Supporting Information

Electrocatalytic properties of a novel ruthenium(II) terpyridine-based complex towards CO_2 reduction

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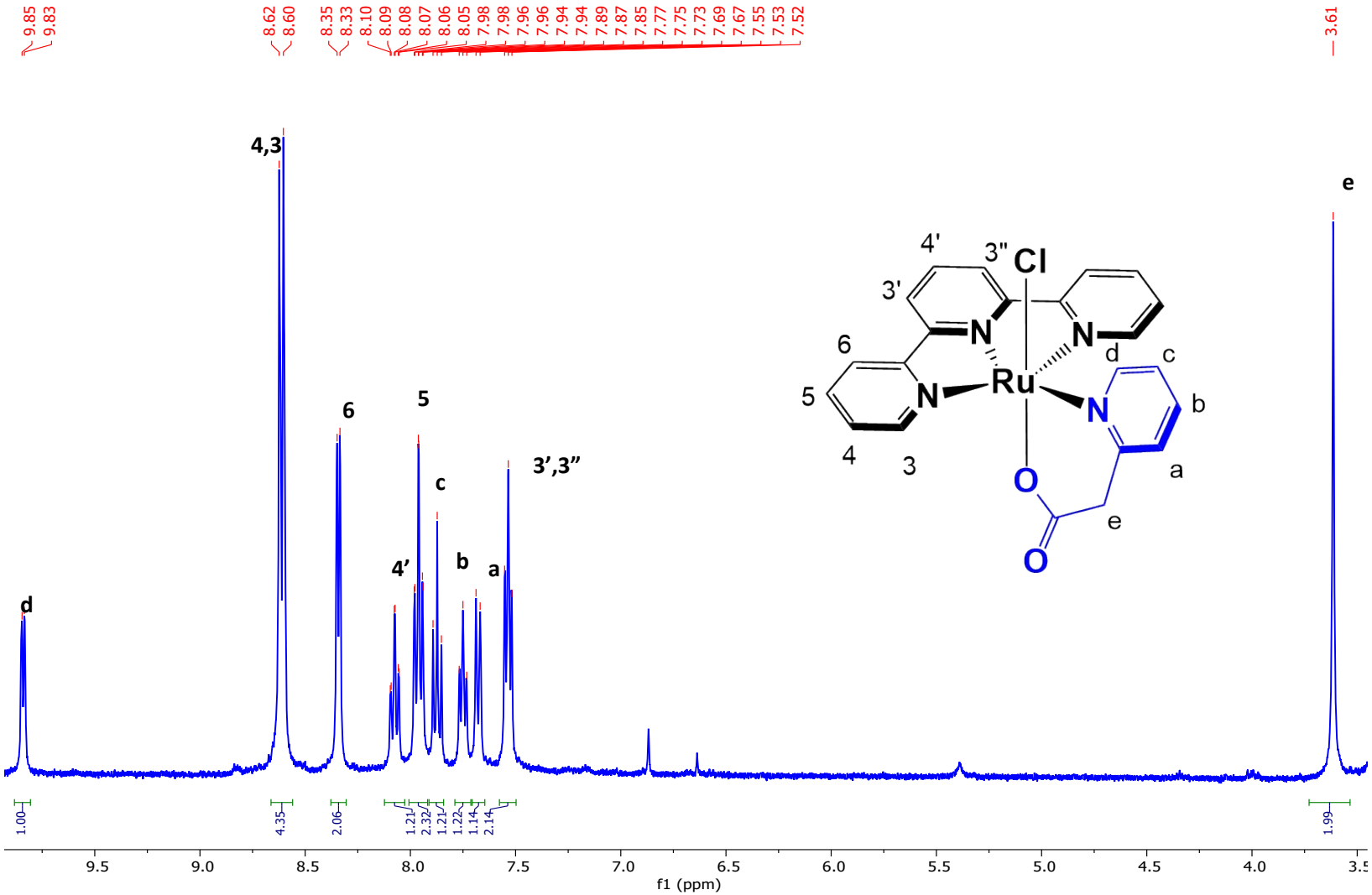

Figure S1. ^{1}H NMR spectrum in DMSO-d_6 of [RuCl(trpy)(acpy)], 298 K and 400 MHz.

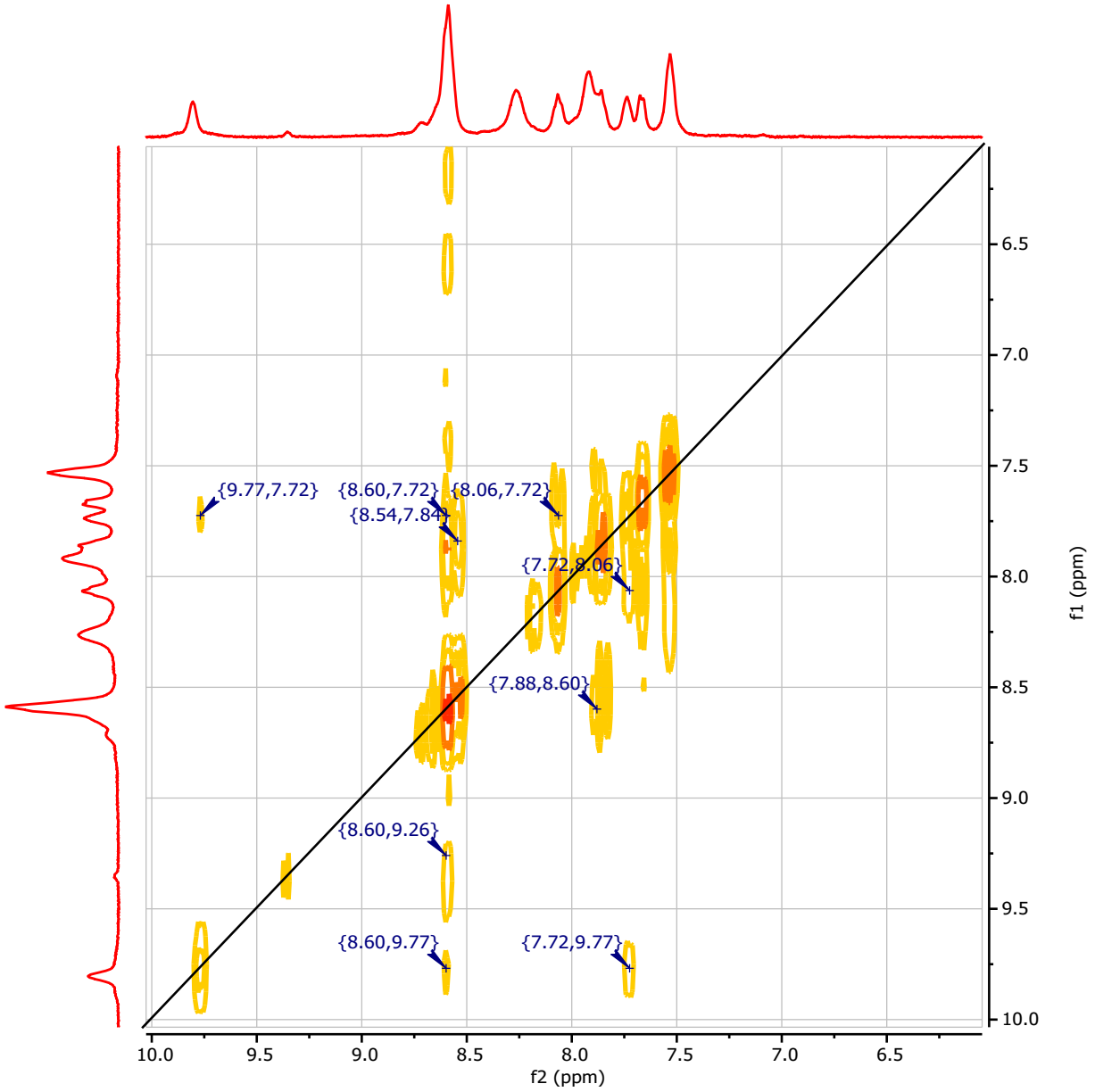

Figure S2. H-H Cosy spectrum in DMSO-d_6 of [RuCl(trpy)(acpy)], 298 K and 400 MHz.

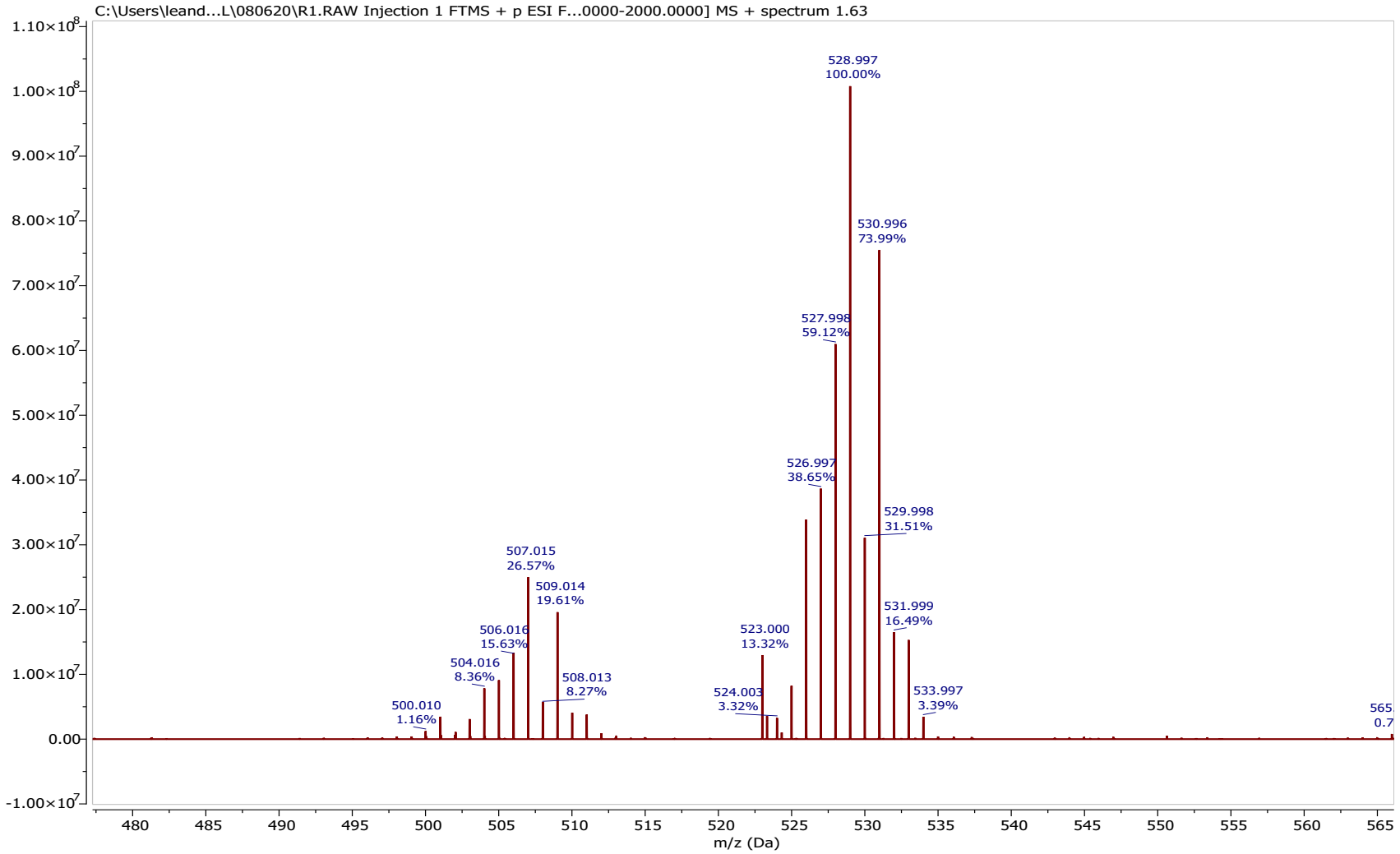

Figure S3. Mass spectrum of [RuCl(trpy)(acpy)] in methanol/water (4:1).

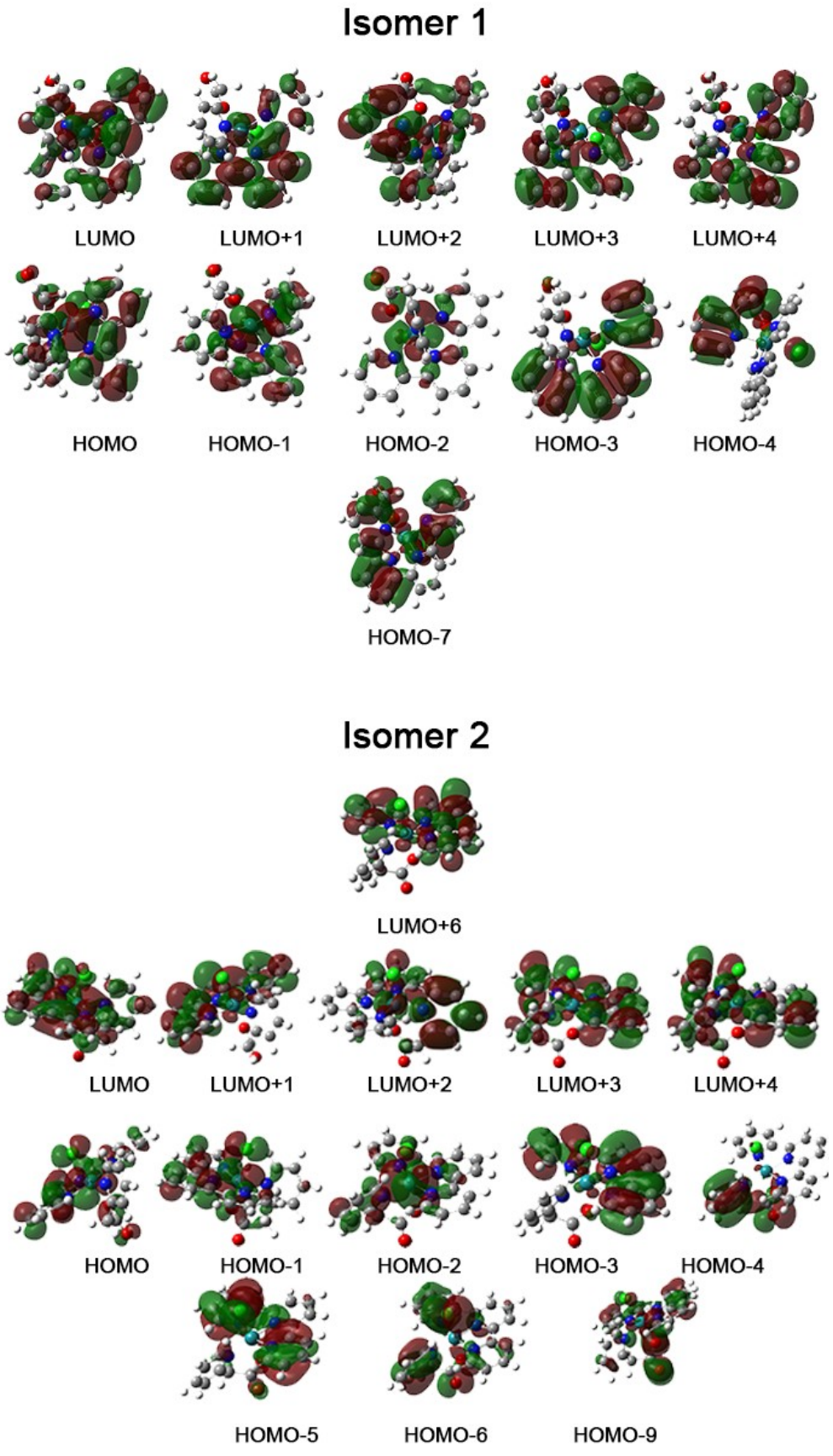

Figure S4. Representative images of electronic transitions of [RuCl(trpy)(acpy)] in acetonitrile.

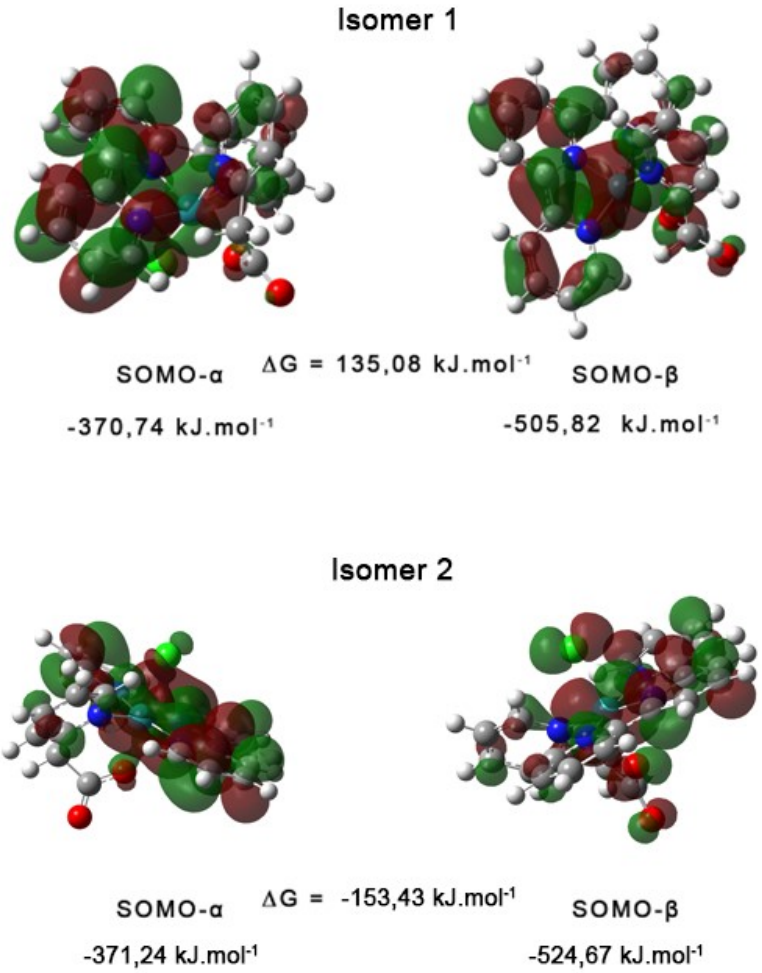

Figure S5. Orbitals SOMO-α and SOMO-β of [RuCl(trpy)(acpy)] reduced by one electron.

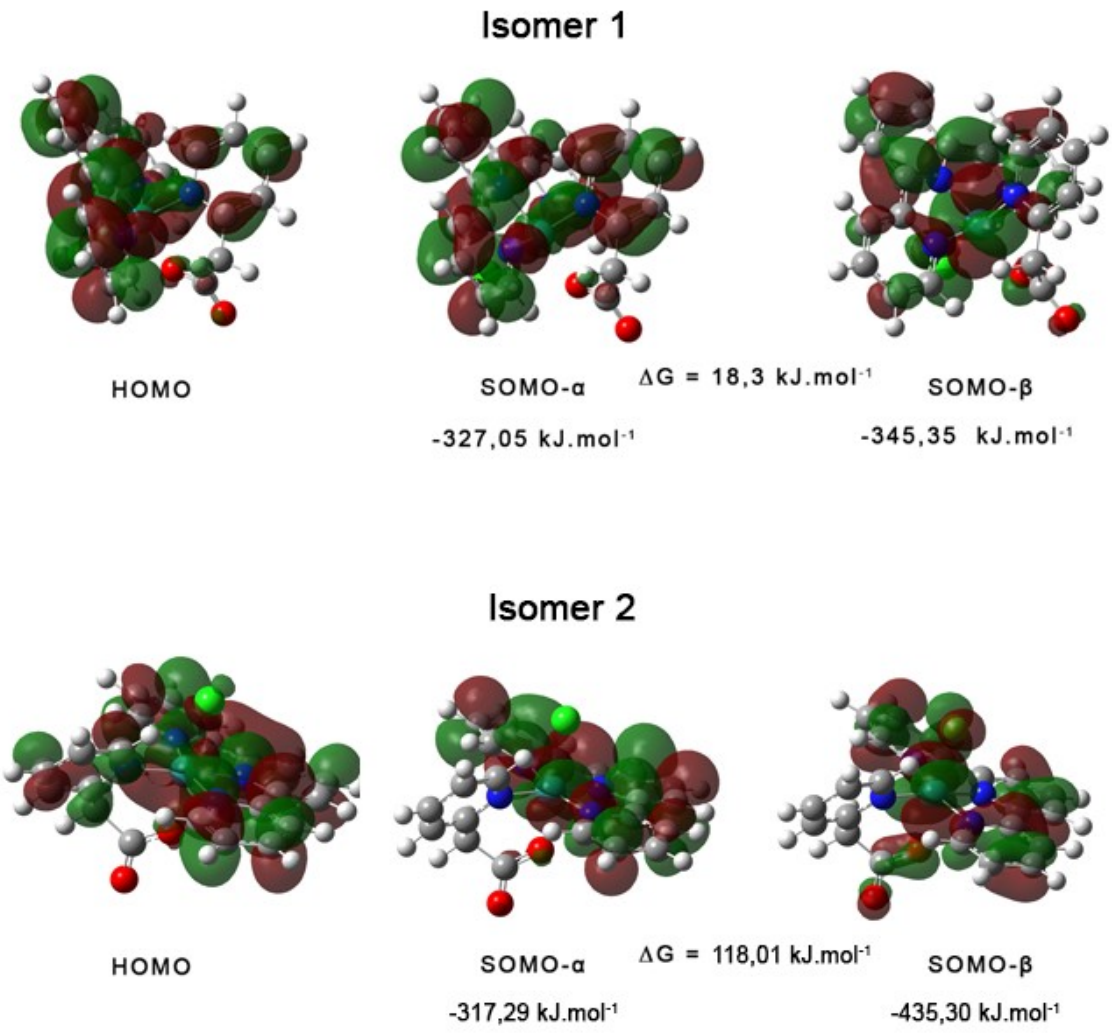

Figure S6. Orbitals HOMO, SOMO-α and SOMO-β of [RuCl(trpy)(acpy)] reduced by two electrons.

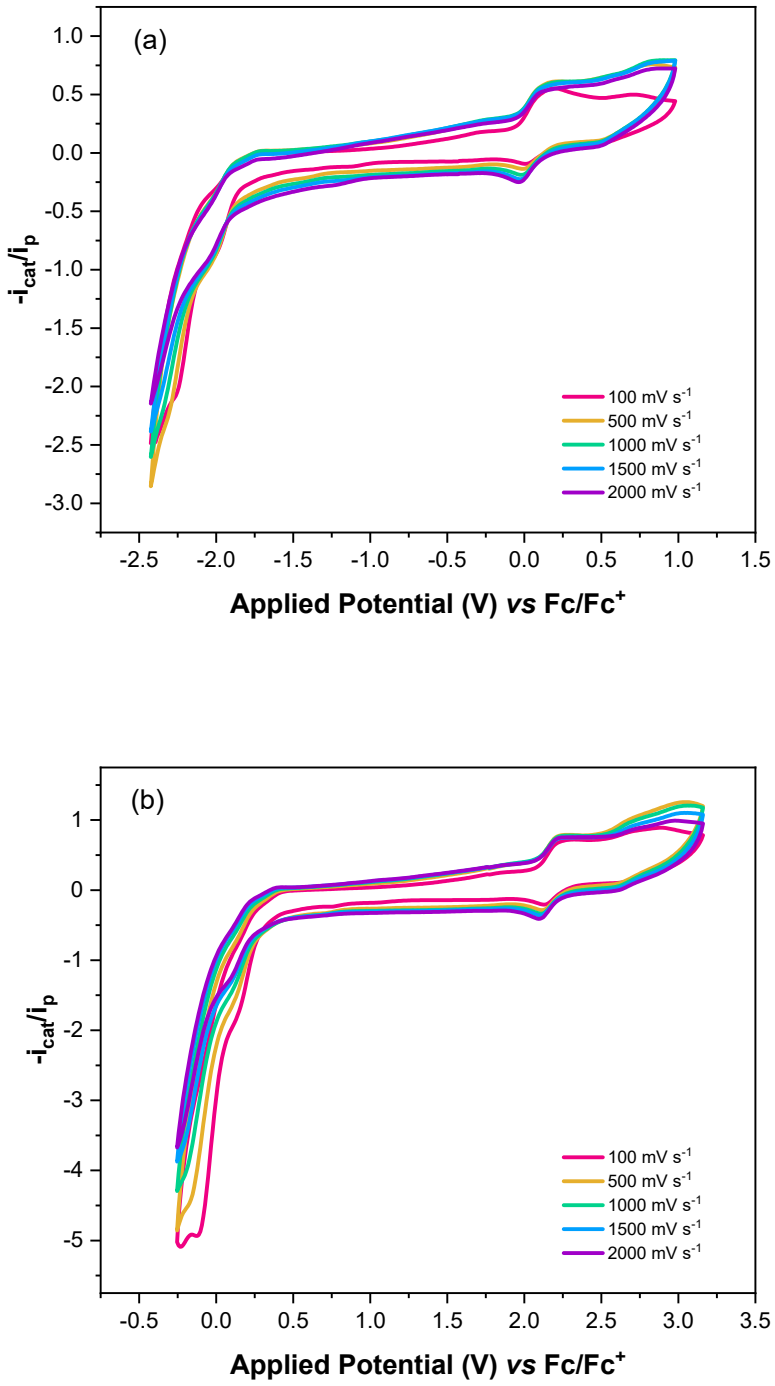

Fig S7. Plots of i_{cat}/i_p at different scan rates (a) in acetonitrile (b) and in 1% H_2O/CH_3CN mixture.

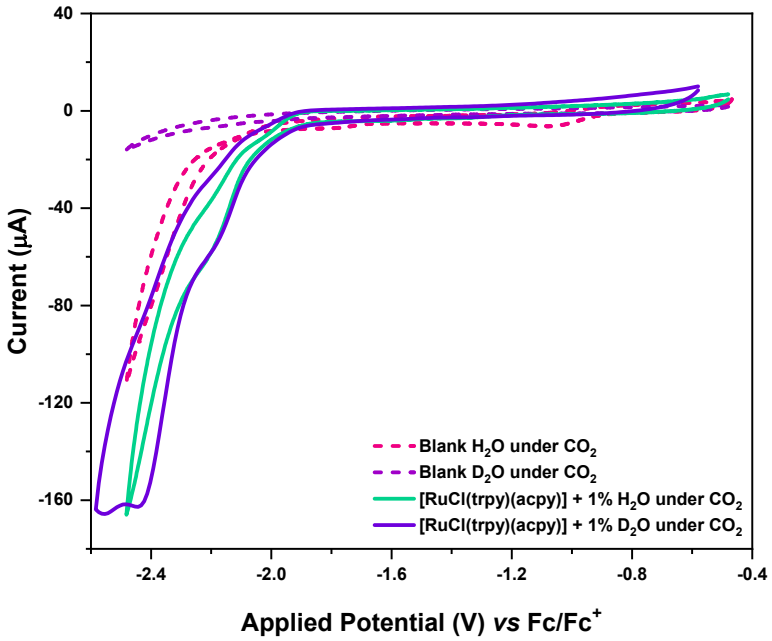

Figure S8. Cyclic voltammetries of 1 mM [RuCl(trpy)(acpy)] in 0.1 M $TBAPF_6/CH_3CN$ under CO_2 atmosphere at 100 mV s^{-1} in the presence of 1% H_2O or D_2O.

Construction of Tafel Plots

Tafel plots for the [RuCl(trpy)(acpy)] catalyst were obtained in bare acetonitrile and 1% H_2O/CH_3CN solutions. The equation below, described by Rountree et al. [1] were employing assuming $TOF_{max} = k_{obs}$ (1.5 s^{-1} for CH_3CN and 2.0 s^{-1} for 1% H_2O/CH_3CN mixture), $E^0_{CO2/CO} = -1.40$ V vs Fc/Fc^+ as reported by Matsubara [2], $E_{cat/2}$ is the potential at which the homogeneous catalytic wave reaches half of its maximum current (-2.14 V vs Fc/Fc^+) and η is the overpotential required to trigger the reaction at a specific rate.

$$TOF = \frac{TOF_{max}}{1 + \exp\left[\frac{F}{RT}\left(E^{0}_{\frac{CO_2}{CO}} - E_{\frac{cat}{2}}\right)\right]\exp\left(-\frac{F}{RT}\eta\right)}$$

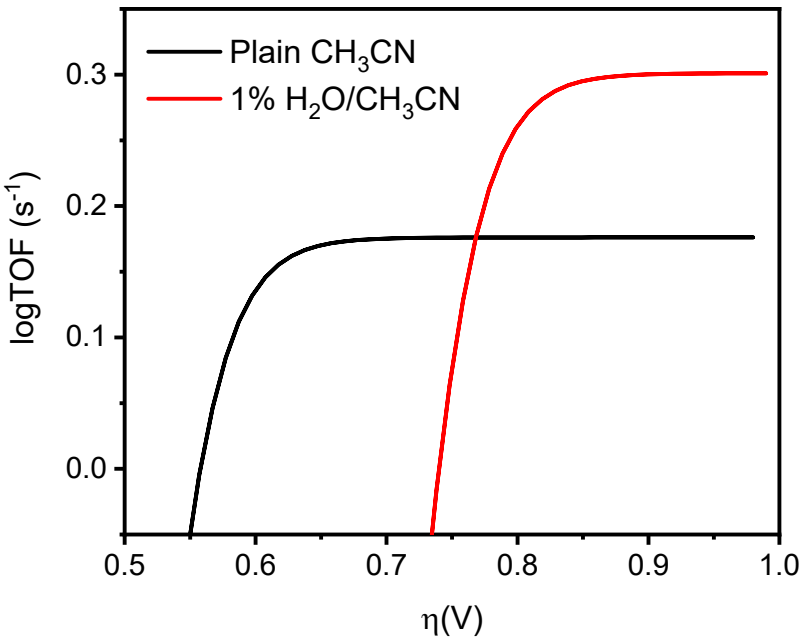

Figure S9. Tafel plot of [RuCl(trpy)(acpy) in plain acetonitrile and mixture of 1% H_2O

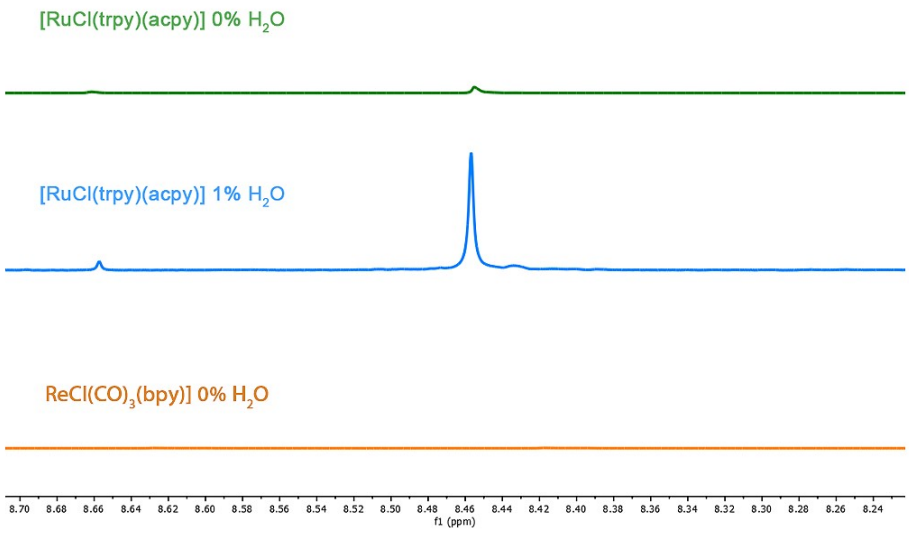

Figure S10. ^1H NMR in D_2O after bulk of electrolysis at -2.18 V vs Fc/Fc+ in 0.1 M $TBAPF_6/CH_3CN$ of 1 mM [RuCl(trpy)(acpy)] in anhydrous and with 1% of H_2O, and the standard *fac*-[$ReCl(CO)_3$(bpy)].

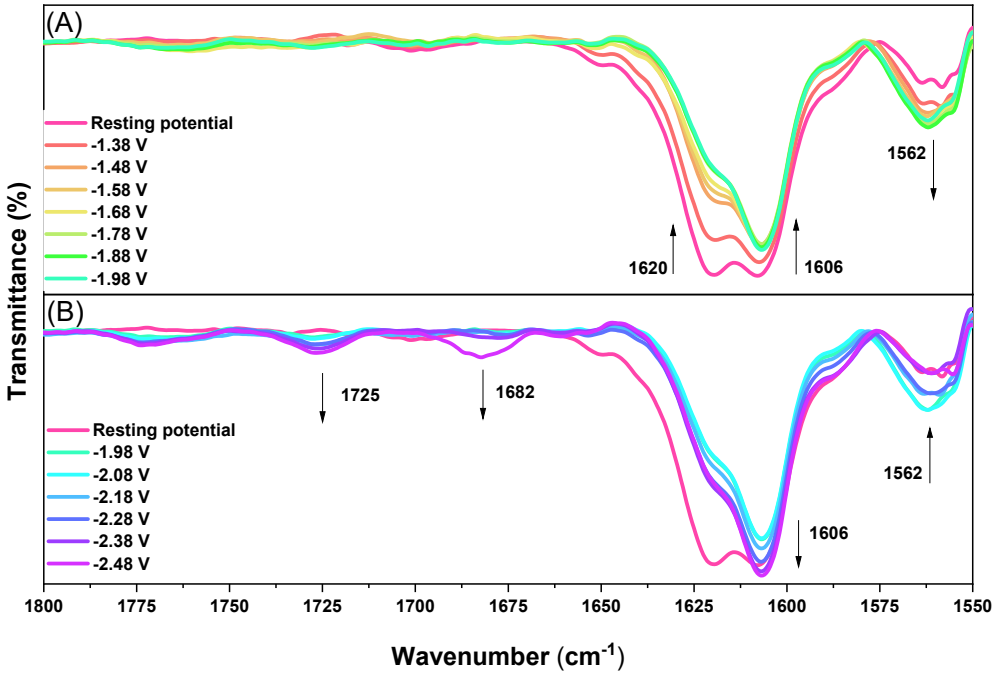

Figure S11. Changes in the FTIR spectra of 1 mM [RuCl(trpy)(acpy)] during the spectroelectrochemistry in 0.1 M $TBAPF_6/CH_2Cl_2$ varying potential under CO_2 atmosphere Δt = 1.5 min.

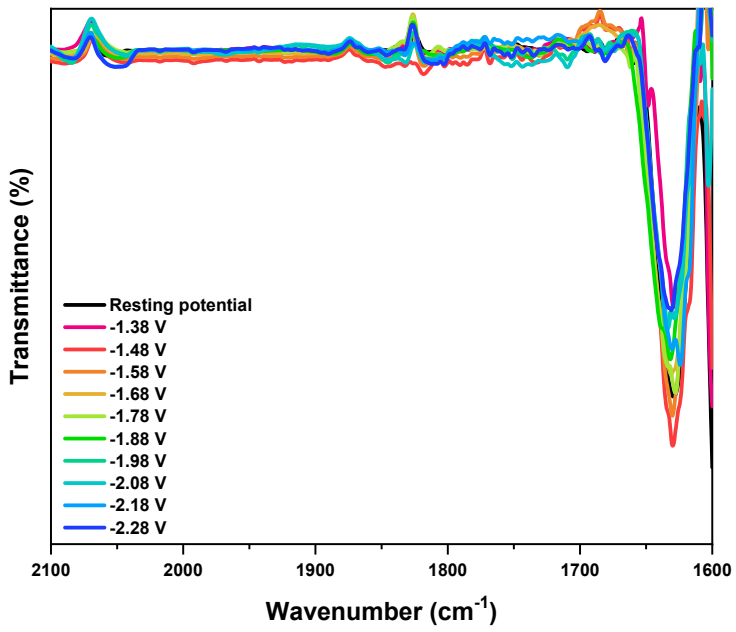

Figure S12. FTIR spectra of the bare electrolyte (0.1 M $TBAPF_6/CH_3CN$) as a function of the applied potential under CO2 atmosphere; Δt = 1.5 min.

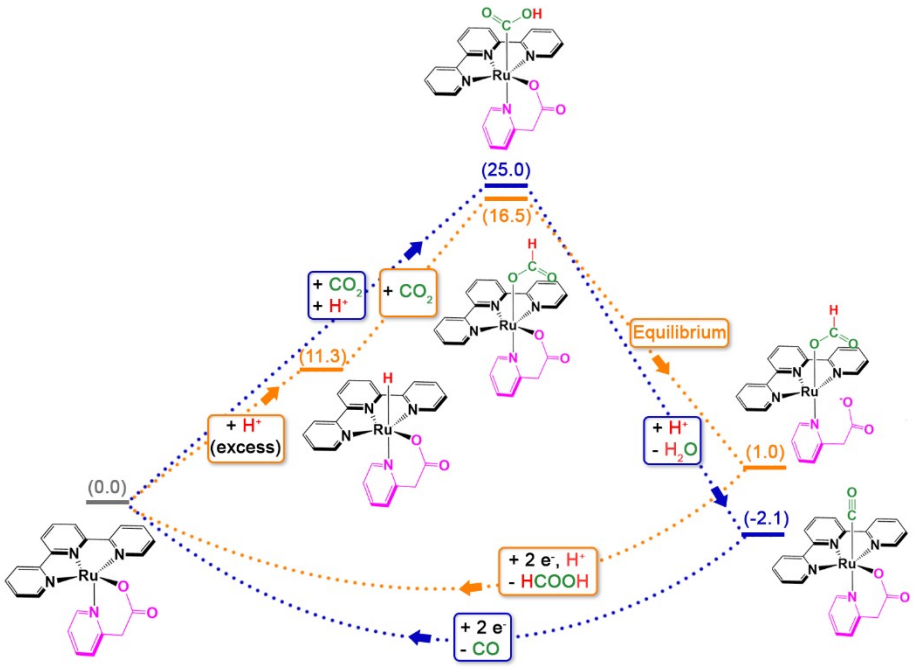

Figure S13. Thermodynamic free energy profile in kcal mol^{-1} obtained through theoretical calculation during CO_2 reduction mediated by the [RuCl(trpy)(acpy)] complex (isomer 1) considering the primary (blue) and the secondary (orange) pathways.

Table S1. ^1H NMR Chemical shifts and coupling constants of [RuCl(trpy)(acpy)].

Structure	Proton		δ / ppm	J / Hz
	H_3	d	8.61	8.0
	H_4	d	8.61	8.0
	H_5	td	7.96	4.0 / 8.0 / 16.0
	H_6	d	8.34	8.0
	$H_{3'/3''}$	td	7.55	4.0 / 8.0 / 12.0
	$H_{4'}$	td	8.07	4.0 / 8.0 / 20.0
	H_a	d	7.68	8.0

	H_b	t	7.75	8.0 / 16.0
	H_c	t	7.87	8.0 / 16.0
	H_d	d	9.84	8.0
	H_e	s	3.61	-

d= doublet, td = triple doublet, t = triplet, s = singlet.

Table S2. Crystal data and structure refinement for [RuCl(trpy)(acpy)].

Identification code	shelx
Empirical formula	C_{22} H_{21} Cl N_4 O_4 Ru
Formula weight	541.95
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 8.9094(8) Å a= 92.649(8)°.
	b = 8.9354(9) Å b= 99.764(7)°.
	c = 13.7859(13) Å g = 98.885(7)°.
Volume	1065.65(18) $Å^3$
Z	2
Density (calculated)	1.689 Mg/m^3
Absorption coefficient	0.899 mm^{-1}
F(000)	548
Crystal size	0.460 x 0.220 x 0.040 mm^3
Theta range for data collection	4.762 to 29.160°.
Index ranges	-12<=h<=12, -12<=k<=12, -17<=l<=18
Reflections collected	11922
Independent reflections	5673 [R(int) = 0.0440]
Completeness to theta = 25.242°	98.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5673 / 4 / 305
Goodness-of-fit on F^2	0.949
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0695
R indices (all data)	R1 = 0.0473, wR2 = 0.0729
Extinction coefficient	n/a
Largest diff. peak and hole	0.783 and -0.957 $e.Å^{-3}$

Table S3. Electronic transitions of [RuCl(trpy)(acpy)] and the correspondent oscillator strength for each isomer.

Isomer 1			
λ nm (eV)	**Oscillator Strength**	**Transition**	**Nature**
655.67 (1.89)	0.0137	H-2→L (39.4%) H-1→L (32.4%) H→L (7.5%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
639.27 (1.94)	0.0199	H-2→L (40.3%) H-1→L (21.5%) H→L (16.%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
540.43 (2.29)	0.0214	H-1→L (40.0%) H→L (24.3%) H→L+1 (30.5%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
513.65 (2.41)	0.1216	H-1→L+1 (13.3%) H→L (27.6%) H→L+1 (56.8%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
459.29 (2.70)	0.0038	H-2→L (15.8%) H-2→L+1 (72.0%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
440.50 (2.81)	0.1192	H-1→L+1 (64.3%) H→L (24.3%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
378.67 (3.27)	0.1100	H-2→L+2 (10.2%) H-1→L+2 (46.9%) H→L+2 (39.0%)	MLCT $_{d\ Ru\rightarrow\pi^*acpy}$ LLCT $_{\pi\ tpy\rightarrow\pi^*\ acpy}$
351.26 (3.53)	0.0966	H→L+3 (100%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
338.02 (3.67)	0.1712	H-2→L+3 (20.4%) H-1→L+3 (79.6%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
275.53 (4.50)	0.3978	H-3→L (54.7%) H-1→L+6 (22.1%) H→L+6 (13.3%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
252.71 (4.90)	0.4477	H-3→L (9.6%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$

		H-3→L+1 (56.3%) H-2→L+6 (9.9%) H→L+6 (8.5%)	IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
242.61 (5.11)	0.1436	H-4→L (77.9%) H-4→L+2 (14.3%)	LLCT $_{\pi\ acpy\rightarrow\pi^*\ tpy}$ LLCT $_{n\ Cl\rightarrow\pi^*\ tpy/acpy}$ IL $_{\pi\ acpy\rightarrow\pi^*\ acpy}$
217.80 (5.69)	0.2491	H-4→L+1 (26.8%) H-3→L+3 (42.3%)	IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$ LLCT $_{\pi\ acpy\rightarrow\pi^*\ tpy}$ LLCT $_{n\ Cl\rightarrow\pi\ tpy}$
214.07 (5.79)	0.1863	H-7→L (18.4%) H-4→L+1 (29.7%) H-3→L+3 (12.6%)	IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$ LLCT $_{\pi\ acpy\rightarrow\pi^*\ tpy}$

Isomer 2

λ nm (eV)	**Oscillator Strength**	**Transition**	**Nature**
748.22 (1.65)	0.0412	H-1→L (74.8%) H→L (25.2%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
589.77 (2.10)	0.0259	H-1→L (50.9%) H→L (18.4%) H→L+1 (19.5%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
518.11 (2.39)	0.0925	H-1→L+1 (58.1%) H→L+1 (41.9%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
464.03 (2.67)	0.1216	H-1→L (20.3%) H-1→L+1 (36.1%) H→L+1 (39.7%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
403.68 (3.07)	0.0079	H-1→L+2 (9.5.8%) H→L+2 (85.2%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$
377.89 (3.28)	0.0184	H-2→L+2 (5.5%) H-1→L+2 (79.0%) H→L+2 (6.9%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ LLCT $_{\pi\ tpy\rightarrow\pi^*\ acpy}$
367.88 (3.37)	0.2040	H→L+3 (81.1%) H→L+4 (81.1%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
353.26 (3.50)	0.0787	H-2→L+2 (8.2%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$

		H-1→L+3 (66.1%) H→L+4 (16.6%)	MLCT $_{d\ Ru\rightarrow\pi\ acpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
346.16 (3.58)	0.2538	H-2→L+2 (57.9%) H-1→L+3 (21.8%) H→L+4 (11.0%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ LLCT $_{\pi\ tpy\rightarrow\pi^*\ acpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
284.84 (4.35)	0.2826	H-3→L (27.4%) H→L+6 (64.6%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ LLCT $_{\pi\ tpy\rightarrow\pi^*\ acpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
276.71 (4.48)	0.2429	H-3→L (68.8%) H→L+6 (31.2%)	MLCT $_{d\ Ru\rightarrow\pi\ tpy}$ LLCT $_{\pi\ tpy\rightarrow\pi^*\ acpy}$ IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$
253.61 (4.89)	0.4298	H-3→L (75.9%) H-2→L+6 (8.2%)	IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$ LLCT $_{n\ Cl\rightarrow\pi^*\ tpy}$ LLCT $_{\pi\ tpy\rightarrow\pi^*\ acpy}$
241.38 (5.13)	0.0729	H-4→L (81.0%) H-4→L+2 (14.8%)	IL $_{\pi\ acpy\rightarrow\pi^*\ acpy}$ LLCT $_{\pi\ acpy\rightarrow\pi^*\ tpy}$
233.92 (5.30)	0.0171	H-6→L (18.4%) H-5→L+1 (29.7%)	IL $_{\pi\ acpy\rightarrow\pi^*\ acpy}$ LLCT $_{\pi\ acpy\rightarrow\pi^*\ tpy}$ LLCT $_{n\ Cl\rightarrow\pi^*\ tpy}$
218.48 (5.67)	0.3172	H-9→L (13.0%) H-5→L+1 (40.8%) H-3→L+3 (20.9%)	IL $_{\pi\ tpy\rightarrow\pi^*\ tpy}$ LLCT $_{n\ Cl\rightarrow\pi^*\ tpy}$

Table S4. Distance bond of reduced species obtained by TD-DFT.

Isomer 1						
Electrons inserted in the structure	**Ru-Cl (pm)**	**Ru-O (pm)**	**Ru-N_{acpy} (pm)**	**Ru-$N_{1(trpy)}$ (pm)**	**Ru-$N_{2(trpy)}$ (pm)**	**Ru-$N_{3(trpy)}$ (pm)**
0	237.152	204.538	204.004	199.381	187.817	200.901
1 (Doublet)	240.750	206.858	199.971	197.829	190.265	200.687
2 (Singlet)	247.117	208.518	194.925	197.153	192.241	197.679
2 (Triplet)	244.155	208.016	196.156	200.535	191.293	200.453
Isomer 2						
Electrons inserted in the structure	**Ru-Cl (pm)**	**Ru-O (pm)**	**Ru-N_{acpy} (pm)**	**Ru-$N_{1(trpy)}$ (pm)**	**Ru-$N_{2(trpy)}$ (pm)**	**Ru-$N_{3(trpy)}$ (pm)**
0	237.790	202.372	206.086	198.999	189.764	200.890
1 (Doublet)	241.137	203.700	202.160	199.015	192.811	197.266
2 (Singlet)	244.295	204.135	197.281	196.045	194.584	197.536
2 (Triplet)	242.729	205.151	198.829	200.826	193.798	201.947

References

1. E. S. Rountree, B. D. McCarthy, T. T. Eisenhart and J. L. Dempsey, *Inorg. Chem.*, 2014, **53**, 9983-10002.
2. Y. Matsubara, *ACS Energy Letters*, 2019, **4**, 1999-2004.