Synthesis and Strong Photooxidation Power of a Supramolecular Hybrid comprising a Polyoxometalate and Ru(II) Polypyridyl Complex with Zinc(II)

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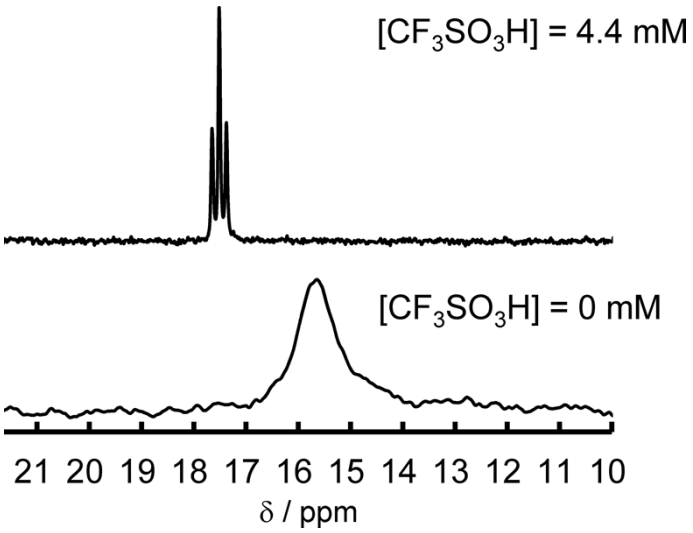

Fig. S1 ^{31}P NMR spectra in dmso-d_6 of **RuP** (4.4 mM) in the absence and presence of trifluoromethanesulfonic acid (160 MHz).

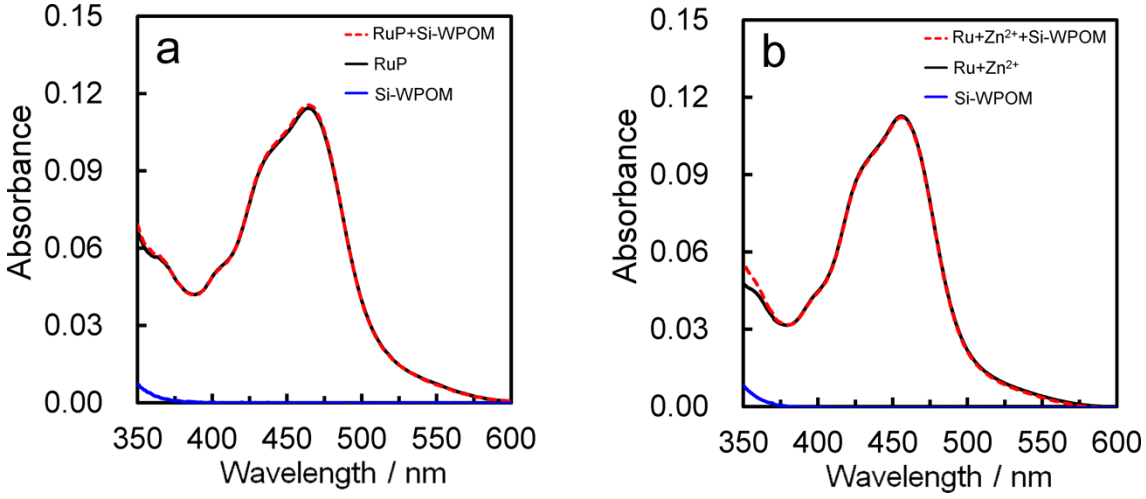

Fig. S2 UV‑Vis absorption spectra of DMSO solutions containing (a) **RuP** (7 μM) plus **Si-WPOM** (3.5 μM), **RuP** (7 μM) and **Si-WPOM**; (b) **Ru** (7 μM) plus Zn^{2+} (3.5 μM) plus **Si-WPOM** (3.5 μM), **Ru** (7 μM) plus Zn^{2+} (3.5 μM) and **Si-WPOM** (7 μM).

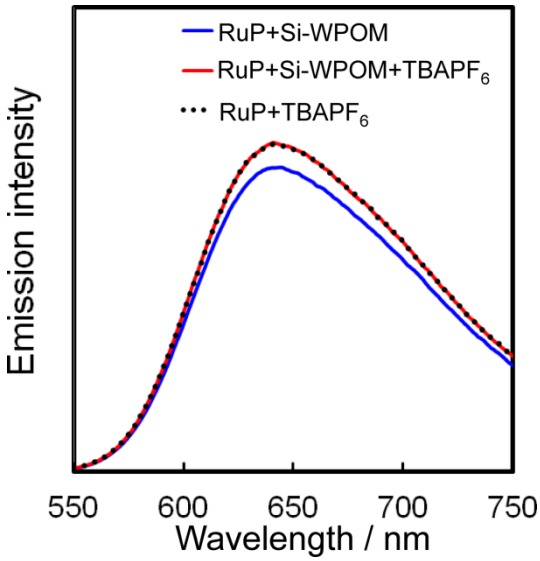

Fig. S3 Emission spectra from DMSO solutions containing **RuP** (7 μM) and **Si-WPOM** (7 μM) in the absence and presence of $TBAPF_6$ (10 mM) and **RuP** (7 μM) and $TBAPF_6$ (10 mM) obtained at 25°C under Ar with λ_{ex} = 510 nm. The emission intensities were normalized with the absorbance at the excitation wavelength.

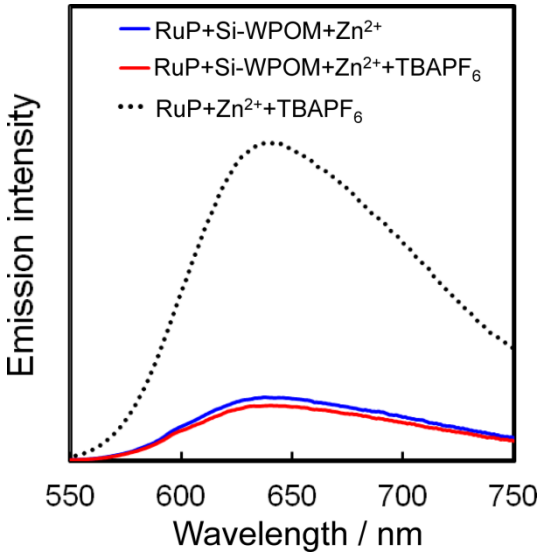

Fig. S4 Emission spectra from DMSO solutions containing **RuP** (7 μM), Zn^{2+} (3.5 μM) and **Si-WPOM** (7 μM) in the absence and presence of $TBAPF_6$ (10 mM) and Ru (7 μM), Zn^{2+} (3.5 μM) and $TBAPF_6$ (10 mM) obtained at 25°C under Ar with λ_{ex} = 510 nm. The emission intensities were normalized with the absorbance at the excitation wavelength.

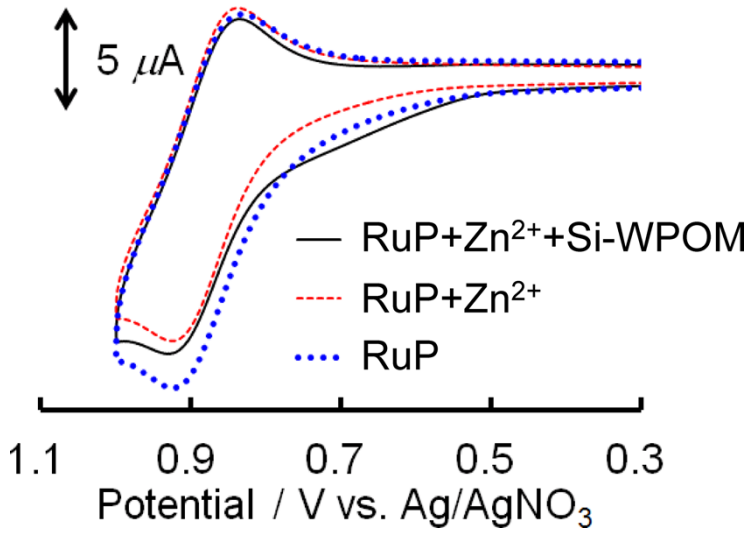

Fig. S5 Cyclic voltammograms of **RuP** (0.5 mM), Zn^{2+} (0.025 mM) and **Si-WPOM** (0.25 mM); **RuP** (0.5 mM) and Zn^{2+} (0.025 mM); and **RuP** (0.5 mM) obtained in DMSO solutions containing $TBAPF_6$ (0.1 mol dm^{-3}) using a glassy carbon working electrode, a Pt counter electrode and a $Ag/AgNO_3$ (0.01 mol dm^{-3}) reference electrode. The scan rate was 200 mV s^{-1}.

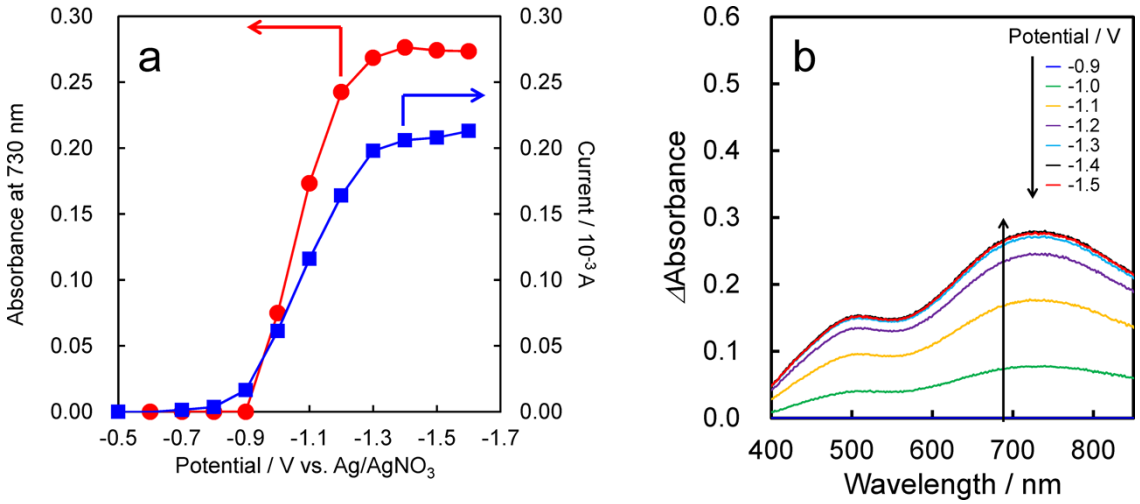

Fig. S6 Absorbance at 730 nm (red line) and the current (blue line) during flow electrolysis of a DMSO solution containing **Si-WPOM** (1.5 mM) and tetrabutylammonium hexafluorophosphate (0.1 M) using a carbon felt working electrode (surface area = 1900 cm^{-2}) in a Vycor glass separator, a $Ag/AgNO_3$ (0.01 M) reference electrode and a Pt counter electrode located outside the separator (VF-2 flow electrolysis cell, EC-FRONTIER Inc.). The flow rate of the solution was 0.11 mL min^{-1}, and the optical pass length was 1.5 mm. The number of electrons accepted by one molecule of **Si-WPOM** was calculated using Eq. S1:

$$N = \frac{i}{CFv} \quad \text{(S1)}$$

where i is the current (A), C is the **Si-WPOM** concentration (1.0 mM), F is the Faraday constant, and v is the flow rate (0.11 mL min^{-1}). The value of N = 1.3 was obtained at the applied voltage of −1.4 V.

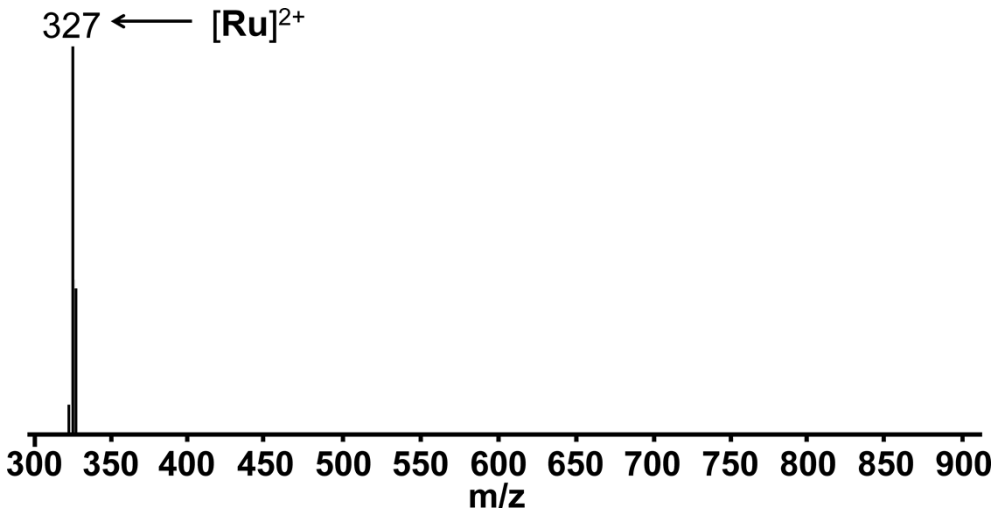

Fig. S7 ESI-MS spectra (eluent; CH_3CN) of **Ru** (4.4 mM) and Zn^{2+} (2.2 mM). Analyzed samples were disolved in DMSO.

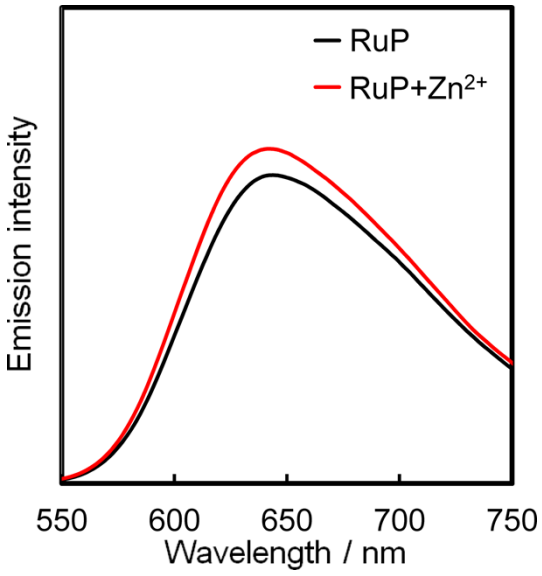

Fig. S8 Emission spectra of DMSO solutions of **RuP** (7 μM) in the absence and presence of Zn^{2+} (3.5 μM) obtained at 25°C in DMSO under Ar. The excitation wavelength was 510 nm, and the emission intensities were normalized to the absorbance at the excitation wavelength.

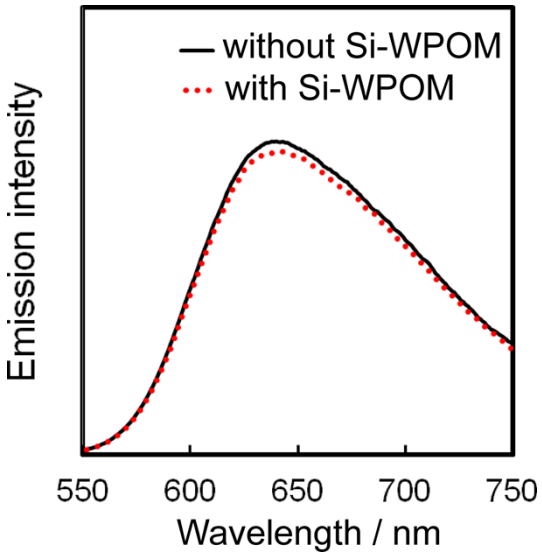

Fig. S9 Emission spectra of DMSO solutions containing $TBAPF_6$ (100 mM), **RuP** (7 μM) and Zn^{2+} (7 μM) obtained in the presence and absence of **Si-WPOM** (7 μM) at 25°C under Ar. The excitation wavelength was 510 nm. The emission intensities were normalized to the absorbance at the excitation wavelength.

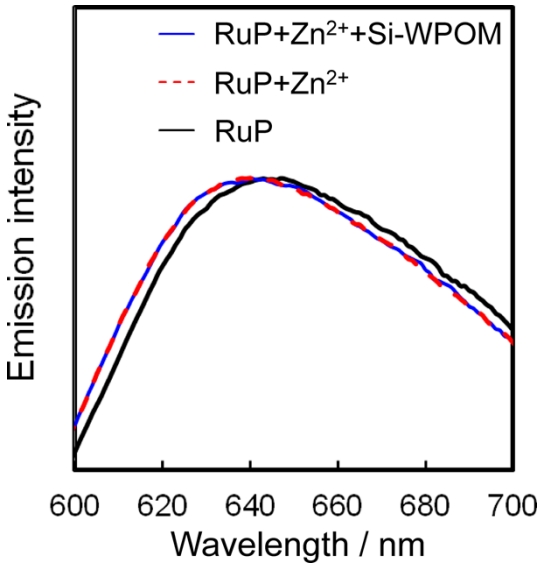

Fig. S10 Emission spectra of DMSO solutions of $TBAPF_6$ (100 mM) containing **RuP** (7 μM), Zn^{2+} (7 μM) and **Si-WPOM** (7 μM); **RuP** (7 μM) and Zn^{2+} (3.5 μM); and **RuP** (7 μM) obtained at 25°C under Ar. The excitation wavelength was 510 nm. The emission intensities were normalized at their peaks.

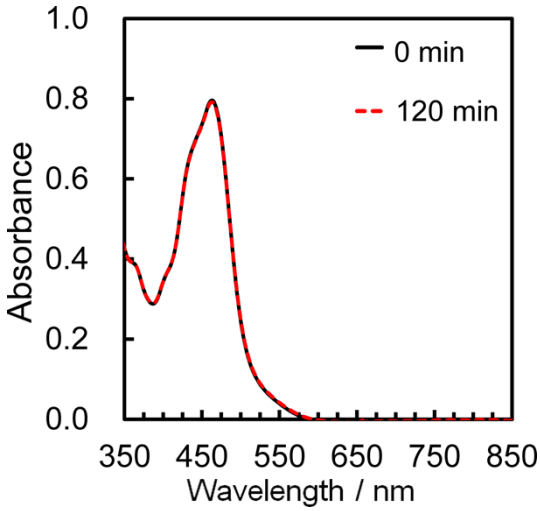

Fig. S11 Steady-state analysis of the absorption spectrum before and after irradiation for 120 min (λ_{ex} = 480 nm) in an Ar-saturated DMSO solution containinig **RuP** (0.05 mM), Zn^{2+} (0.025 mM) and DEOA (2 M).