

Supporting Information

A Bis-Bipyridine Osmium(II) Complex with an N,S-Chelating 2-Aminoethanesulfinate: Photoinduced Conversion of Amine to Imine Donor Group by Air Oxidation

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Experimental Section

(a) [Os(aesi)(bpy)₂]₂PF₆ ([1]PF₆).

To a solution containing 1.00 g (1.74 mmol) of [Os(bpy)₂Cl₂]₂·2H₂O in 300 mL of 1:1 ethanol/water was added 0.15 g (1.97 mmol) of Haet and 0.08 g (1.9 mmol) of NaOH. The mixture was refluxed for 1 h under a nitrogen atmosphere, followed by allowing to stand at room temperature for 1 h in air, which gave a dark brown solution. This solution was concentrated to dryness with a rotary evaporator. The residue was dissolved in a small amount of water and then chromatographed on an SP-Sephadex C-25 column (K⁺ form, φ 3.5 cm × 22 cm). After the column had been washed with water, a brown band was eluted with a 0.05 M aqueous solution of KCl. The brown eluate was concentrated to dryness with a rotary evaporator, and 300 mL of ethanol was added to it. After removal of deposited KCl by filtration, a 0.3 M aqueous solution of KPF₆ (10 mL) was added to the filtrate. The filtrate was concentrated to dryness with a rotary evaporator, and 200 mL of ethanol was added to it. After removal of deposited KPF₆ by filtration, diethyl ether was slowly diffused into the filtrate. The resulting dark green powder ([1]PF₆·3H₂O) was collected by filtration. Yield 0.57 g (40%).

Anal. Calcd for [1]PF₆·3H₂O: C, 32.63; H, 3.49; N, 8.65%. Found: C, 32.51; H, 3.21; N, 8.44%. UV-vis [H₂O, λ_{max}, nm (ε, 10³ mol⁻¹ dm³ cm⁻¹): 547 (2.17), 414 (7.51), 371 (6.30)^{sh}, 285 (52.4), 244 (19.0). ¹H NMR (400 MHz, D₂O): δ, ppm 10.04 (1H, d, *J* = 5.9 Hz), 8.93 (1H, d, *J* = 5.6 Hz), 8.48 (2H, d, *J* = 7.8 Hz), 8.41 (1H, d, *J* = 8.5 Hz), 8.31 (1H, d, *J* = 8.3 Hz), 8.13 (1H, t, *J* = 7.9 Hz), 7.99 (1H, t, *J* = 7.9 Hz), 7.88 (1H, t, *J* = 7.8 Hz), 7.81 (1H, d, *J* = 5.1 Hz), 7.78 (1H, d, *J* = 7.8 Hz), 7.74-7.72 (2H, m), 7.53 (1H, d, *J* = 5.9 Hz), 7.24 (1H, t, *J* = 6.7 Hz), 7.12 (1H, t, *J* = 6.7 Hz), 5.43 (1H, s), 3.06-3.03 (3H, m), 2.80 (1H, s). ¹³C NMR (125 MHz, D₂O): δ, ppm 161.42, 160.87, 159.63, 158.20, 154.01, 152.43, 151.83, 150.66, 139.14, 138.31, 137.75, 137.10, 128.33, 128.16, 127.44, 127.32, 124.97, 124.65, 124.16, 123.85, 66.32, 44.12 (CH of bpy); 66.32 (NC of aesi); 44.12 (SC of aesi). IR (KBr disk, cm⁻¹): 1604 (ν_{C=C, C=N}), 1114 (ν_{asym S=O}), 1006 (ν_{sym S=O}), 844 (PF₆⁻), 766 (δ_{C=C, C=N}), 558 (PF₆⁻).

(b) [Os(iesi)(bpy)₂]₂PF₆ ([2]PF₆).

A solution containing 0.25 g (0.30 mmol) of [1]PF₆·3H₂O in 200 mL of water was irradiated at 0 °C for 45 h using a high pressure Hg lamp (Riko UVL-100HA, 100W). The reaction solution was placed in a Pyrex tube in a distance of 2.5 cm from the lamp without a cut filter in a temperature-controlled bath containing an ethanol/water solution as the cooling medium. After irradiation, the solution was concentrated to dryness with a rotary evaporator. The residue was dissolved into 100 mL of ethanol, and diethyl ether was slowly diffused to the solution, which afforded [2]PF₆·3H₂O as a dark brown powder. Yield 0.15 g (61%).

Anal. Calcd for [2]PF₆·3H₂O: C, 32.71; H, 3.24; N, 8.67%. Found: C, 32.66; H, 3.04; N,

8.66%. UV-vis [H_2O , λ_{max} , nm (ϵ , $10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 520 (2.51)^{sh}, 394 (7.91), 284 (45.6), 244 (19.4). ^1H NMR (400 MHz, D_2O): δ , ppm 12.20 (1H, d, $J = 10.7$ Hz), 9.94 (1H, d, $J = 5.9$ Hz), 8.60 (1H, d, $J = 5.6$ Hz), 8.51 (1H, d, $J = 8.1$ Hz), 8.50 (1H, d, $J = 7.8$ Hz), 8.46 (1H, d, $J = 8.3$ Hz), 8.39 (1H, d, $J = 8.3$ Hz), 8.20 (1H, s), 8.13 (1H, t, $J = 7.9$ Hz), 8.03 (1H, t, $J = 7.9$ Hz), 7.95 (1H, t, $J = 7.9$ Hz), 7.84 (1H, t, $J = 7.9$ Hz), 7.72 (1H, d, $J = 5.9$ Hz), 7.71 (1H, t, $J = 6.6$ Hz), 7.66 (1H, t, $J = 6.7$ Hz), 7.56 (1H, d, $J = 5.6$ Hz), 7.28 (1H, t, $J = 6.6$ Hz), 7.19 (1H, t, $J = 6.7$ Hz), 3.99 (1H, d, $J = 18.8$ Hz), 3.78 (1H, d, $J = 18.8$ Hz). ^{13}C NMR (125 MHz, D_2O): δ , ppm 175.17 (NC of iesi); 160.23, 159.32, 159.03, 158.27, 154.62, 151.61, 150.92, 150.57, 139.49, 138.56, 138.06, 137.89, 128.35, 127.96, 127.53, 127.33, 124.79, 124.55, 124.30, 124.04 (CH of bpy); 74.08 (SC of iesi). IR (KBr disk, cm^{-1}): 1606 ($\nu_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 1140 ($\nu_{\text{asym S}=\text{O}}$), 1014 ($\nu_{\text{sym S}=\text{O}}$), 843 (PF_6^-), 766 ($\delta_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 558 (PF_6^-).

X-ray Structure Determinations.

For $[\mathbf{1}]\text{ClO}_4 \cdot \text{NaClO}_4$, one complex-cation, two sodium cations with the site occupancy of 0.5, and two disordered perchlorate anions were crystallographically independent. All non-hydrogen atoms except for the disordered atoms were refined anisotropically, while the other atoms were refined isotropically. The hydrogen atoms of the amine group, H1 and H2, were found in a difference Fourier map and were refined with [$U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$], while the other H atoms were included in calculated positions. DFIX restraints were used to model a perchlorate anion.

For $[\mathbf{2}]\text{PF}_6 \cdot \text{NH}_4\text{PF}_6$, one complex-cation, one ammonium cation, and two hexafluorophosphate anions were crystallographically independent. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. The hydrogen atom of the imine group, H1, and those of ammonium cations, H21-H24, were found in a difference Fourier map and were refined with [$U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N}_{\text{imine}})$ and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{N}_{\text{ammonium}})$], while the other H atoms were included in calculated positions. SADI restraints were used to model an ammonium cation.

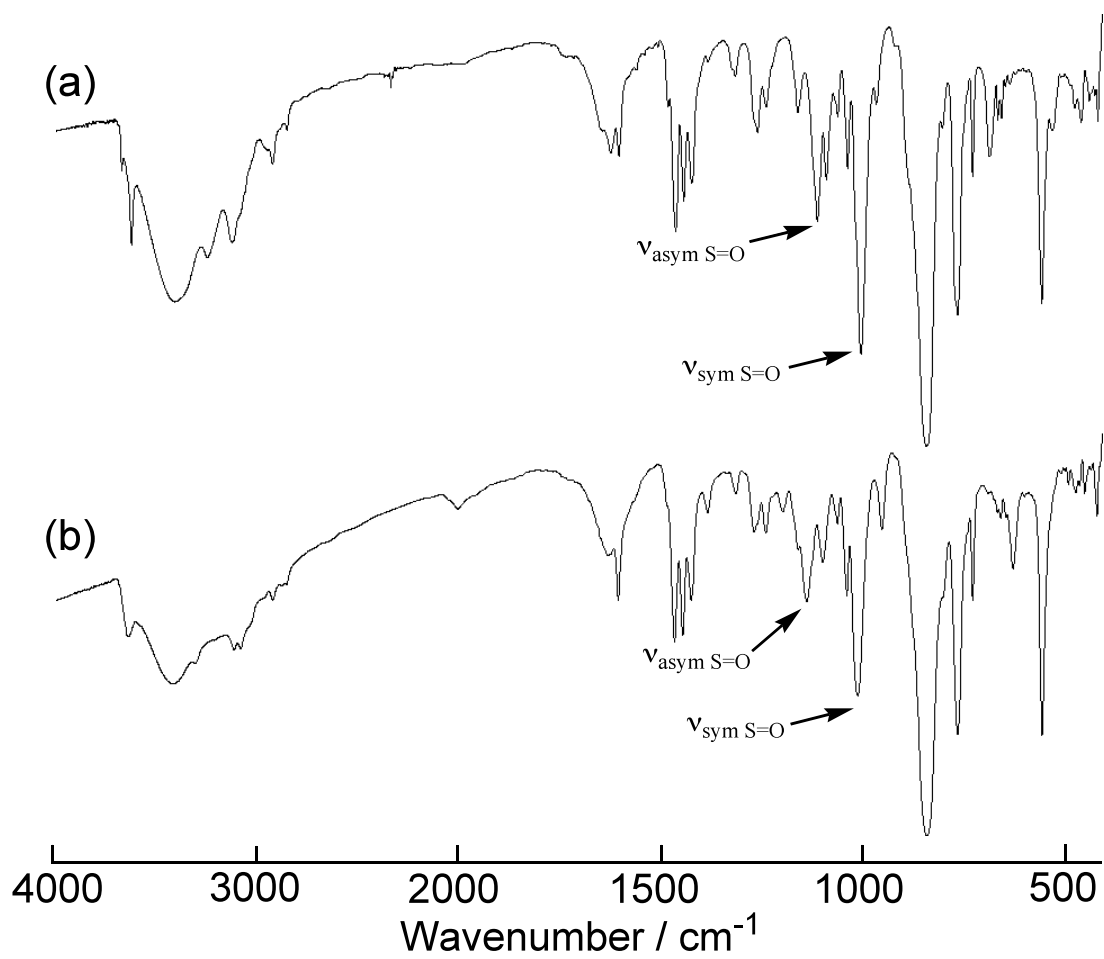


Figure S1. IR spectra of (a) $[1]\text{PF}_6$ and (b) $[2]\text{PF}_6$ (KBr disk).

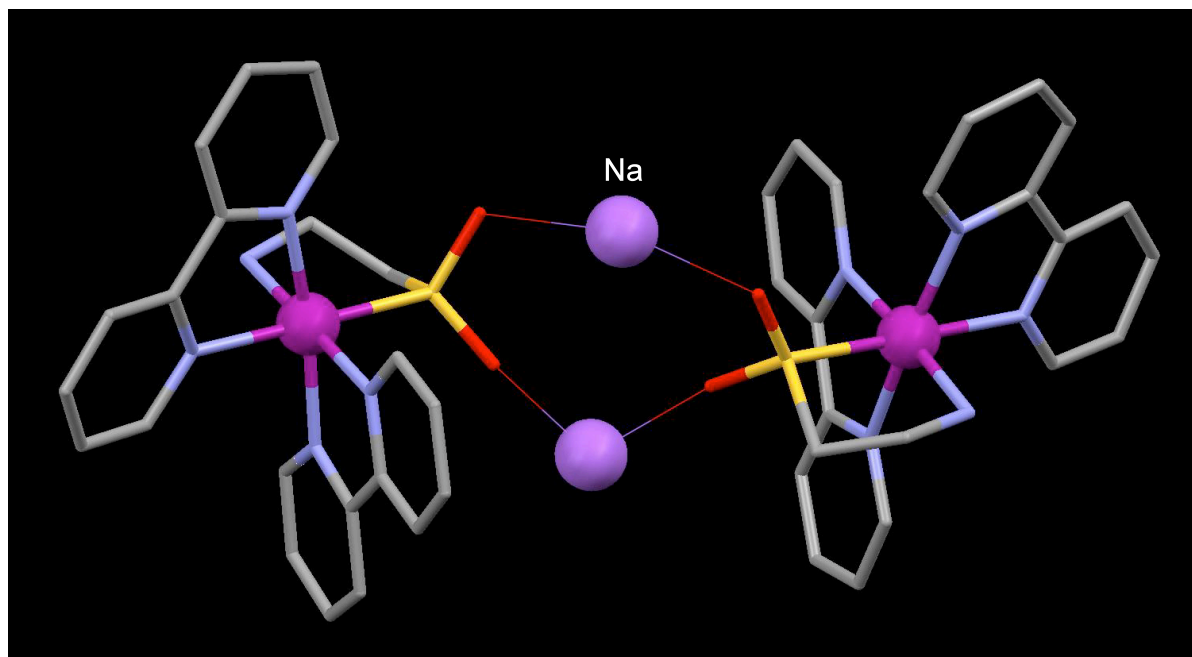


Figure S2. Dimeric structure in $[1]ClO_4 \cdot NaClO_4$ having two bridging Na^+ ions. Hydrogen atoms are omitted for clarity.

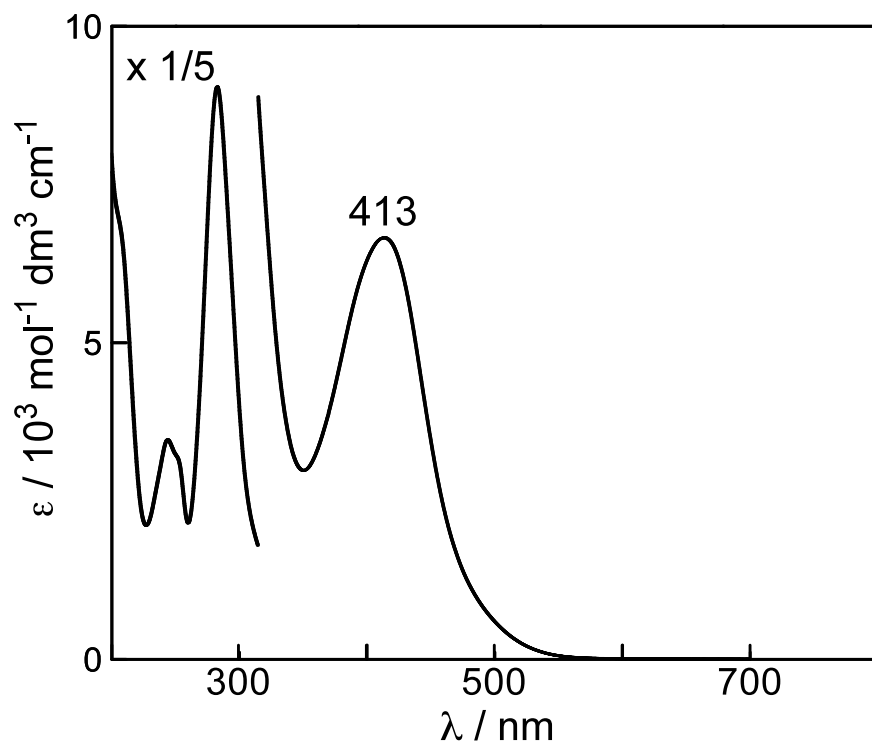


Figure S3. Electronic absorption spectrum of [Ru(aesi)(bpy)₂]PF₆ in H₂O.

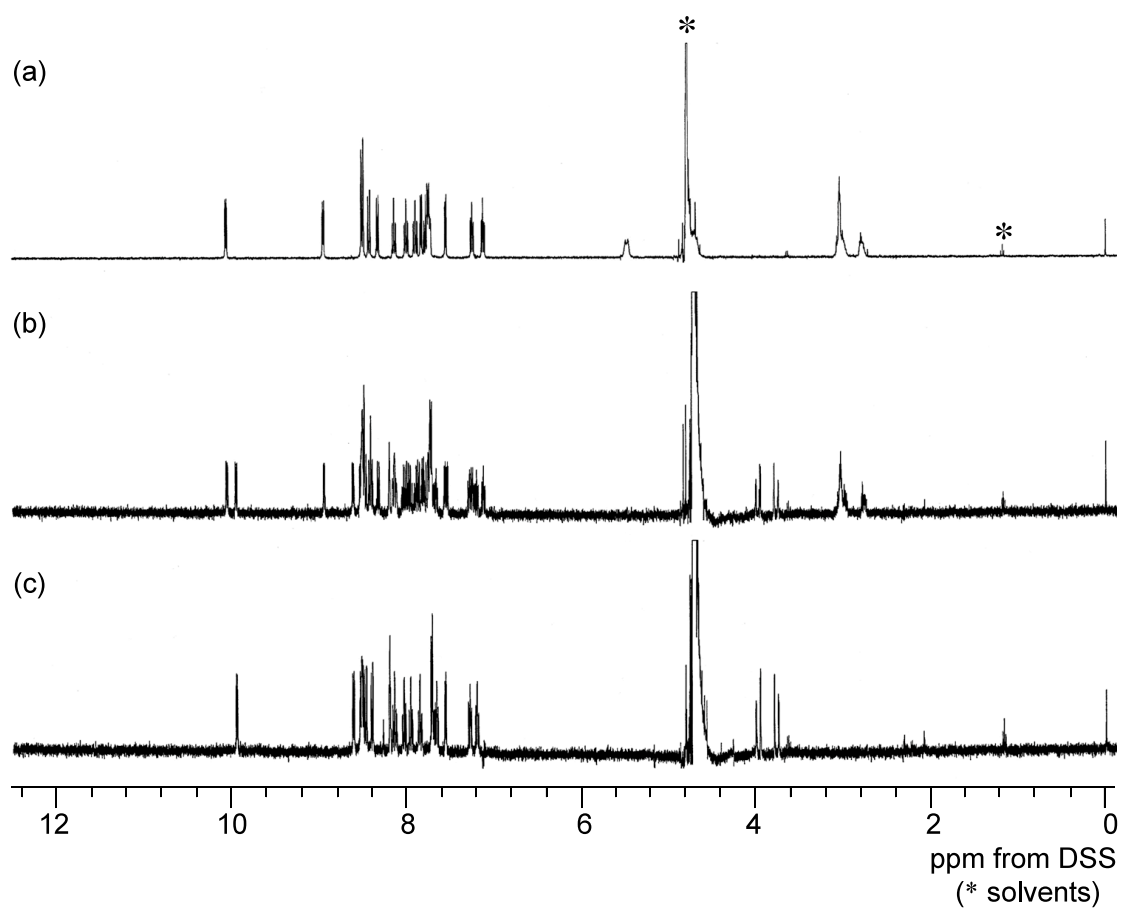


Figure S4. ^1H NMR spectra of $[\mathbf{1}]\text{PF}_6$ at $0\text{ }^\circ\text{C}$ in D_2O under aerobic conditions; (a) 0 hour, (b) after irradiation for 20 hours, and (c) after irradiation for 32 hours. The NMR tube containing the reaction solution was placed in a distance of 2.5 cm from a high pressure Hg lamp (Riko UVL-100HA, 100W).

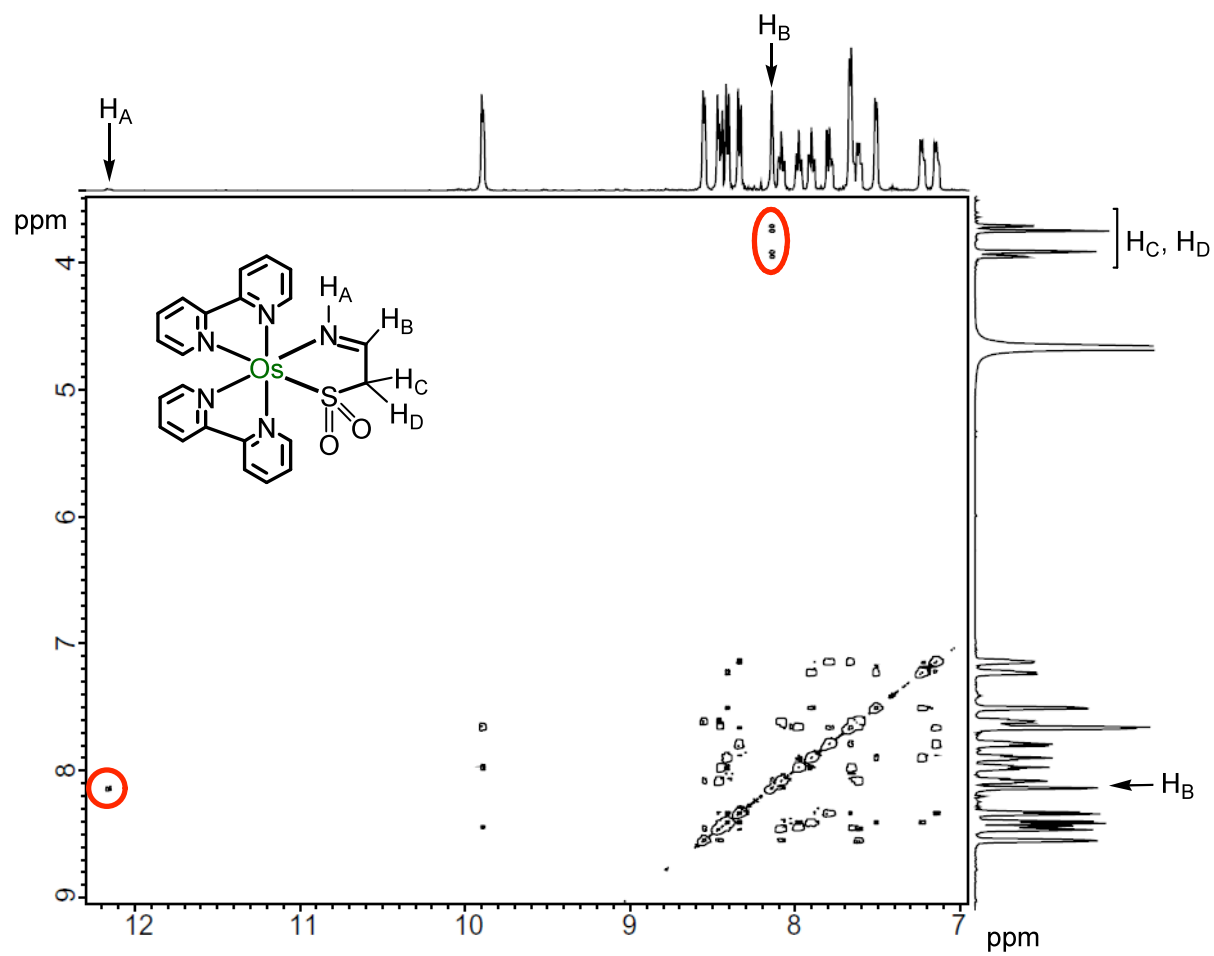


Figure S5. ^1H - ^1H COSY spectrum of $[\mathbf{2}]\text{PF}_6$ in D_2O .

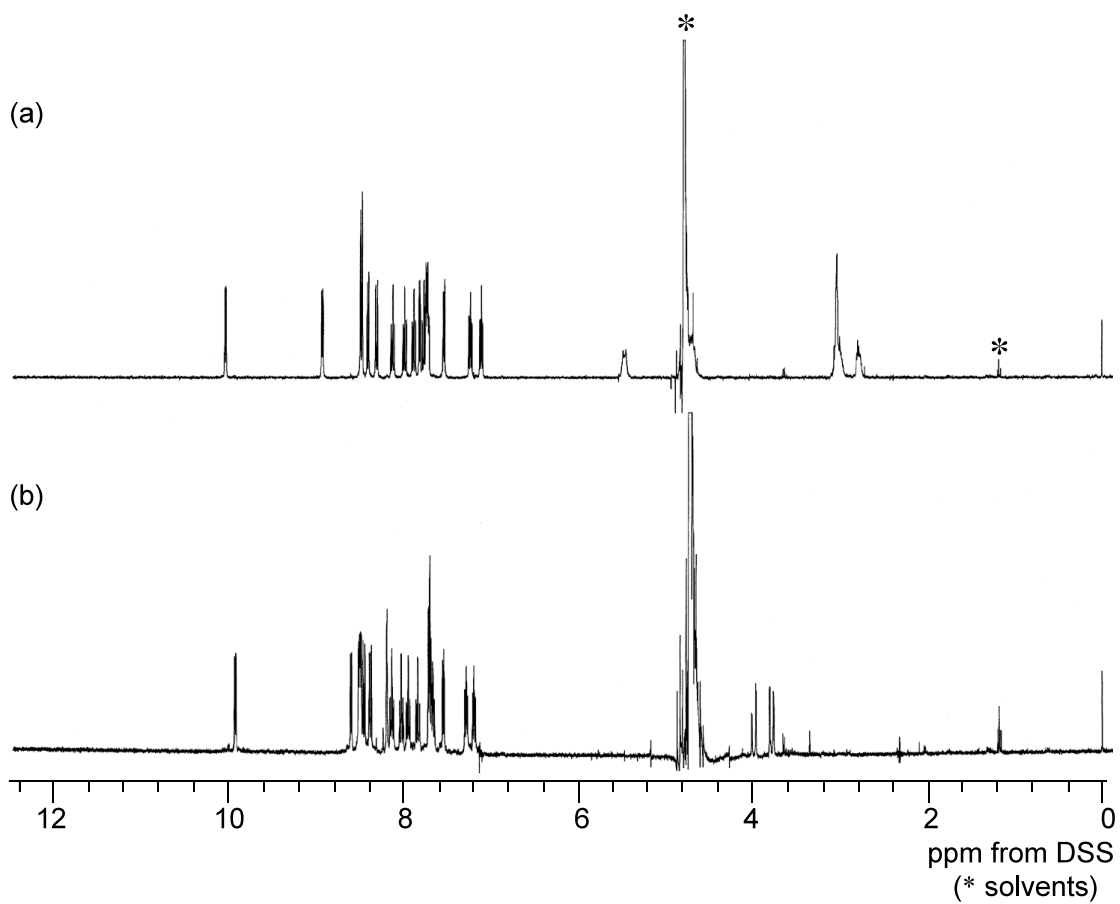


Figure S6. ^1H NMR spectra of $[\mathbf{1}]\text{PF}_6$ in D_2O under aerobic conditions after the addition of 10 molar equiv of AgClO_4 ; (a) 0 h and (b) after 1 h.

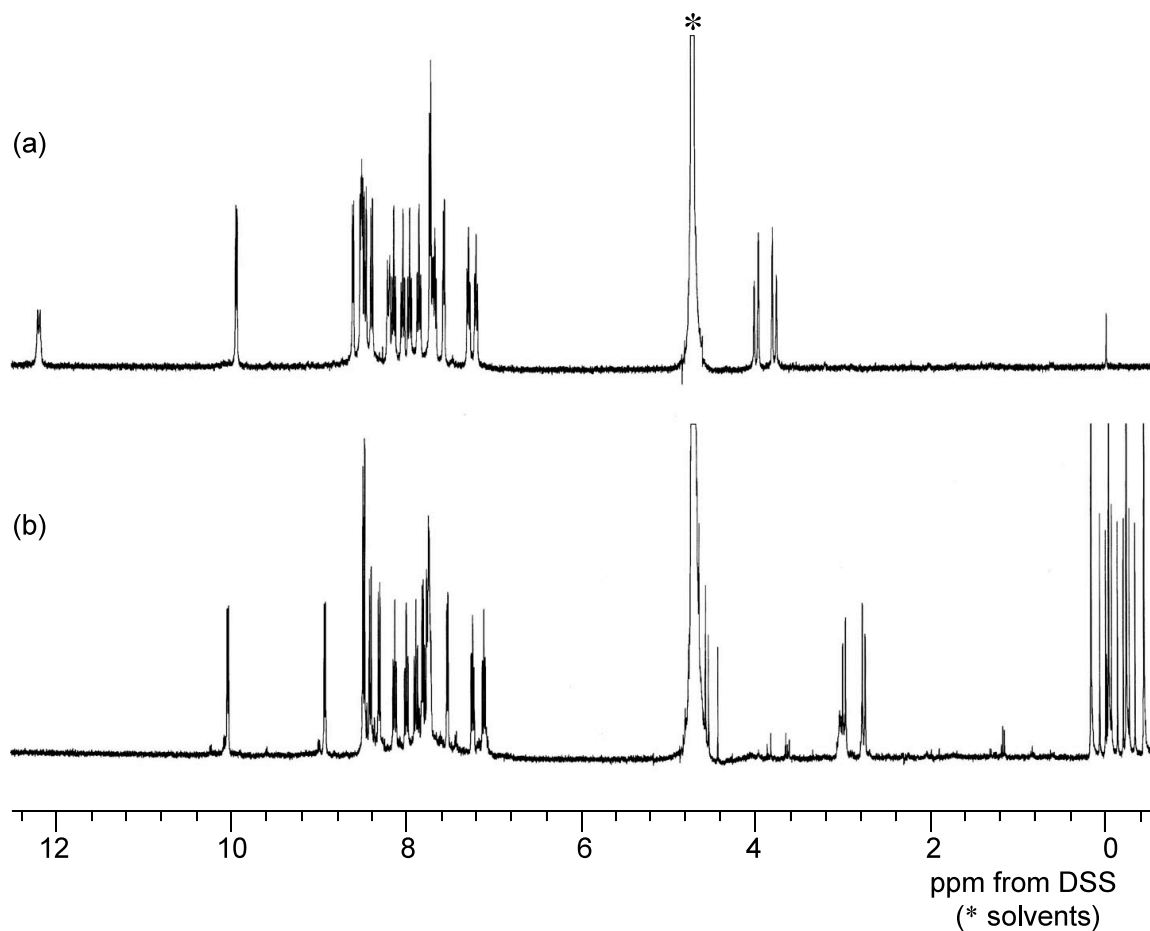


Figure S7. ^1H NMR spectra of $[\mathbf{2}]\text{PF}_6$ in D_2O under aerobic conditions after the addition of 5 molar equiv of NaBH_4 ; (a) 0 h and (b) after 1.5 h.

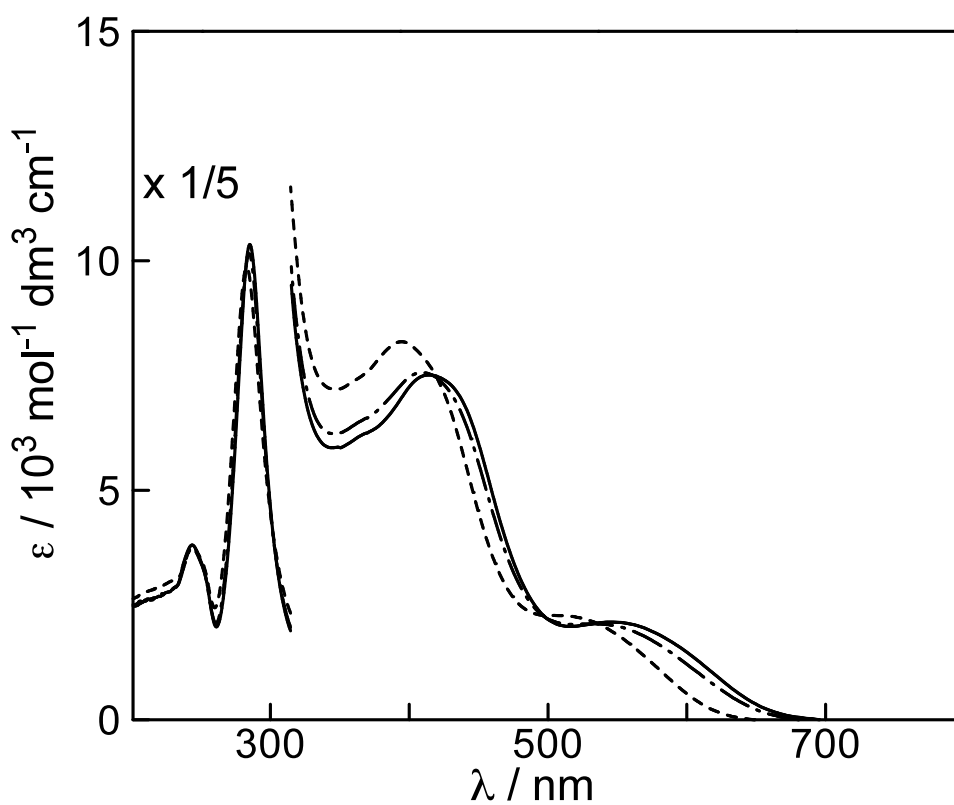


Figure S8. Electronic spectral change of the solution of [1]PF₆ (0.9 mM) in 0.1 M H₂O/NaNO₃ during potentiostatic electrolysis using an optically transparent thin-layer electrode cell; at (a) 0 V (—), (b) +0.30 V (---), and (c) +0.45 V (-----) (vs. Ag/AgCl).

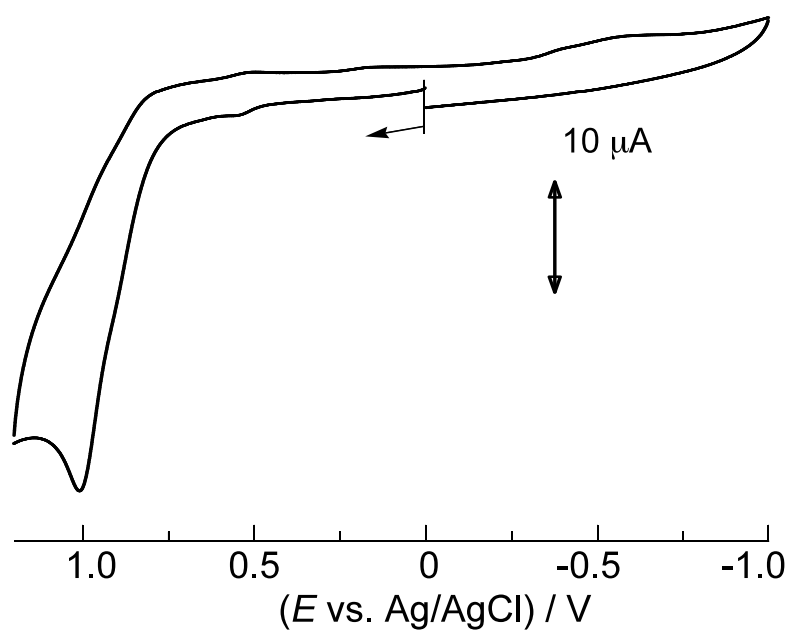


Figure S9. Cyclic voltammogram of $[\text{Ru}(\text{aesi})(\text{bpy})_2]\text{PF}_6$ in a 0.1 M aqueous solution of NaNO_3 at 25 °C with a scan rate of 100 mV s^{-1} . The complex concentration is 1.0 mM.

Table S1. Crystallographic data of [1]ClO₄·NaClO₄ and [2]PF₆·NH₄PF₆.

	[Os(aesi)(bpy) ₂]ClO ₄ ·NaClO ₄ ([1]ClO ₄ ·NaClO ₄)	[Os(iesi)(bpy) ₂]PF ₆ ·NH ₄ PF ₆ ([2]PF ₆ ·NH ₄ PF ₆)
formula	C ₂₂ H ₂₂ Cl ₂ N ₅ NaO ₁₀ OsS	C ₂₂ H ₂₄ F ₁₂ N ₆ O ₂ OsP ₂ S
fw	832.60	916.67
crystal color, habit	black, platelet	red, block
crystal system	Monoclinic	Monoclinic
space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	9.5421(3)	15.9170(3)
<i>b</i> (Å)	16.8001(7)	9.4043(2)
<i>c</i> (Å)	34.0526(10)	20.2031(5)
β (deg)	96.6130(10)	100.5150(10)
<i>V</i> (Å ³)	5422.6(3)	2973.38(11)
<i>Z</i>	8	4
<i>T</i> (K)	200(2)	200(2)
radiation λ (Å)	0.71075	0.71075
ρ_{calcd} (g cm ⁻³)	2.040	2.048
crystal size (mm)	0.40 × 0.20 × 0.01	0.20 × 0.10 × 0.05
μ (Mo <i>K</i> α) (cm ⁻¹)	50.59	45.77
<i>R</i> ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0462	0.0262
<i>R</i> _w ^b (all data)	0.1253	0.0637
<i>GOF</i> (all data)	1.095	1.045

^a $R = \sum |(|F_{\text{ol}}| - |F_{\text{cl}}|) / \sum (|F_{\text{ol}}|)$. ^b $R_w = [\sum w (F_{\text{o}}^2 - F_{\text{c}}^2)^2 / \sum w (F_{\text{o}}^2)^2]^{1/2}$.