Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Self-oscillating Micelles

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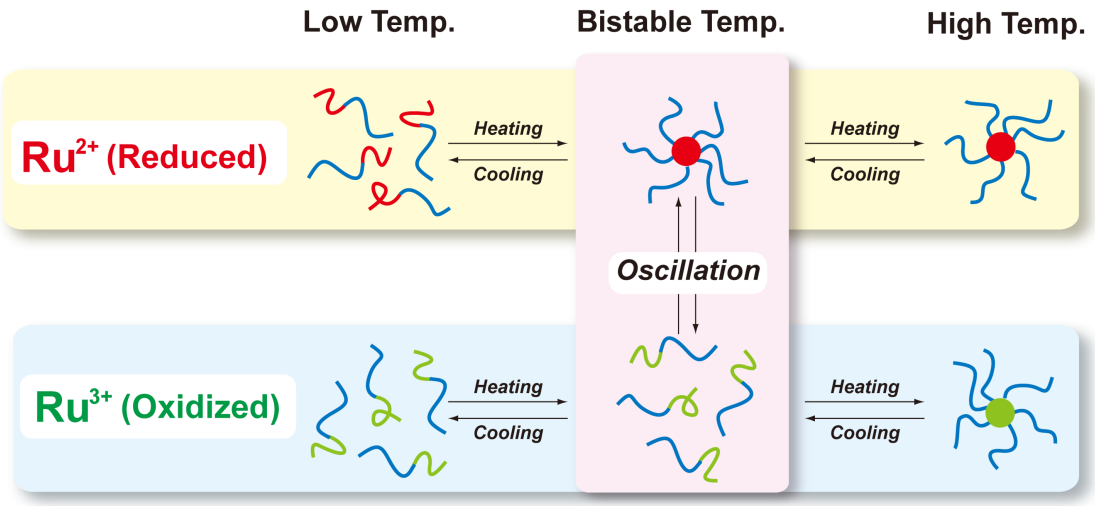
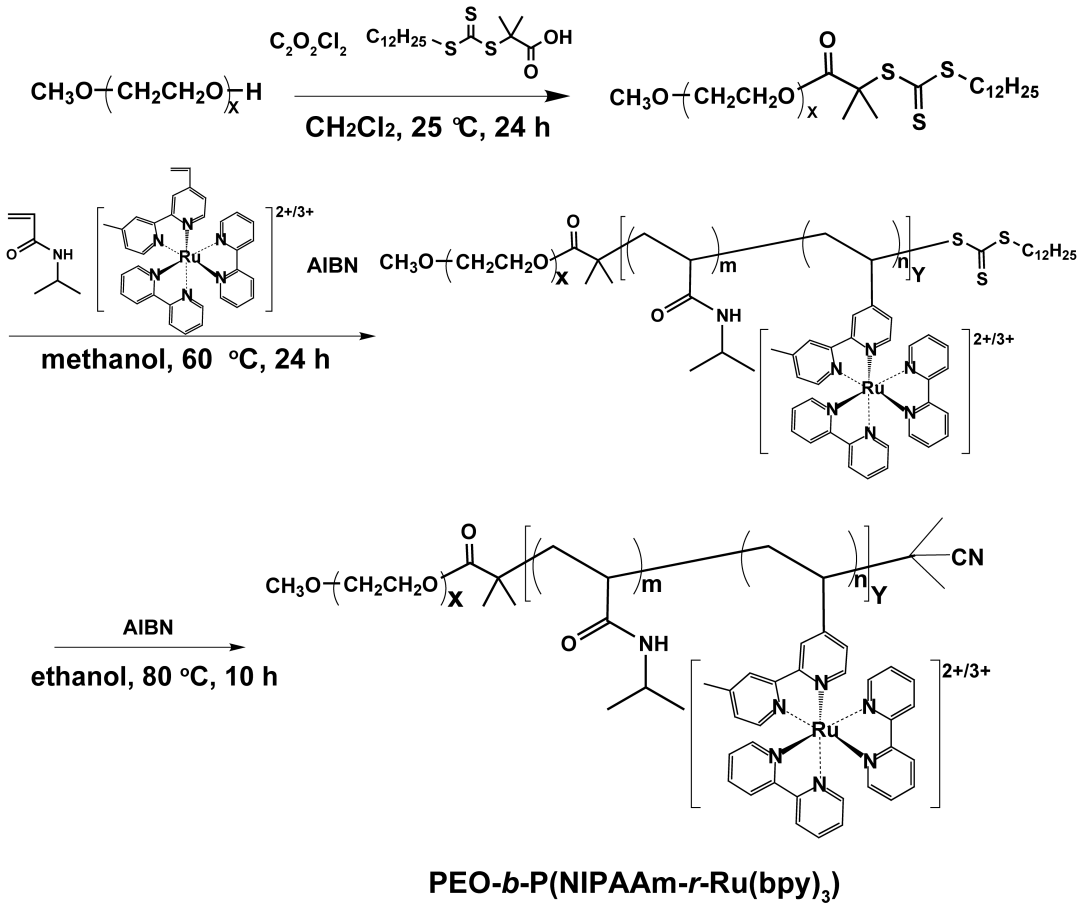


Scheme S1. A Conceptual illustration for the self-oscillating micelles.



Scheme S2. Preparation of PEO-*b*-P(NIPAAm-*r*-Ru(bpy)$_3$).

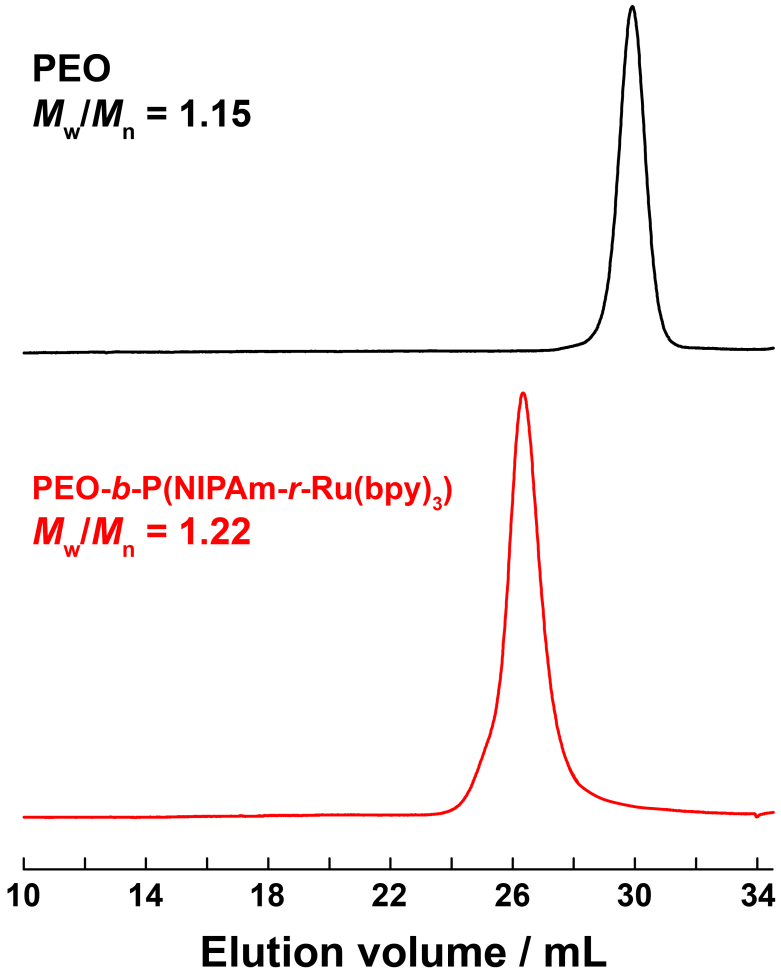


Figure S1. GPC traces for PEO and PEO-*b*-P(NIPAAm-*r*-Ru(bpy)$_3$).

Table S1. Characterization results of PEO and PEO-*b*-P(NIPAAm-*r*-Ru(bpy)$_3$).

Polymer	M_n / kDa	M_w/M_n	[Ru(bpy)$_3$]/[NIPAAm]
PEO	5.0	1.15	
PEO-*b*-P(NIPAAm-*r*-Ru(bpy)$_3$)	25.0	1.22	2.8/97.2

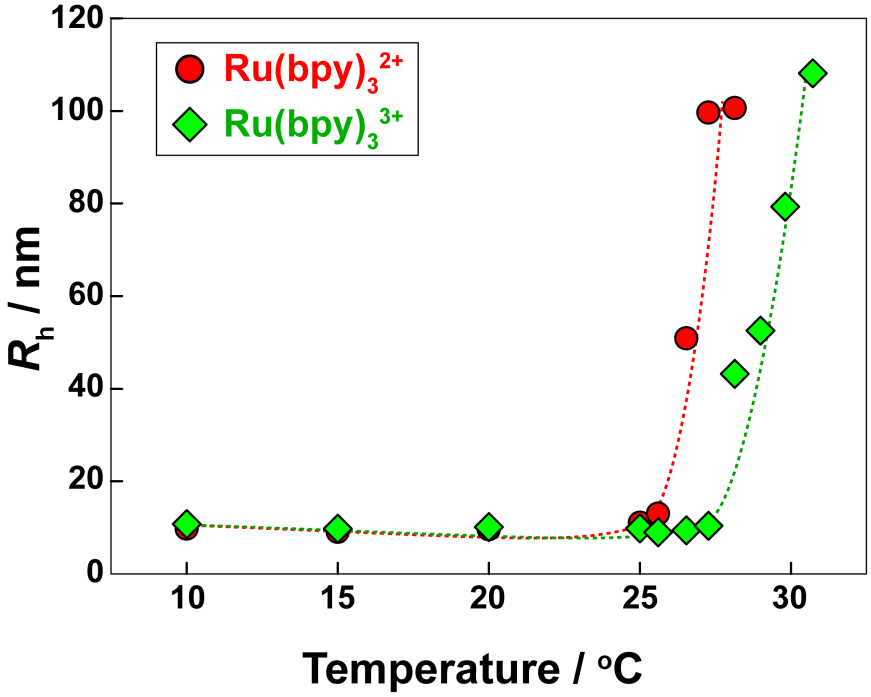


Fig. S2 Hydrodynamic radius (R_h) of the diblock copolymer (0.5 wt%) in the reduced and oxidized states of the $Ru(bpy)_3$ side chain as a function of temperature. The redox states were achieved by adding 0.2 M NaCl and 0.3 M HNO_3 (reduced state, $Ru(bpy)_3^{2+}$) and 0.3 M $NaBrO_3$ and 0.3 M HNO_3 (oxidized state, $Ru(bpy)_3^{3+}$), respectively.

Dynamic light scattering (DLS) measurements

All sample solutions for DLS measurements were passed through 0.20 μm filters to eliminate dust prior to use. DLS measurements were performed on a DLS/SLS-5000 compact goniometer (ALV, Langen, Germany) coupled with an ALV photon correlator. A 22 mW He–Ne laser (Uniphase Co. Ltd., U.S.A.) was used as the light source. The wavelength of the light in vacuum was λ = 632.8 nm. Although the laser power was relatively weak, the output photon-count rate was enhanced approximately 50 times compared to the conventional pinhole system. This was achieved by employing a set of static and dynamic enhancers (devices to enhance the photon counting rate) and a high quantum efficient avalanche photodiode detection system. Experiments were performed at different temperatures (15 °C–32 °C) within an accuracy of ±0.1 °C, and the intensity autocorrelation functions $g_2(q, t)$ were recorded at a scattering angle of 90° at each temperature for 120 s. Samples were equilibrated at constant temperature for at least 30 min before data collection. In the case of the study involving the BZ oscillation reaction, both autocorrelation function and time average scattering intensities were collected every 2 s.

For solutions containing monodisperse particles, the electric field correlation function $g_1(q, t)$ displays a single exponential decay.

$$g_1(q, t) = \exp(-\Gamma t) = \exp(-D_0 q^2 t) \qquad (1)$$

where q is the scattering vector ($q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent, λ is the wavelength of the light in vacuum, and θ is the scattering angle), Γ is the decay rate, and D_0 is the translational diffusion coefficient. The recorded intensity correlation function $g_2(q, t)$ is calculated from the Siegert relation.[S1] The hydrodynamic radius, R_h, can be estimated with knowledge of the solvent viscosity, η, by using the Stokes-Einstein equation,

$$R_h = (k_b T)/6\pi\eta D_0 \qquad (2)$$

For solutions that contain a unimodal distribution of polydisperse particles, $g_1(q, t)$ can be analyzed using the method of cumulants:[S2]

$$g_1(q, t) = A\exp(-\Gamma t)(1 + (1/2!)\mu_2 t^2 - (1/3!)\mu_3 t^3)$$

where Γ is the mean decay rate of μ_2/Γ^2 and characterizes the width of the distribution. In this work, the apparent R_h, was calculated using equation (2) by substituting the $D = \Gamma/q^2$ of 0.1 wt% solutions for D_0. The distribution of R_h was also examined by applying the inverse Laplace transformation to $g_1(q, t)$ with the well established CONTIN program, and by fitting to a sum of two exponentials.

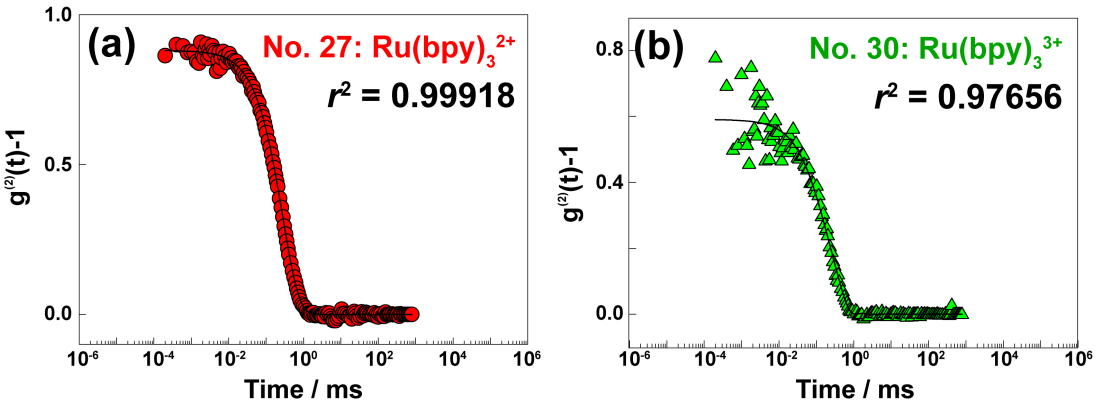


Fig. S3 Representative autocorrelation functions for the measurements obtained at (a) reduced state (plot number 27) and at (b) oxidized state (plot number 30) are also shown. The BZ substrates for the measurements in the feed are as follows: [$NaBrO_3$] = 0.2 M, [HNO_3] = 0.3 M, and [MA] = 0.3 M.

References and Notes

S1. Dynamic light scattering: The method and some applications; W. Brown, Ed.; Clarendon Press: Oxford, England, 1993.

S2. D. E. Koppel, *J. Chem. Phys.*, 1972, **57**, 4814.