Supporting Information

Soft Actuators of Organized Self-Oscillating Microgels

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Experimental Section

Unless stated otherwise, all materials were purchased from Wako Pure Chemical Industries, Ltd, and used as received. Ruthenium(II)(4-vinyl-4'-methyl-2,2'-bipyridine)bis(2,2'-bipyridine)bis (hexafluoro-phosphate) [Ru(bpy)₃ monomer] was synthesized according to the previous work.¹ 10 *N*-(3-aminopropyl) methacrylamide hydrochloride (APMA) was purchased from Polysciences, Inc., and used without further purification. Glutaric dialdehyde (50 wt.% solution in water) was purchased from Sigma-Aldrich, and used as received. Water for all reactions, solution preparation, and polymer purification was first distilled then ion-exchanged.

- The oscillating microgels were synthesized by surfactant-free aqueous radical precipitation 15 polymerization.² SI Figure 1 shows the chemical structure of the microgel. A mixture of *N*-isopropylacrylamide Ruthenium(II)(4-vinyl-4'-methyl-2,2'-bipyridine) (NIPAm) (1.613)g), bis(2,2'-bipyridine)bis(hexafluorophosphate) [Ru(bpy)₃ monomer] (0.270 g), APMA (0.027 g), N,N'-methylenebisacrylamide (BIS) (0.046 g), and water (195 mL) was poured into a 300-mL three-neck, round-bottom flask equipped with a stirrer, a condenser, and a nitrogen gas inlet. Under a 20 stream of nitrogen to purge oxygen and with constant stirring at 250 rpm, the solution was heated in an oil bath to 70 °C. After stabilizing the solution for 1 h, the azobis-amidinopropane dihydrochloride (V-50) initiator (0.109 g) dissolved in 5 mL water was added to the flask to initiate the polymerization, which then continued for 4 hrs. In this polymerization, total NaCl concentration was 50 mM. After the polymerization, the dispersion was cooled to room temperature. The obtained microgels were purified 25 by centrifugation/re-dispersion with water two times using a relative centrifugal force (RCF) of 50000
- x g for approximately 3 hrs, and by daily changes of water by means of dialysis for 5 days. Ru(bpy)₃ monomer was incorporated in microgels ~60 %.

Hydrodynamic diameter of the microgels was determined by dynamic light scattering (DLS, Malvern, ZetasizerNanoS). Diluted microgels were analysed in a quartz cuvette. The samples were 30 allowed to equilibrate at the desired temperature for 10 min before data collection. Scattered light was collected at 173°.

Scattering intensity of microgel oscillations in dispersions were collected on a JASCO V-630 spectrophotometer. The microgels (0.25 wt%) were dispersed in the aqueous solution containing the reactants of the BZ reaction: MA (100 mM), NaBrO₃ (150 mM), and HNO₃ (500 mM). Under constant 35 temperature and stirring conditions, the time course of scattering intensity was monitored. The 570 nm wavelength was selected to detect the intensity changes of the microgels (see **SI Figure 2**).

To form macrogels from the microgels, 2µL of the glutaric dialdehyde aqueous solution was added to concentrated microgel dispersions (10 mg, final concentration: 4-6 wt%) containing 5 mM NaBrO₃ at 35°C in order to induce a chemical reaction between the amino groups located on microgel 40 exterior. After mixing the dispersion for 2 min, temperature decreased rapidly to 4 °C. The reaction was carried out in a micro tube. The reaction tube was mixed at 900 rpm with thermomixer R

(Eppendorf). The reaction continued for 2 days at 4 °C. In this study, the macrogels were used after cutting them (ca.1mm×1mm). Unstructured oscillating macrogels were synthesized as described in previous papers.^{3,4}

Deswelling kinetics of the macrogels were measured with an optical microscope (BX51, 5 Olympus) equipped with a digital camera (ImageX Earth Type S-2.0M, Kikuchi-Optical Co., Ltd) and a temperature controller (NCB-1200, Eyela). The square-shaped macrogels soaked in a 1900µL solution were observed using a computer running ImageX Earth Type S-2.0M Version 3.0.5 software. First, the macrogel was equilibrated in an aqueous solution containing 650 mM HNO₃ at 20 °C. Then temperature increased quickly to 40 °C. Swelling ratios defined as the sizes of the macrogels 10 normalized by the size of each swollen macrogel at 20 °C were calculated as a function of time.

The oscillation behavior of the macrogels was recorded with the optical microscope equipped with the digital camera. First, the macrogels were immersed in aqueous solutions (900 μ L) containing NaBrO₃ and HNO₃. After 30 min to equilibrate the macrogels, 100 μ L of MA solution was injected to the solution to start the BZ reaction. One-line images along the size of the macrogel were collected 15 every 20 s, and the time series of the frames was pictured as a spatiotemporal pattern.

Reference

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SI movie 1. The oscillating behavior of the organized macrogel at 22 °C in Fig. 4a. (speed up image: 100 times faster than the real image)

SI movie 2. The oscillating behavior of the organized macrogel at 24 °C in Fig. 4a. (speed up image: 30 100 times faster than the real image)

SI movie 3. The oscillating behavior of the organized macrogel in 1M HNO₃ in Fig. 4b. (speed up image: 200 times faster than the real image)

35 **SI movie 4.** The oscillating behavior of the unstructured macrogel. The reaction condition is the same as Fig.4a, 22 °C. (speed up image: 200 times faster than the real image)

SI movie 5. The oscillating behavior of the unstructured macrogel. The reaction condition is the same as Fig.4b, 1M HNO₃. (speed up image: 200 times faster than the real image)

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SI Figure 1. Chemical structure of the microgel.

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SI Figure 2. Oscillation profiles of scattering intensity, *I*, for the microgel dispersions, as measured by 10 UV-vis spectroscopy. The microgels (0.25 wt.%) were dispersed in aqueous solutions containing MA (100 mM), NaBrO₃ (150 mM), and HNO₃ (500 mM). The profiles were measured at the different temperatures: 15 °C (black), 20 °C (blue), 22 °C (red), 23 °C (orange), 24 °C (green), and 25 °C (grey). The isosbestic point between Ru(II) and Ru(III) of 570 nm wavelength was used to detect swelling/deswelling or flocculating/dispersing changes of the microgels. The sudden increase in 15 scattering intensity at 23 °C is due to flocculating/dispersing oscillation of microgels.



SI Figure 3. Comparison of swelling/deswelling oscillations for the macrogels. (red) data shown in Fig.4a, 22 °C. (black) control experiment, i.e., unstructured gel. Both macrogels were immersed in 1 mL aqueous solutions containing MA, NaBrO₃, and HNO₃. *L*₀ is each size before the MA addition to 5 start the chemical reaction. MA (100 mM), NaBrO₃ (150 mM), and HNO₃ (500 mM). **SI movie 4** shows the volume oscillation of the unstructured gel.



10 SI Figure 4. Comparison of swelling/deswelling oscillations for the macrogels. (red) data shown in Fig.4b, 1M HNO₃. (black) control experiment, i.e., unstructured gel. Both macrogels were immersed in 1 mL aqueous solutions containing MA, NaBrO₃, and HNO₃ at 20 °C. L₀ is each size before the MA addition to start the chemical reaction. MA (100 mM), NaBrO₃ (150 mM), and HNO₃ (1 M). SI movie 5 shows the volume oscillation of the unstructured gel.