were purchased from SEIKO EG&G Co., Ltd. (Tokyo, Japan).

### General methods.

$^1$H-nuclear magnetic resonance (NMR) spectra were collected at room temperature using a JEOL JNM-ECS400 spectrometer. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) was performed using SHIMADZU IRSpirit-X spectrophotometer. Cyclic voltammograms were measured on a Bio-Logic SAS SP-50 electrochemical analyzer.

ITO electrodes with polymer modifications, platinum wire, and Ag/AgCl electrode ([KCl] = 3.4 M) were used as the working, auxiliary, and reference electrodes, respectively. All electrochemical measurements were conducted under air. Confocal microscope images of the redox-responsive polymer-modified ITO electrode were obtained using OLYMPUS FLUOVIEW FV3000 equipped with three electrodes electrochemistry setup while sweeping the electrode potential (reference electrode: Ag/AgCl ([KCl] = 3.4 M, counter electrode: platinum wire, medium: 0.01 M nitric acid). The excitation wavelength ($\lambda_{ex}$) was 488 nm, and the emission was collected between 550 nm and 650 nm, corresponding to the phosphorescence of $Ru(bpy)_3^{2+}$. The potential was scanned over a range of 0.6 V to 1.4 V with a scan rate of 10 mV $s^{-1}$.

### Electrochemical QCM (EQCM) measurement

Electrochemical QCM (EQCM) measurement were conducted using SEIKO EG&G QCM922A with three electrodes electrochemistry setup while sweeping the electrode potential (reference electrode: Ag/AgCl ([KCl] = 3.4 M, counter electrode: platinum wire, medium: 0.01 M nitric acid). The observed resonance frequency shift (Δf) were converted to mass changes ($\Delta m$) using Sauerbrey equation: $\Delta f = -2 f_0^2 \Delta m / (\mu_\mathrm{q} \rho_\mathrm{q})^{1/2}$, where $f_0$ is the resonance frequency, which is 9.08 MHz for the quartz oscillator used in this study; $\mu_\mathrm{q}$ is the shear modulus of quartz, which is $2.95 \times 10^{11}$ g $cm^{-1}$ $s^{-2}$; and $\rho_\mathrm{q}$ is the density of quartz, which is 2.65 g $cm^{-3}$. Δf values were calculated based on the plateau regions in the resonance frequency before or after the current peaks. The QCM data shown in Figure 4b and 4c were smoothed by averaging the 4 preceding and 4 following points for each data point. During the EQCM measurement were conducted, the temperature of the cell was controlled by an EYELA NCB-1210A water bath.

### Estimation of the influence of electrolyte incorporation and hydration/dehydration of Ru(bpy)$_3$ complexes on EQCM results

The molecular weight of the electrolyte anion ($NO_3^-$) is 62. Therefore, the mass change related to the incorporation of the counter anion corresponds to only 1.2% of the total mass change. To the best of our knowledge, there is no literature that reports the difference in the number of hydration water molecules between $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ in water. However, the first solvation shell of $Ru(bpy)_3^{2+}$ is estimated to contain approximately 35 well-oriented water molecules.[1] Even if the number of hydrated water molecules is doubled through the oxidation of $Ru(bpy)_3^{2+}$, the contribution would only account for 12%. Based on these considerations, we conclude that the mass changes associated with these minor contributions do not dominate.

### Preparation of polymer brush-immobilized ITO electrodes

Poly(NIPAAm-*co*-NAPMAm-*co*-NAPMAm[Ru(bpy)$_3$]) was prepared on the surface of ITO substrates or ITO-modified QCM chips according to the literature with modifications[2].

### Synthesis of poly(NIPAAm-*co*-NAPMAm) brush on ITO.

An ATRP initiator (CMPETMS) was immobilized on ITO substrates (ITO electrodes or ITO-modified QCM chips) by the silanization reaction. ITO substrates were cleaned by a mixed solution of 30% $H_2O_2$ (20 mL), 25% $NH_4OH$ (24 mL) and $H_2O$ (96 mL) at 60 °C for 30 min to activate the surface. The ITO substrates were then placed in a separable flask (500 mL), and it was purged with argon gas by argon gas flushing for 30 min. CMPTEMS (20 μL) were dissolved in 1 mL toluene and then added into a separable flask while flushing with argon gas. Under an argon atmosphere, immobilization of CMPTEMS proceeded for 20 h at 150 °C. After the reaction, the ITO substrates were washed with toluene and acetone and finally dried in a vacuum oven at 110 °C for 2 h.

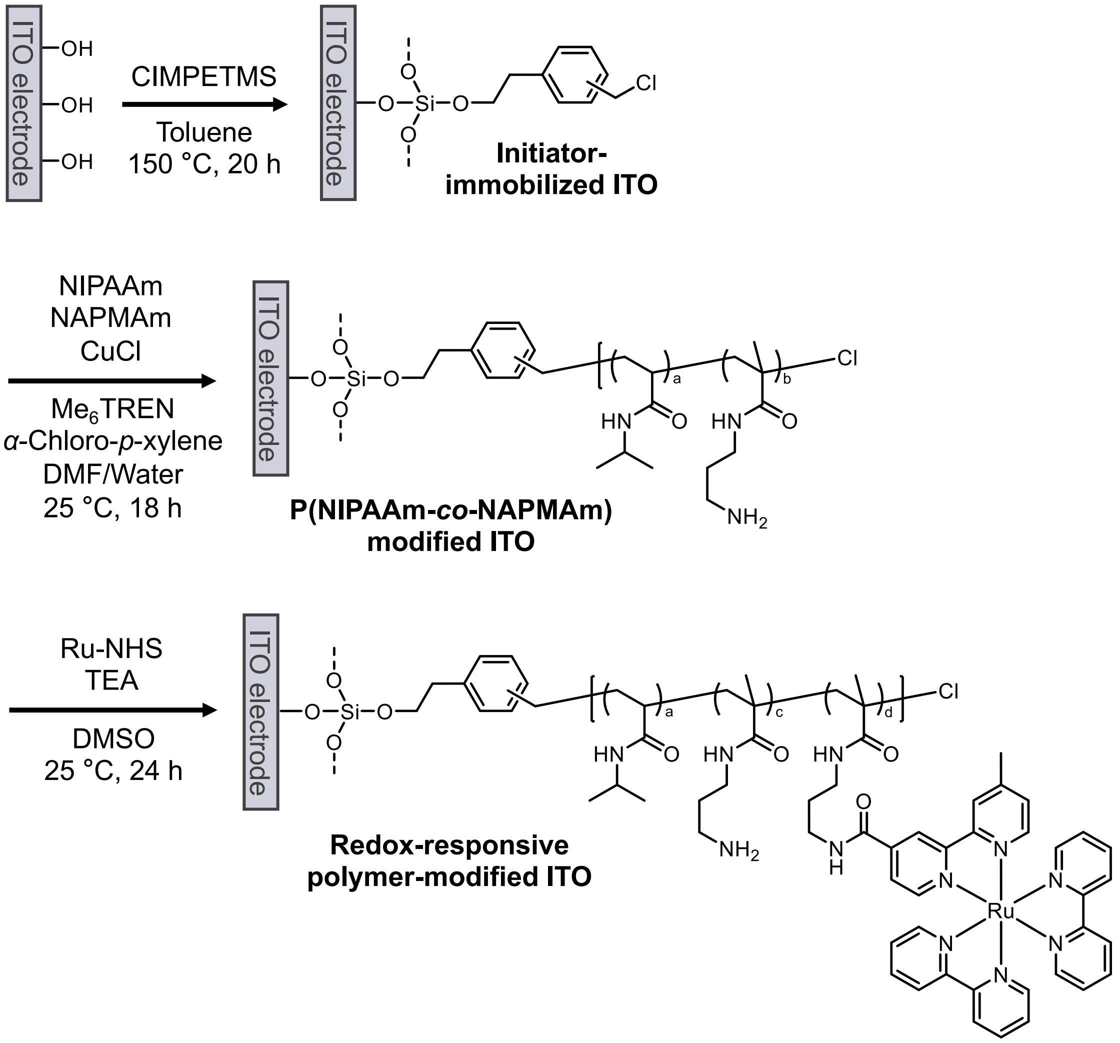
NIPAAm (3.23 g, 28.5 mmol) and NAPMAm (0.27 g, 1.5 mmol) were dissolved in a mixed solution of DMF (10 mL) and water (10 mL) and then deoxygenated by argon bubbling for 20 min. CuCl (19.8 mg, 0.2 mmol) and $Me_6$TREN (58.8 μL, 0.22 mmol) were added to the solution and stirred for 30 min under an argon atmosphere to form a complex between CuCl and $Me_6$TREN. The initiator-immobilized substrates and *α*-Chloro-*p*-xylene (2.64 μL, 0.02 mmol) were added into the prepared ATRP solution and deoxygenated by argon bubbling for another 10 min. α-Chloro-p-xylene was added to the solution to polymerize an untethered free polymer. The reaction was performed at 25 °C for 18 h. After the polymerization, the reaction mixture was exposed to the air to terminate the reaction. The poly(NIPAAm-*co*-NAPMAm)-modified substrates were rinsed with methanol and water, followed by sonication in a solution of 50 mM EDTA aqueous solution and then water for 5 min. The substrates were then immersed in 0.1 M $Na_2CO_3$ aqueous solution for 1 h to deprotonate the primary ammonium group of the NAPMAm. The substrates were washed with deionized water and finally dried in a vacuum oven at 100 °C for 2 h.

The obtained ATRP reaction mixture was dialyzed against deionized water for 3 days using a dialysis membrane with a molecular weight cutoff of 14 kDa and then lyophilized to recovery the untethered poly(NIPAAm-*co*-NAPMAm). The molecular weight and composition of the polymer were estimated to be 92 kDa and P(NIPAAm$_{0.94}$-*co*-NAPMAm$_{0.06}$)$_{786}$, respectively, from the $^1$H-NMR results of the untethered polymer in $D_2O$ by analysing the integrated intensity of the characteristic peaks: NIPAAm (1H, $\delta$ = 3.5−3.9 ppm), NAPMAm (4H, $\delta$ = 2.5−3.3 ppm) and the terminal *p*-xylene moiety (4H, $\delta$ = 7.0−7.3 ppm).

### Synthesis of poly(NIPAAm-*co*-NAPMAm-*co*-NAPMAm[Ru(bpy)$_3$]) brush on ITO.

Ru(bpy)$_3$-NHS (15.2 mg, 15.0 μmol) and triethylamine (6.3 μL, 45 μmol) were dissolved in dimethylsulfoxide (DMSO) (75 μL). The reaction solution was cast on the poly(NIPAAm-*co*-NAPMAm)-modified substrates and reacted with the amino group of NAPMAm at 25 °C for 24 h. After the reaction, the poly(NIPAAm-*co*-NAPMAm-*co*-NAPMAm[Ru(bpy)$_3$])-modified substrates were washed with DMSO and acetone and then dried in a vacuum oven at 60 °C for 1 h.

## Fabrication of the self-oscillating polymer-modified ITO electrode



**Scheme S1**. Fabrication of the self-oscillating polymer-modified ITO electrode.

## $^1$H-NMR spectrum

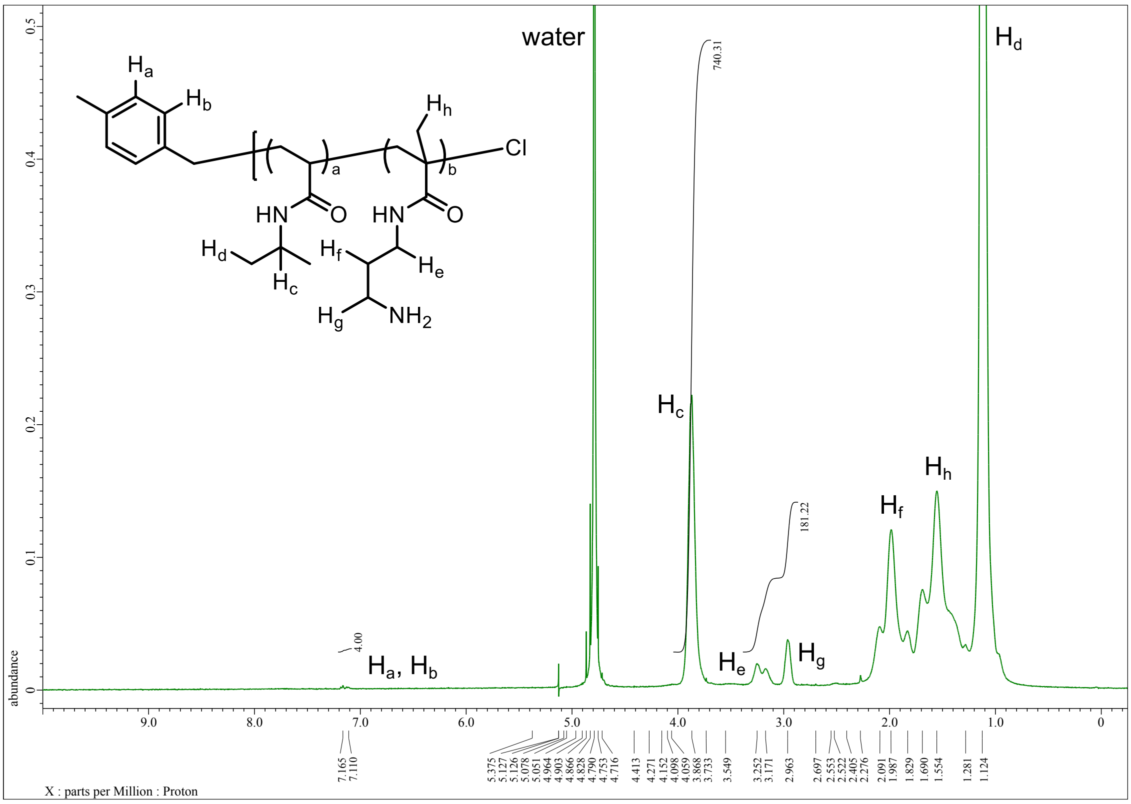


**Figure S1.** $^1$H-NMR spectrum of P(NIPAAm-*co*-NAPMAm) in $D_2O$.

**ATR-FT-IR spectrum**

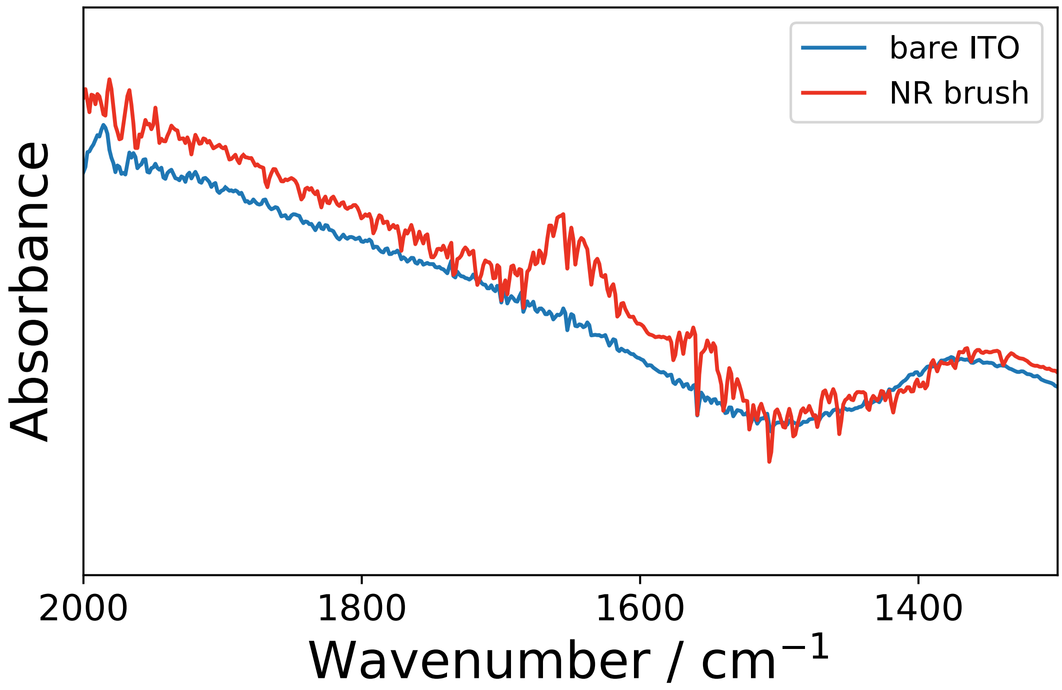


**Figure S2.** ATR-FT-IR spectrum of the poly(NIPAAm-*co*-NAPMAm-*co*-NAPMAm[Ru(bpy)$_3$])-modified ITO surface.

**EQCM result**

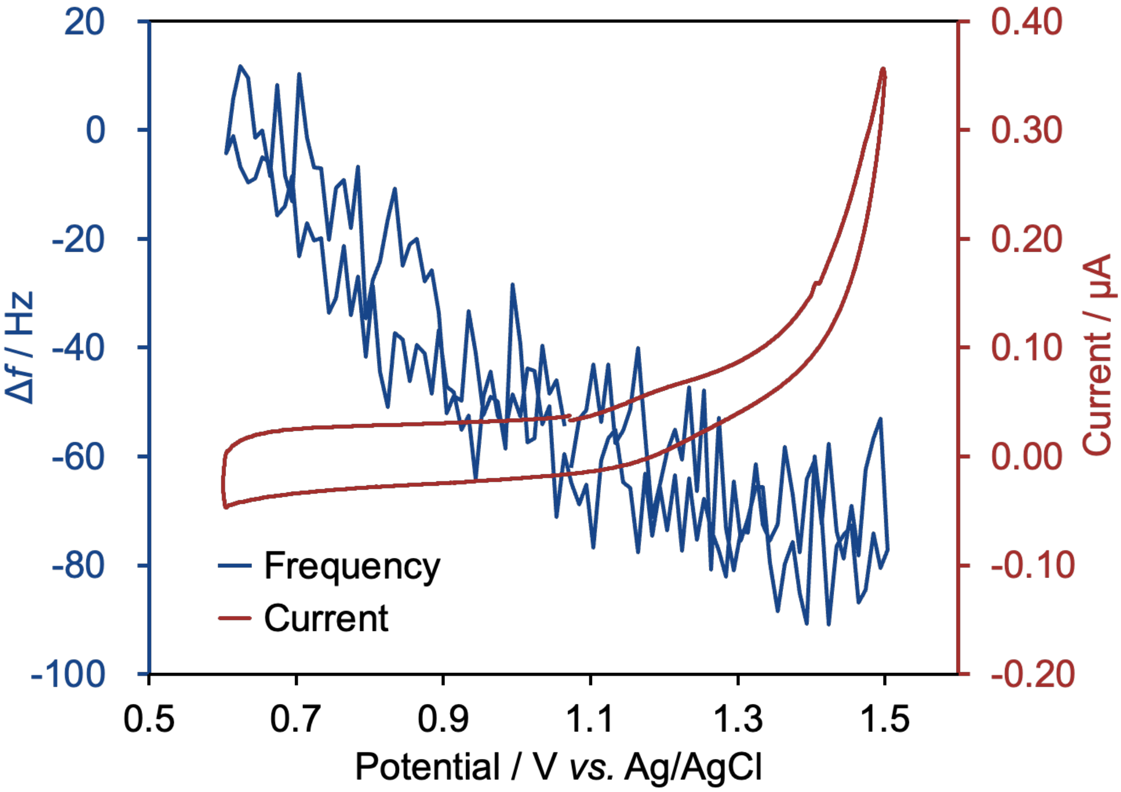


**Figure S3.** Cyclic voltammogram and the corresponding resonance frequency change (*Δf*) of the PNIPAAm-based redox-responsive polymer electrode in water containing nitric acid (0.01 M) obtained at a scan rate of 10 mV $s^{-1}$ and a temperature of 25 °C.

## References

(1) M. E. Moret, I. Tavernelli and U. Rothlisberger, *J. Phys. Chem. B*, 2009, **113**, 7737.

(2) K. Homma, Y. Ohta, K. Minami, G. Yoshikawa, K. Nagase, A. M. Akimoto, R. Yoshida, *Langmuir* 2021, **37**, 4380.