Supporting Information

Temporal Control of Self-Oscillation for Microgels
by Crosslinking Network Structure

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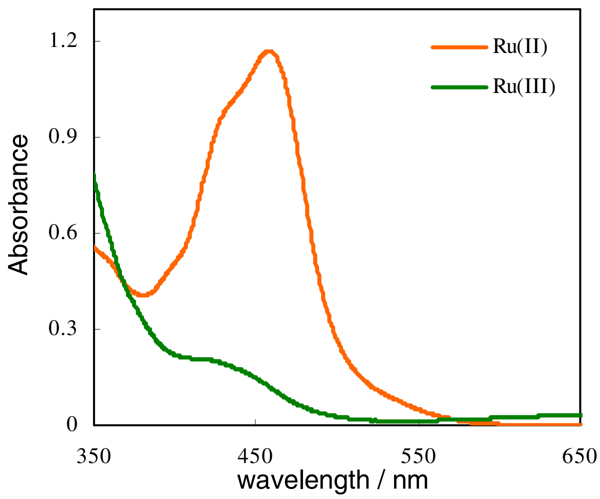
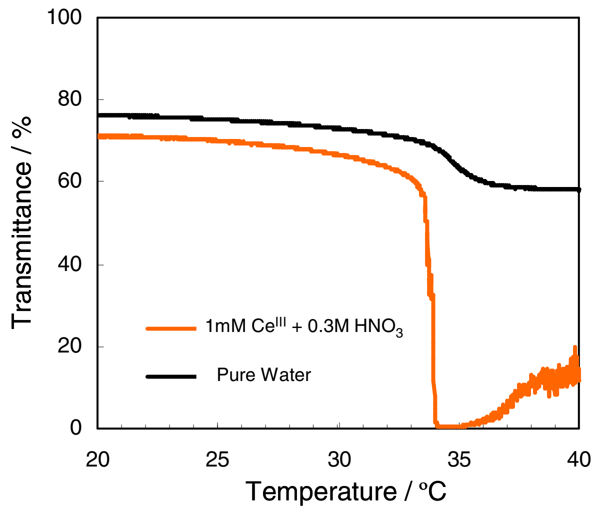
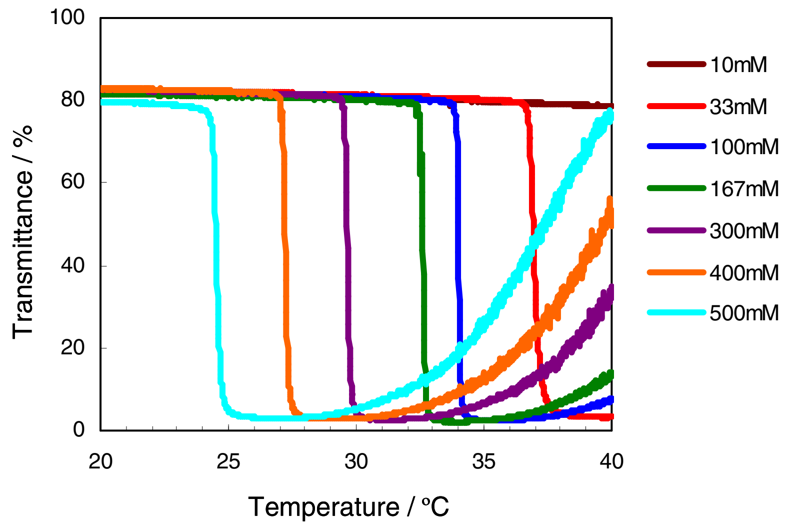


SI Figure 1. Absorption spectra for Ru(bpy)$_3$ monomer for the reduced Ru^{II} state in 1 mM Ce^{III} and 0.3 M HNO$_3$ solution (orange line), and the oxidized Ru^{III} state in 1 mM Ce^{IV} and 0.3 M HNO$_3$ solution (green line). Each Ru(bpy)$_3$ monomer concentration was 0.01 wt.%.

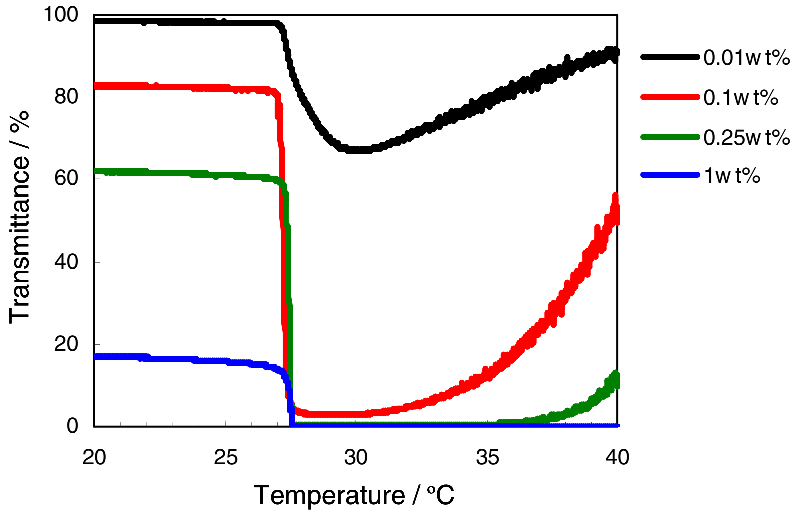
As shown in SI Figure 1, the Ru(bpy)$_3$ complex has different absorption spectra in the reduced Ru^{II} state and the oxidized Ru^{III} state as an inherent property. The solution has isosbestic point at 570 nm. In this study, our aim is to detect the optical transmittance changes based on swelling/deswelling changes of the microgels. Therefore, the 570 nm wavelength was used for detecting the swelling/deswelling oscillation of the microgels.



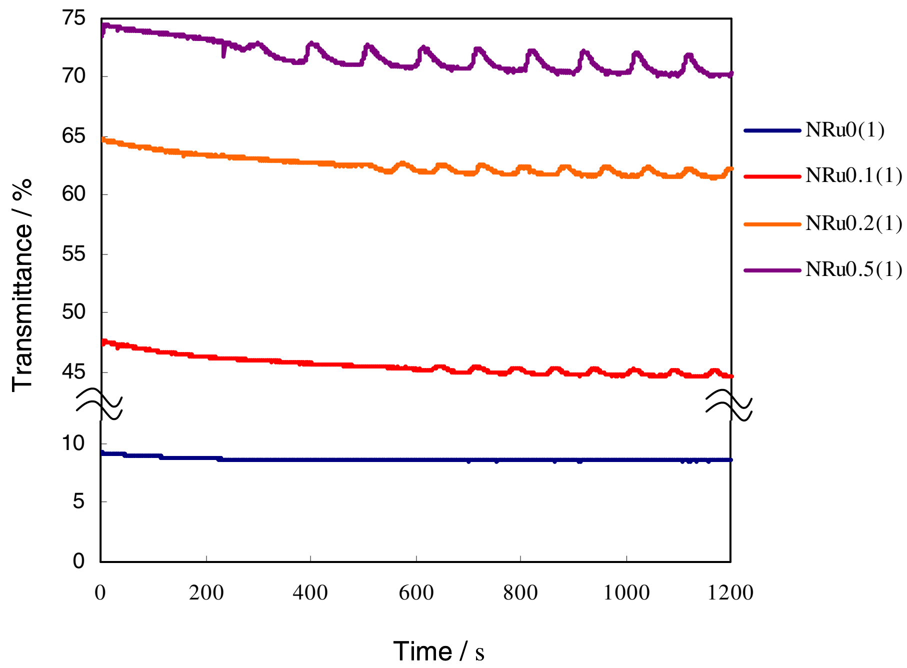
SI Figure 2. Temperature dependence of optical transmittance for the Ru(bpy)$_3$ copolymerized pNIPAm microgels [NRu0.1(1)] under the different conditions; the reduced state Ru^{II} in 1mM Ce^{III} and 0.3M HNO_3 solution (orange line), and the reduced state Ru^{II} in pure water (black line). The dispersion concentration was 0.1 wt% in both cases. The 570 nm wavelength was used for the measurement. The solutions were heated at a rate of 1 ºC/min with a constant stirring.



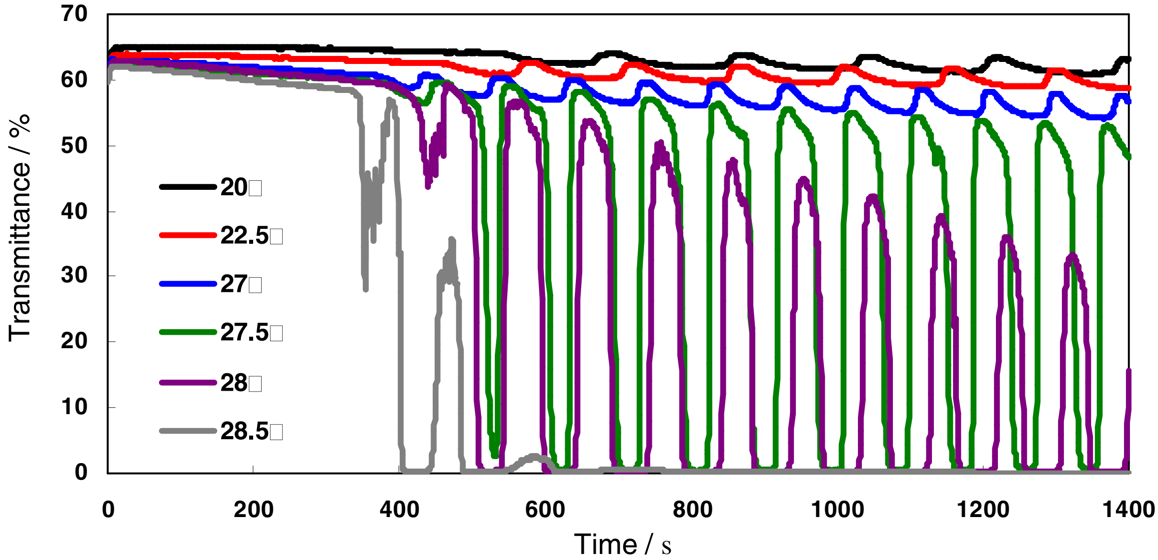
SI Figure 3. Temperature dependence of optical transmittance for the $Ru(bpy)_3$ copolymerized pNIPAm microgels [NRu1(10)] dispersed in different $NaBrO_3$ solutions. The microgels were not flocculated at low $NaBrO_3$ concentration (10 mM). The dispersion concentration was 0.1 wt% in all cases. The 570 nm wavelength was used for the measurement. The solutions were heated at a rate of 1 ºC/min with a constant stirring. Note that cloud point sifted to lower temperatures with increasing [$NaBrO_3$] (i.e., 36.6 ºC in 33 mM, 33.8 ºC in 100 mM, 32.4 ºC in 167 mM, 29.4 ºC in 300 mM, 27.0 ºC in 400 mM, and 24.3 ºC in 500 mM).



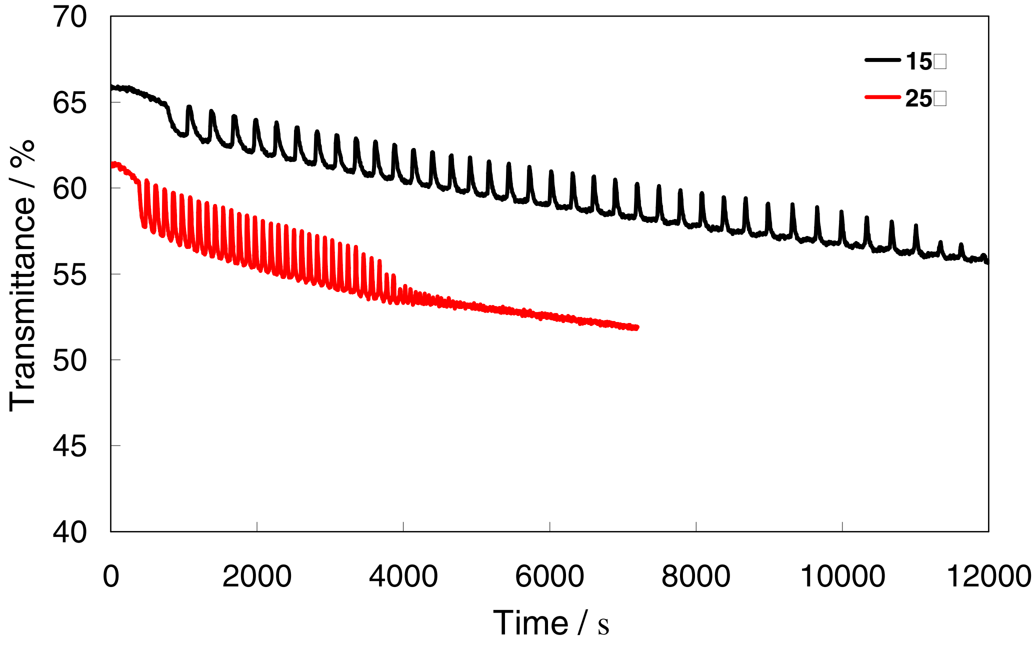
SI Figure 4. Temperature dependence of optical transmittance for the Ru(bpy)$_3$ copolymerized pNIPAm microgels [NRu1(10)] in 400 mM $NaBrO_3$ solution measured at different microgel dispersion concentrations. The 570 nm wavelength was used for the measurement. The solutions were heated at a rate of 1 ºC/min with a constant stirring. Different from [$NaBrO_3$] dependence, microgel concentration did not affect cloud point so much (i.e., 27.2 ºC in 0.01 wt%, 27.1 ºC in 0.1 wt%, 27.3 ºC in 0.25 wt%, and 27.3 ºC in 1 wt%).



SI Figure 5. Self-oscillating profiles of optical transmittance for NRu0.1(1) (red line), NRu0.2(1) (orange line), NRu0.5(1) (purple line), and control NRu0(1) microgels (blue line). The microgels (0.25-wt%) were dispersed in the aqueous solutions containing MA (62.5 mM), $NaBrO_3$ (84 mM), and HNO_3 (0.3 M) at 25 ºC.



SI Figure 6. Self-oscillating profiles of optical transmittance for NRu1(4) microgel dispersions. The microgels (100 μM of $Ru(bpy)_3$) were dispersed in the aqueous solutions containing MA (62.5 mM), $NaBrO_3$ (84 mM), and HNO_3 (0.3 M). The profiles were measured at the different temperatures: 20 ºC (black line), 22.5 ºC (red line), 27 ºC (blue line), 27.5 ºC (green line), 28 ºC (purple line) and 28.5 ºC (gray line).



SI Figure 7. Typical self-oscillating profiles of optical transmittance for many hours for NRu1(4) microgel dispersions. The microgels (100 μM of $Ru(bpy)_3$) were dispersed in aqueous solutions containing MA (62.5 mM), $NaBrO_3$ (84 mM), and HNO_3 (0.3 M). The profiles were measured at the different temperatures: 15 ºC (black line) and 25 ºC (red line). At the same substrate concentrations, duration of the oscillation at lower temperature (15 ºC, ~5 h) is longer than that at higher temperature (25 ºC, ~ 1 h).