Supporting Information

for

Synthesis and Characterization of an Azido-Bridged Dinuclear Ruthenium(II)-Polypyridylamine Complex Forming a Mixed-Valence State

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X-ray Crystallography on $[Ru^{II}(ClO_4)(N4Py)](PF_6)$ and $[Ru^{II}(N4Py)(NCCH_3)](PF_6)_2$.

The crystals of $[Ru^{II}(ClO_4)(N4Py)](PF_6)$ and $[Ru^{II}(N4Py)(NCCH_3)](PF_6)_2$ were mounted on a mounting loop with epoxy resin. All measurements were performed on a Bruker APEXII diffractometer at −153 °C with a graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The data were collected up to 2θ = 55.0°. The structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and the refinement was carried out with full-matrix least-squares on F. All calculations were performed using the Yadokari-XG crystallographic software package,[1] and structure refinements were made by using SHELX-97.[2] Crystallographic data for $[Ru^{II}(ClO_4)(N4Py)](PF_6)$: $C_{23}H_{21}N_5RuClO_4 \cdot PF_6$, FW = 712.94, orange, orthorhombic, space group *Pnma*, cell parameters: a = 9.7449(10) Å, b = 21.936(2) Å, c = 13.4714(14) Å, V = 2888.6(5) Å^3, T = 120(2) K, Z = 4, D_c = 1.639 g cm^{-3}, 15712 reflections measured, 3546 unique (R_{int} = 0.0331), R_1 = 0.0442 ($I > 2\sigma(I)$) and wR_2 = 0.1345 (all the reflections), GOF = 1.113. Crystallographic data for $[Ru^{II}(N4Py)(NCCH_3)](PF_6)_2$: $C_{25}H_{24}N_6Ru \cdot 2PF_6$, FW = 799.51, orange-red, orthorhombic, space group $P\ \bar{1}$, cell parameters: a = 12.529(2) Å, b = 12.734(2) Å, c = 18.789(3) Å, α = 89.976(2)°, β = 89.898(3)°, γ = 89.418(2) Å, V = 2997.4(8) Å^3, T = 120(2) K, Z = 4, D_c = 1.772 g cm^{-3}, 16155 reflections measured, 12077 unique (R_{int} = 0.0555). R_1 = 0.0669 ($I > 2\sigma(I)$) and wR_2 = 0.1489 (all the reflections), GOF = 0.949.

Reference and Notes

(1) Kabuto, C.; Akine, S.; Nemoto, T.; Kwon, E. *J. Cryst. Soc. Jpn.* **2009**, *51*, 218.

(2) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.

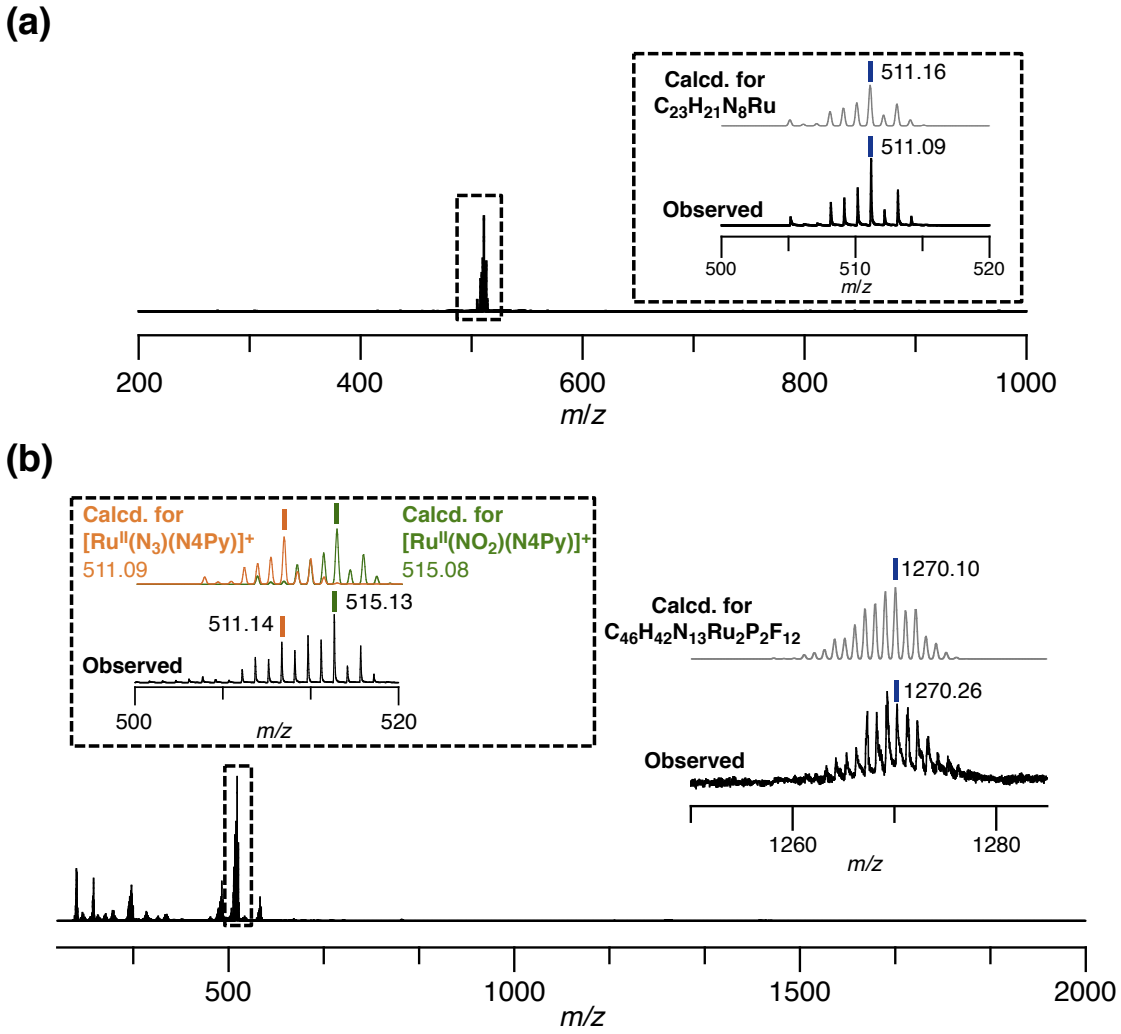

Figure S1. ESI-TOF-MS spectra of **1** (a) in MeOH and **2** (b) in acetone. Inset: magnified spectra of the experimental (above), and the simulated (below).

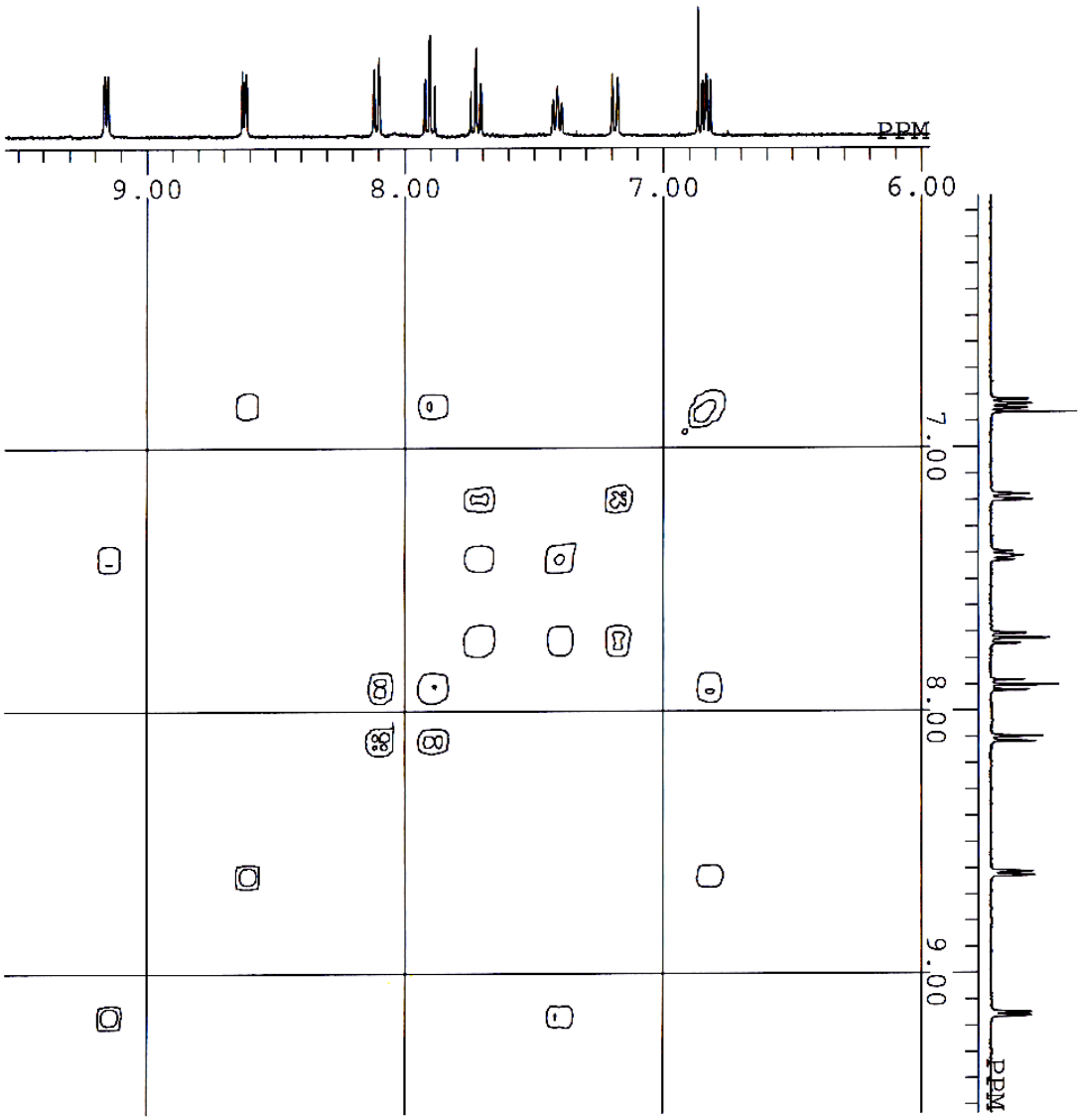

Figure S2. ^{1}H-^{1}H COSY 2D spectrum of **2** in acetone-d_6.

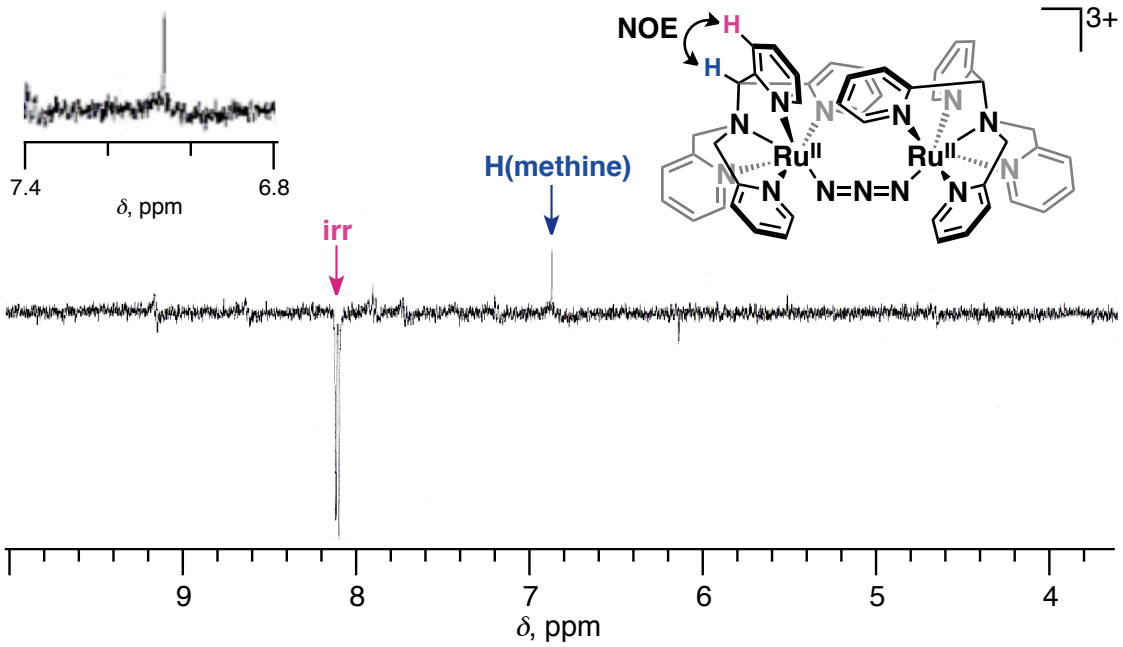

Figure S3. Differential 1-D NOE spectrum of **2** in acetone-d_6.

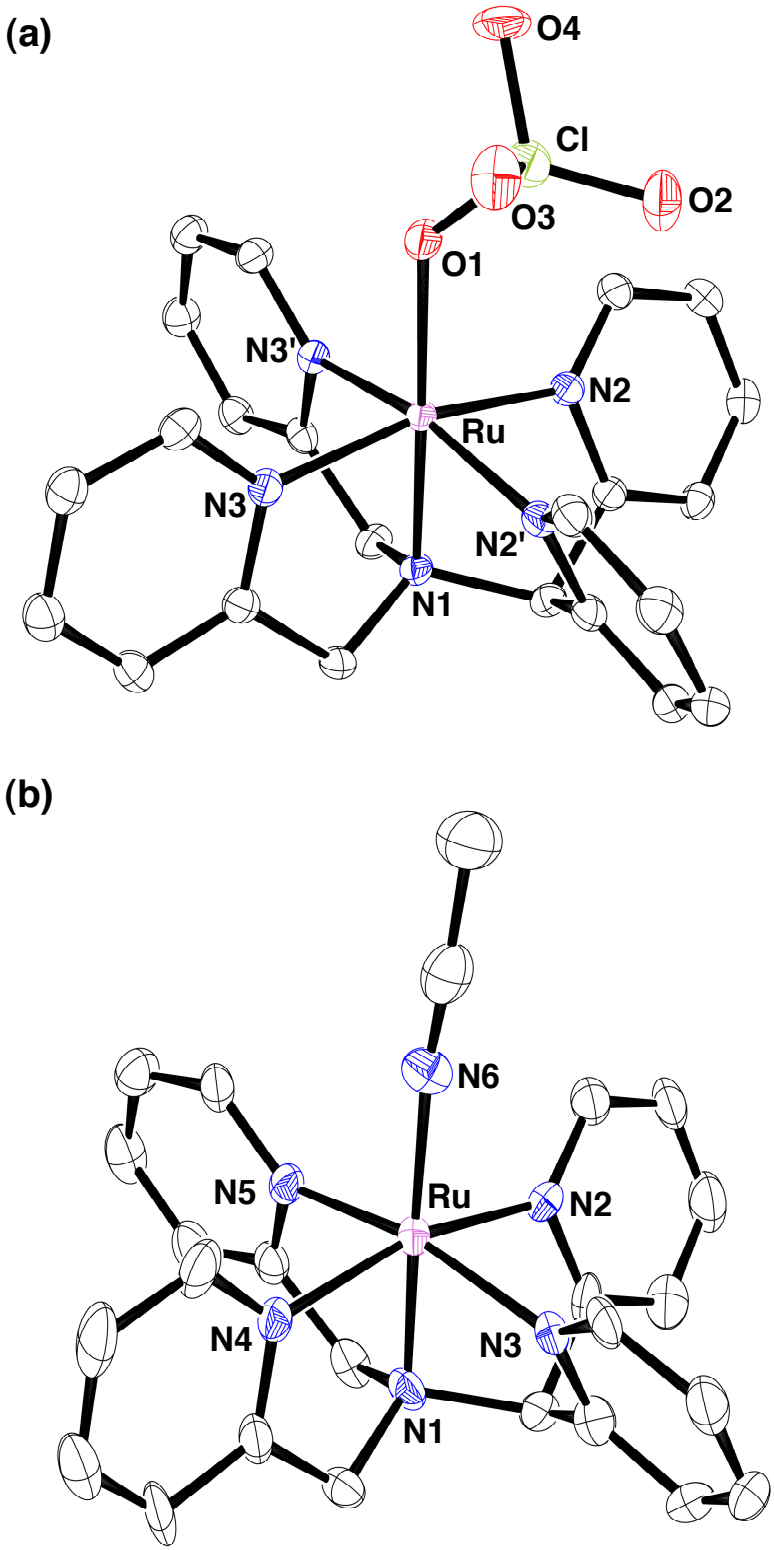

Figure S4. ORTEP drawings of crystal structures of the cation parts of $[Ru^{II}(ClO_4)(N4Py)](PF_6)$ (a) and $[Ru^{II}(N4Py)(NCCH_3)](PF_6)_2$ (b).

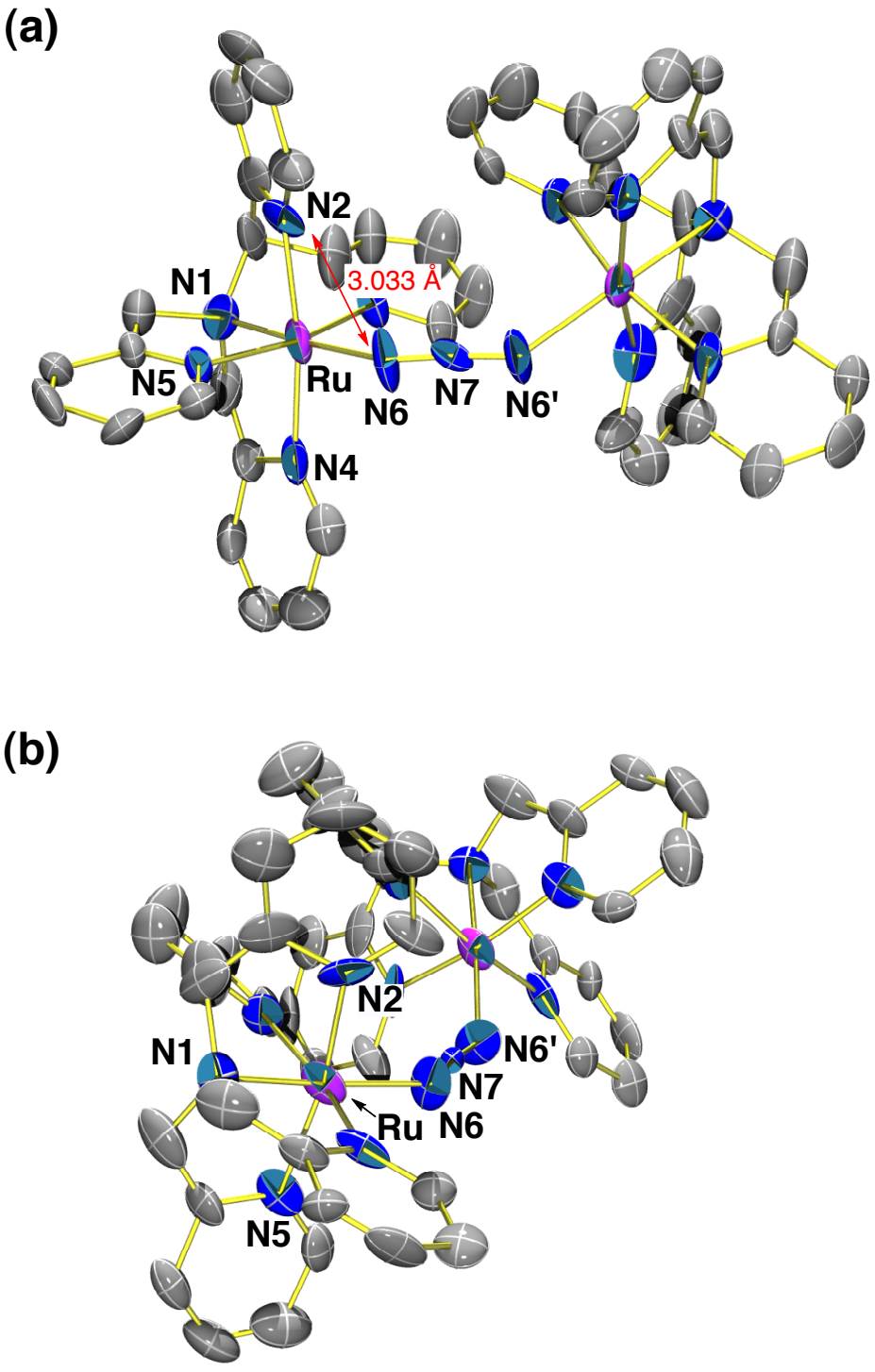

Figure S5. ORTEP drawings of the crystal structure of the cation part of **2** to show the spatial locations of the μ-azido ligand and the N2-pyridine rings of the N4Py ligand: (a) A side view; (b) a top view.

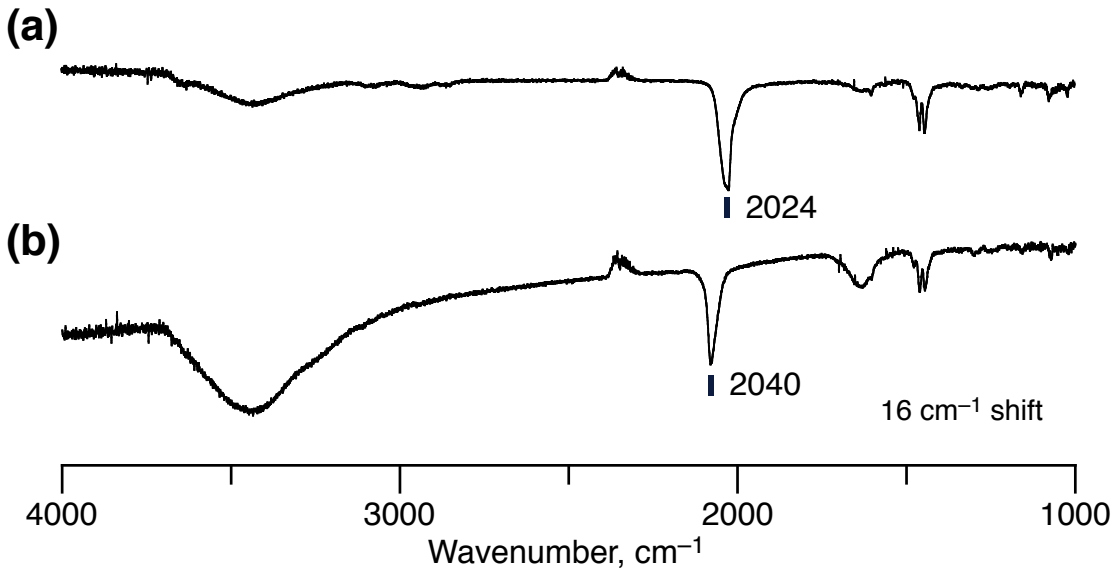

Figure S6. IR spectra of **1** (a) and **2** (b) in KBr pellet.

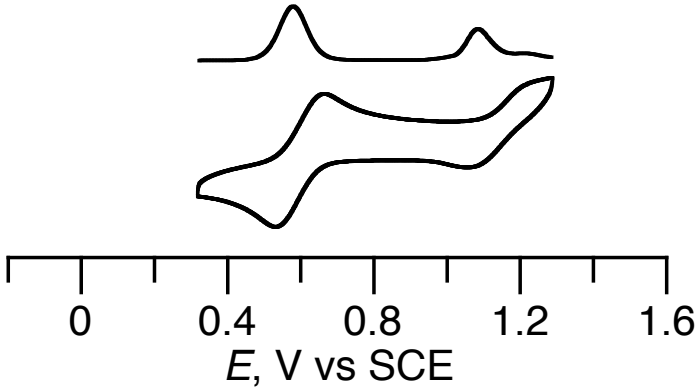

Figure S7. Cyclic (below) and differential pulse (above) voltammograms of **2** in CH_3CN in the presence of $[(n\text{-}Bu)_4N](PF_6)$ as an electrolyte at –40 ºC. Scan rate: 5 V s^{-1}.

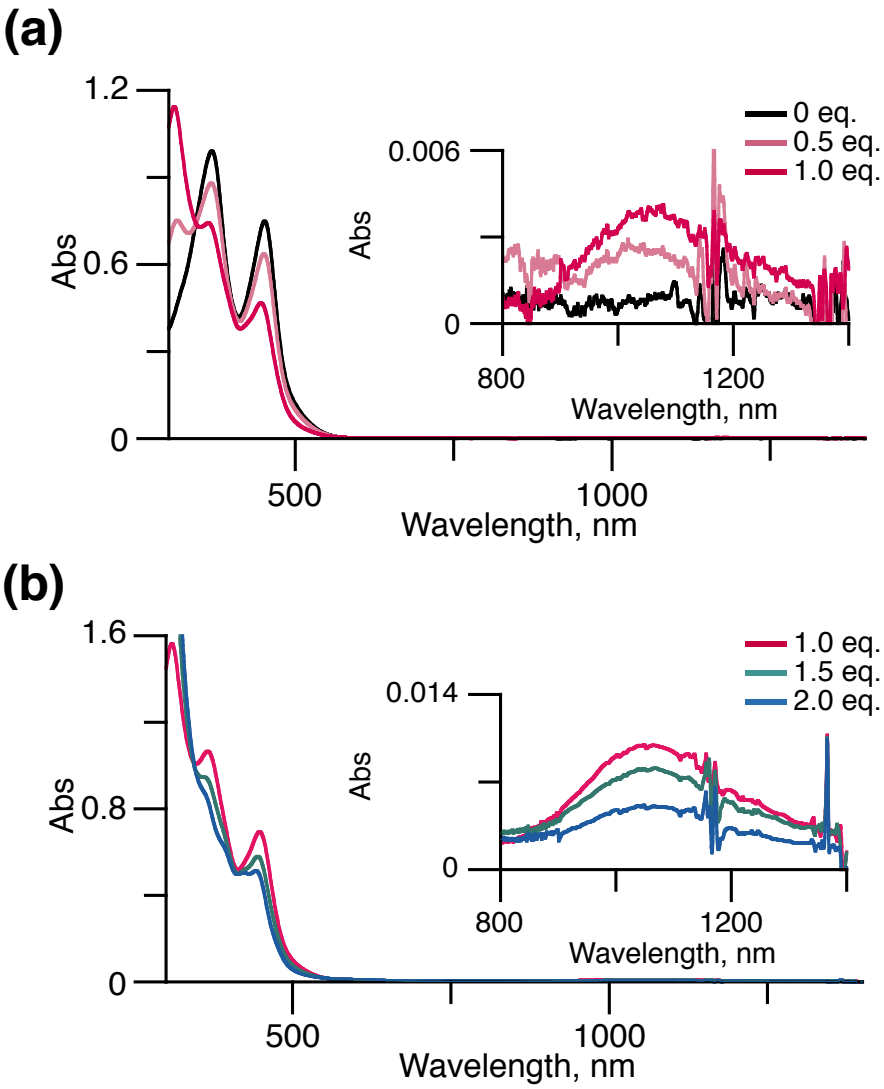

Figure S8. UV-Vis spectral changes upon titration of **2** with TBAH 0 – 1 eq (a) and 1 – 2 eq (b) in CH_3CN at room temperature. The experiments using 0 – 1 eq of TBAH and those using 1 – 2 eq of the oxidant were performed separately due to the instability of the oxidant in CH_3CN.

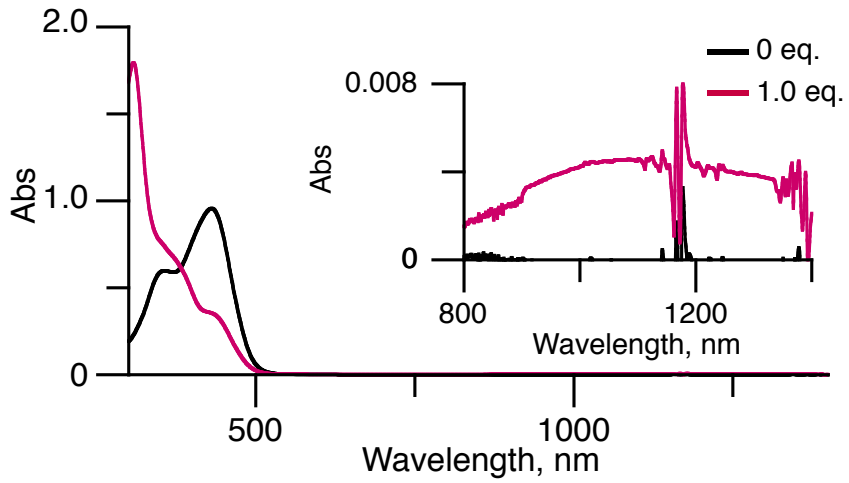

Figure S9. UV-Vis spectra of **8** (black line) and 1e$^-$-oxidized form of **8** (purple line) in CH_3CN at room temperature. The 1e$^-$-oxidized form of **8** was formed *in situ* by addition of 1 equiv of TBAH.

Table S1. Comparison of Bond Lengths (Å) among Related Ru(II)-N4Py Complexes.

	1		**2**	$[RuCl(N4Py)]ClO_4$[a]	$[Ru(ClO_4)(N4Py)]PF_6$	$[Ru(N4Py)(NCCH_3)](PF_6)_2$		**3**[b]
Ru-N1	2.039(3)	2.030(3)	2.022(10)	2.036(3)	2.009(4)	2.012(6)	2.016(6)	1.968(5)
Ru-N2	2.058(3)	2.049(3)	2.011(10)	2.059(2)	2.050(3)	2.059(6)	2.048(6)	2.057(4)
Ru-N3	2.043(3)	2.058(3)	2.067(8)	2.046(3)	—	2.061(6)	2.066(6)	2.053(5)
Ru-N4	2.053(3)	2.051(3)	2.056(10)	2.061(2)	2.055(3)	2.053(6)	2.056(6)	2.061(5)
Ru-N5	2.065(3)	2.046(3)	2.057(8)	2.063(3)	—	2.047(6)	2.060(6)	2.060(5)
Ru-N6	2.158(3)	2.122(3)	2.121(10)	2.416(1) (RuCl)	2.167(4) (RuO)	2.027(6) (RuN)	2.025(7) (RuN)	2.172(5) (RuO)
N6-N7	1.138(5)	1.181(4)	1.103(9)	—	—	—	—	
N7-N8	1.172(6)	1.171(5)	—	—	—	—	—	

[a] Kojima, T.; Weber, D. M.; Choma, C. T. *Acta Cryst.* **2005**, *E61*, m226. [b] Ohzu, S.; Ishizuka, T.; Hirai, Y.; Jiang, H.; Sakaguchi, M.; Ogura, T.; Fukuzumi, S.; Kojima, T. *Chem. Sci.* **2012**, *3*, 3421.