Supporting Information

Control of swelling-deswelling behavior of self-oscillating gel by designing the chemical structure

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Experimental

Preparation of the calibration curve to determine the amount of Ru(bpy)$_3$ conjugated to the polymer

The calibration curve was independently made from aqueous solutions of Ru(bpy)$_3$Cl$_2$ with known concentrations. The absorbance spectra of the aqueous solutions of Ru(bpy)$_3$Cl$_2$ were measured by using a UV-vis measurement spectroscopy. Here, the absorbance at 700 nm ($A_{700}$) was defined as the baseline (i.e. $A_{700} = 0$), because there are no peak at 700 nm.

Measurements of swelling and deswelling kinetics

The kinetics of the ternary self-oscillating gel was measured as the following reference. The gel was immersed in the aqueous solution containing HNO$_3$ (810 mM) and NaCl (104 mM), and stabilized at 20 °C. Swelling kinetics were measured by exchanging the external solution to the aqueous solution containing HNO$_3$ (810 mM) and NaBrO$_3$ (104 mM). Deswelling kinetics were measured by exchanging the solution to the solution containing HNO$_3$ (810 mM), NaCl (104 mM), and MA (84 mM). Swelling or deswelling process of the gels were recorded by a digital video recorder through a CCD camera (Toshiba Teli, CS5270B) attached to a microscope (MZ16, Leica).

Reference:
Supporting Results

**Fig. S1** Calibration curve to determine the amount of Ru(bpy)₃ conjugated to the polymer. The calibration curve was independently made from aqueous solutions of Ru(bpy)₃Cl₂ with known concentrations.

**Fig. S2** Absorbance spectra for poly(NIPAAm-co-NAPMAm-co-Ru(bpy)₃NAPMAm) solutions (0.05 wt%) under the different conditions of the reduced Ru(II) state and oxidized Ru(III) state.
Fig. S3 Temperature dependence of optical transmittance for (a) the ternary self-oscillating polymer and poly(NIPAAm-co-NAPAm) (black line), and (b) the conventional self-oscillating polymer (poly(NIPAAm-co-Ru(bpy)$_3$) and polyNIPAAm (black line) in aqueous solution containing 1 M HNO$_3$.

Fig. S4 Arrhenius plot of the self-oscillation of linear polymer.
**Fig. S5** The kinetics of PNNR-5-(100%) in (a) swelling process and (b) deswelling process. The initial rates were shown in the figure.

**Table S1** Kinetics of ternary self-oscillating gel (PNNR5-(100%)) and conventional gel.

<table>
<thead>
<tr>
<th>Gel</th>
<th>Swelling process</th>
<th>Deswelling process</th>
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<tbody>
<tr>
<td>Ternary self-oscillating gel</td>
<td>0.37 µm s(^{-1})</td>
<td>0.36 µm s(^{-1})</td>
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<tr>
<td>(PNNR-5-(100%))</td>
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<tr>
<td>Conventional gel (^{S1})</td>
<td>0.11 µm s(^{-1})</td>
<td>0.07 µm s(^{-1})</td>
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**Fig. S6** Oscillating profile of the gray value of PNNR-10-(100%) at 20 °C.