Chiroptical switching behavior of heteroleptic ruthenium complexes bearing acetylacetonato and tropolonato ligands

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ESI-MS spectrum

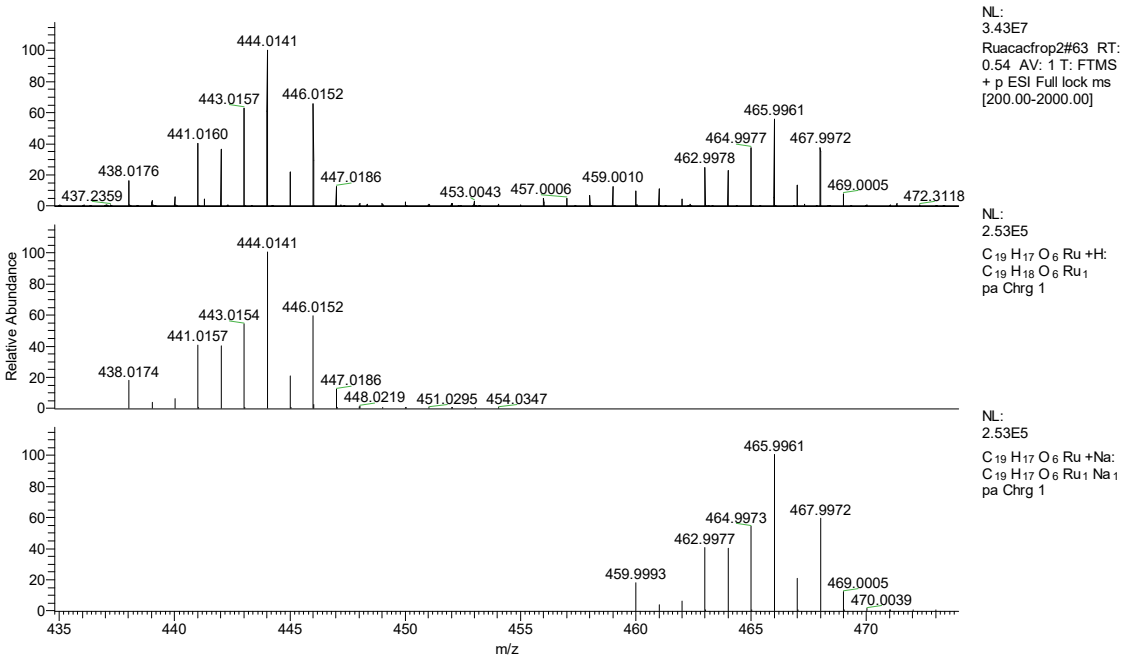


Figure S1 Experimental isotropic pattern of **Ru-2** (top) and theoretical isotopic patterns for $[C_{19}H_{17}O_6Ru+H]^+$ (middle) and $[C_{19}H_{17}O_6Ru+Na]^+$ (bottom).

HPLC charts

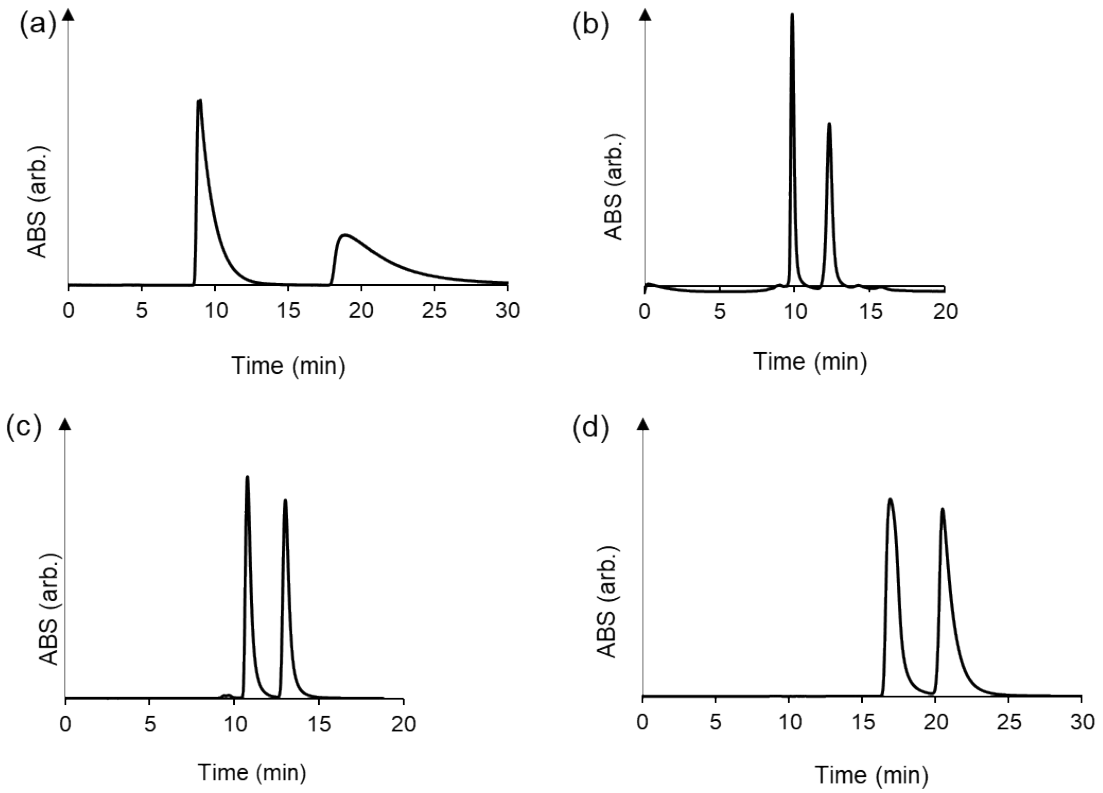


Figure S2 The HPLC chromatograms of (a) **Ru-0**, (b) **Ru-1**, (c) **Ru-2**, and (d) **Ru-3** obtained in the following conditions; (a) RU-1 column (Shiseido Corp., Japan), methanol, flow rate = 1 ml min^{-1}, (b, c) CHIRALPAK-IA column (Daicel Chemical Industries Co., Ltd. Japan), chloroform/hexane = 2/1 (v/v), flow rate = 6 ml min^{-1}, and (d) CHIRALPAK-IA column, chloroform/hexane = 3/2 (v/v), flow rate = 6 ml min^{-1}.

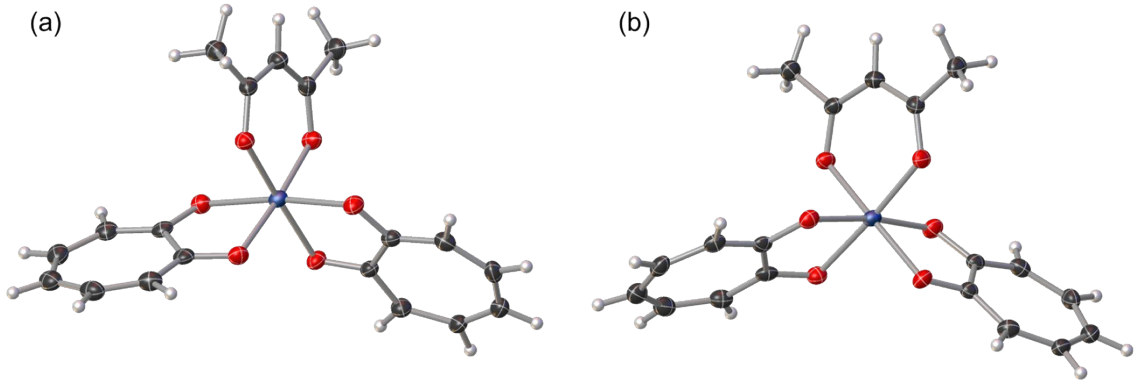


Figure S3 ORTEP representations of (a) Δ-**Ru-2** and (b) Λ-**Ru-2** (50% probability level), which correspond to 2nd and 1st fractions in the HPLC chromatogram.

Table S1 Crystallographic and experimental data for Δ- and Λ-**Ru-2** (CCDC 2099739 and 2099741).

Compound	Δ-**Ru-2**	Λ-**Ru-2**
Formula	$C_{19}H_{17}O_6Ru$	$C_{19}H_{17}O_6Ru$
Formula weight	442.39	442.39
$D_{calc.}$/ g cm^{-3}	1.701	1.700
μ / mm^{-1}	7.649	7.648
Size / mm^3	0.13×0.10×0.07	0.047×0.038×0.02
T / K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Flack Parameter	-0.014(5)	-0.019(5)
Hooft Parameter	-0.022(4)	-0.024(4)
Space group	C_2	C_2
a / Å	28.6206(4)	28.5743(4)
b / Å	7.38672(13)	7.3986(1)
c / Å	8.17443(13)	8.1753(1)
α / °	90	90
β / °	91.0315(15)	90.911(1)
γ / °	90	90
V / Å^3	1727.90(5)	1728.12(4)
Z	4	4
Wavelength/Å	1.54184	1.54184
Radiation type	CuK_α	CuK_α
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10058, 3444, 3421	9684, 3411, 3316
R_{int}	0.027	0.027
No. of parameters	238	237
GooF	1.108	1.118
wR_2	0.052	0.052
R_1	0.020	0.020

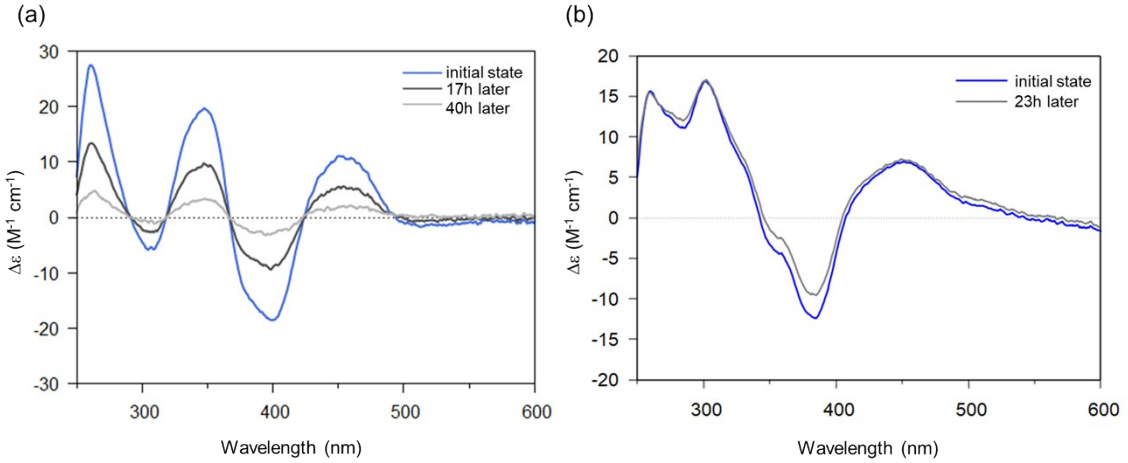


Figure S4 The time-course CD spectral changes of the acetonitrile solutions containing (a) [Ru(trop)$_3$] (**Ru-3**) and (b) [Ru(acac)(trop)$_2$] (**Ru-2**).

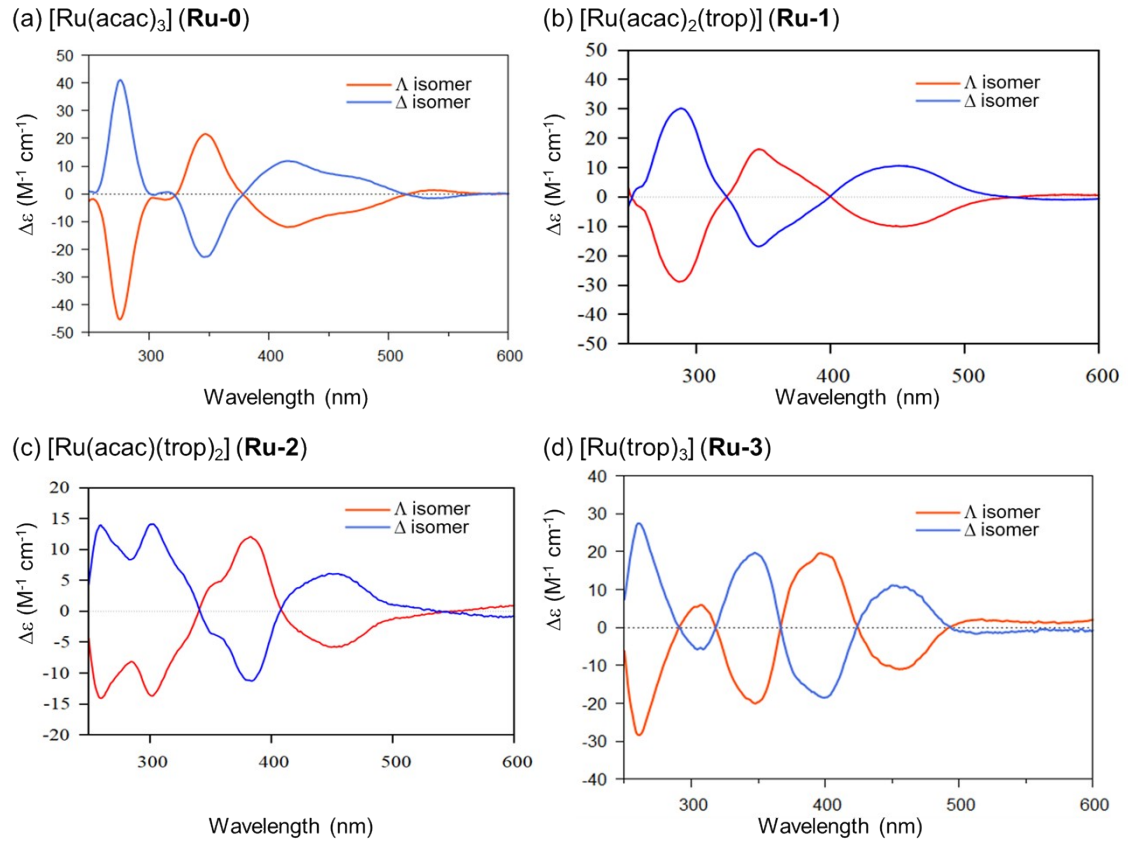


Figure S5 ECD spectra of Δ and Λ isomers of **Ru-0**, **Ru-1**, **Ru-2**, and **Ru-3**. The 1st and 2nd fractions in the HPLC chromatograms of ruthenium complexes were all assigned to Λ and Δ isomers, respectively.

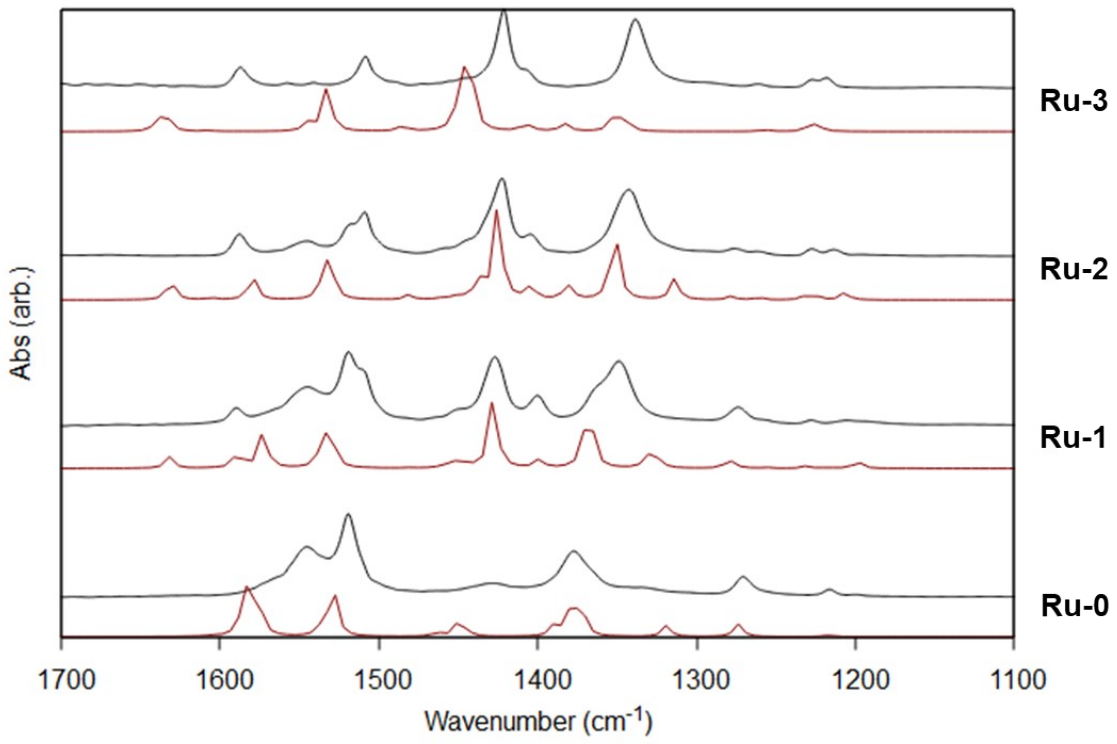


Figure S6 Experimental (black) and DFT-calculated (red) IR spectra of (a) **Ru-0**, (b) **Ru-1**, (c) **Ru-2**, and (d) **Ru-3** (Scale = 0.97 for calculated spectra).

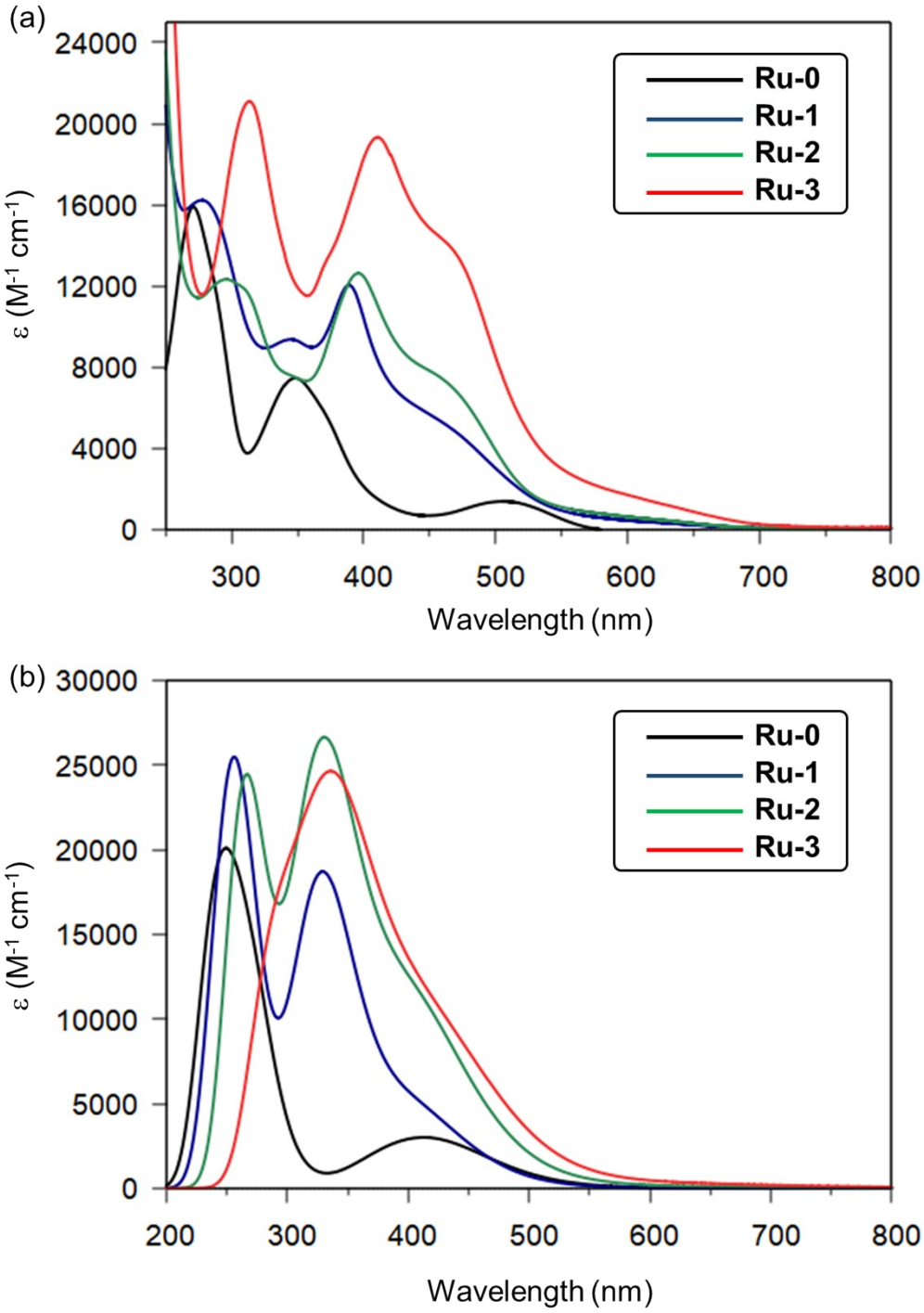


Figure S7 (a) Experimental and (b) calculated UV-vis spectra of **Ru-0**, **Ru-1**, **Ru-2**, and **Ru-3**.

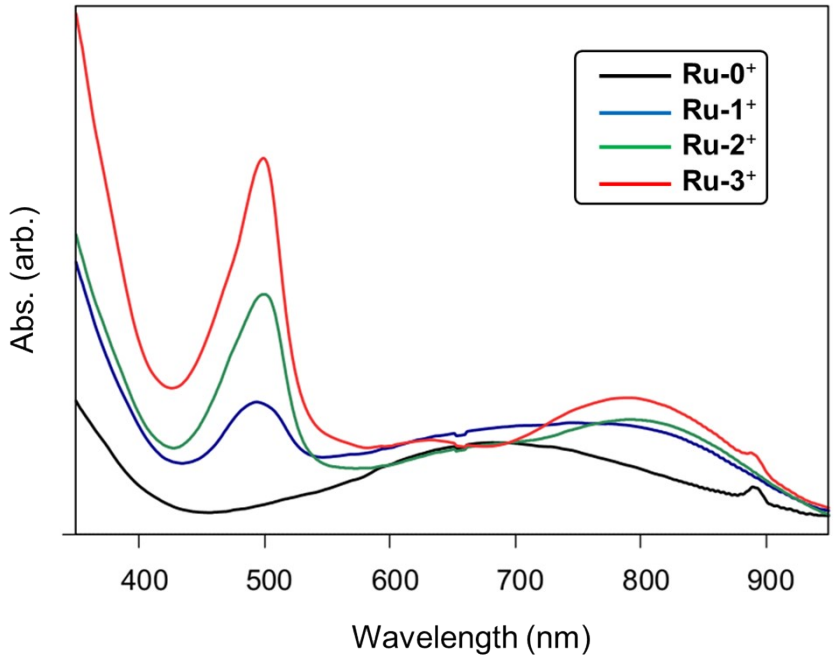
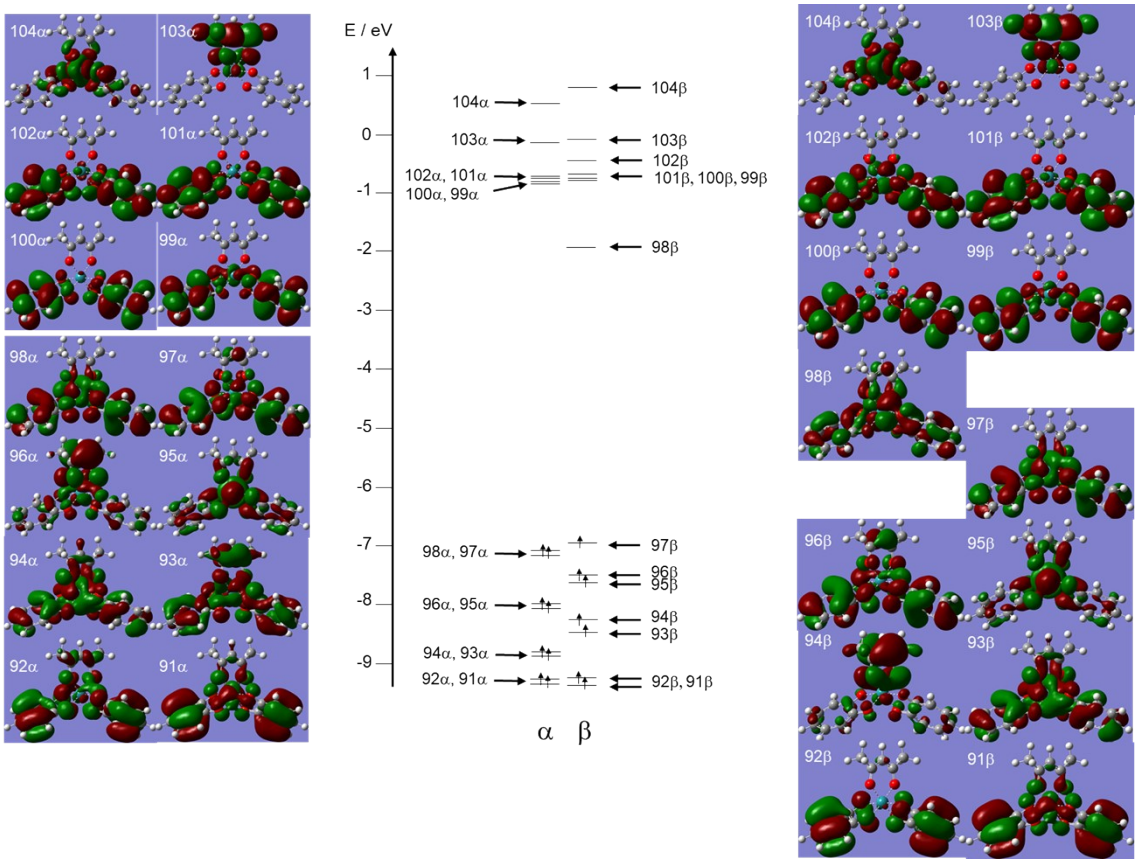


Figure S8 UV-vis spectra of **Ru-0**$^{+}$, **Ru-1**$^{+}$, **Ru-2**$^{+}$, and **Ru-3**$^{+}$, which were in-situ prepared by the addition of 1.0~2.5 equiv. of CAN to the acetonitrile solution containing each neutral complex.



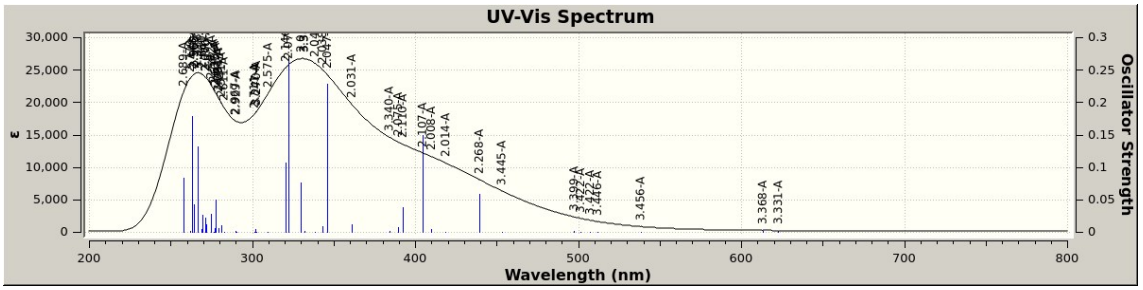
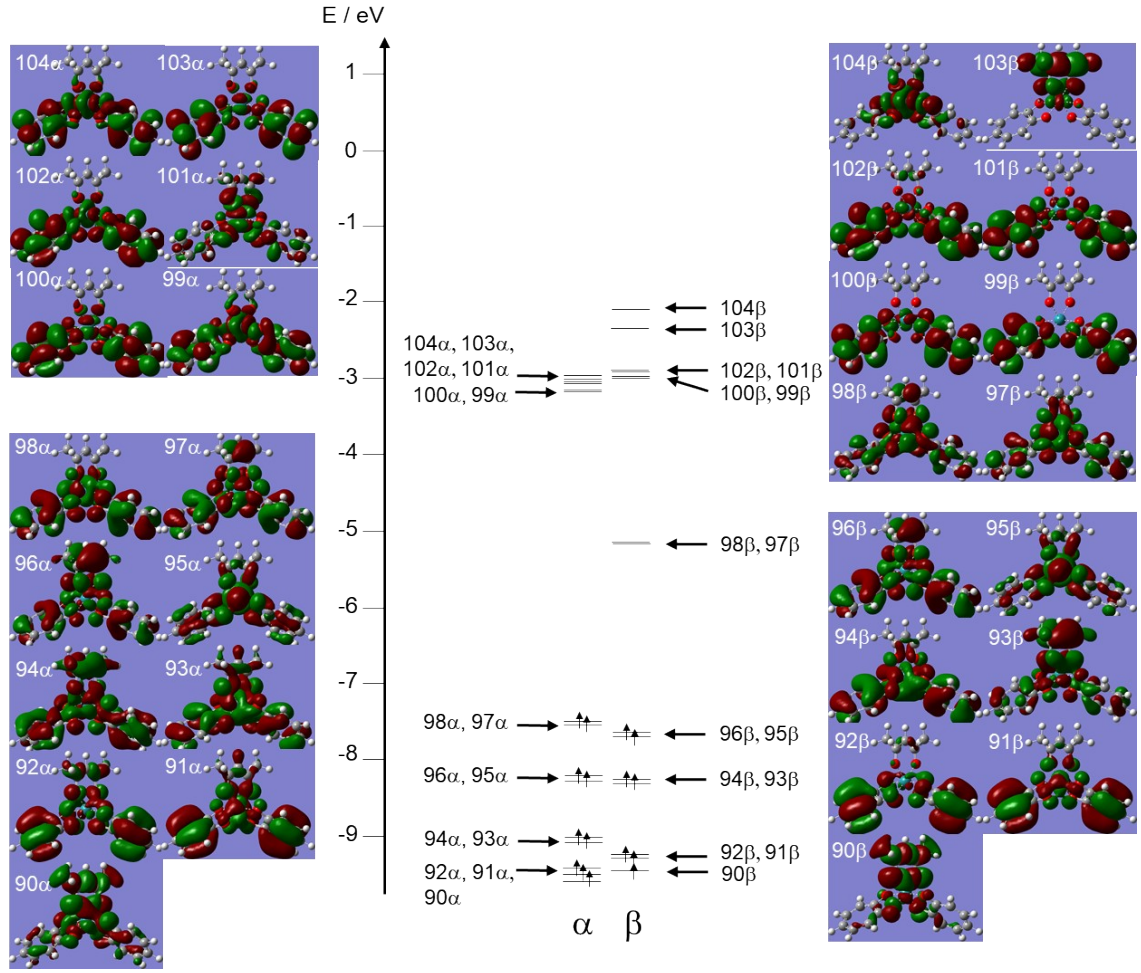


Figure S9 Frontier MO diagram and UV-vis spectrum of **Ru-2** calculated by TD-DFT/ucam-b3lyp. The HOMO(SOMO)-LUMO band gap is 4.939 eV.



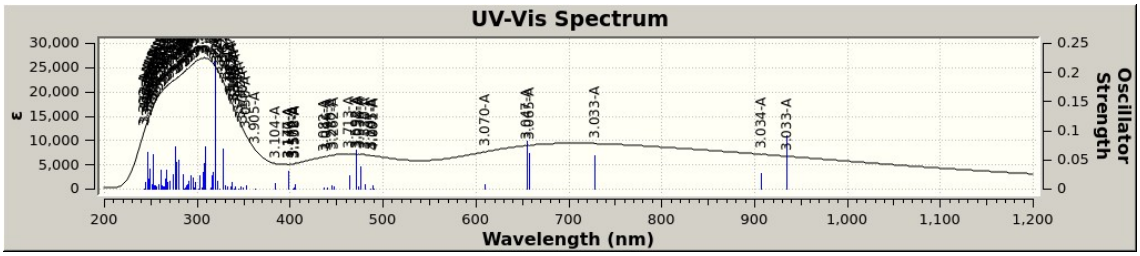


Figure S10 Frontier MO diagram and UV-vis spectrum of **Ru-2**$^{+}$ calculated by TD-DFT/ucam-b3lyp. The HOMO(SOMO)-LUMO band gap is 2.505 eV.

Table S2 Part of the excitation energies and oscillator strengths obtained from the TD-DFT calculation of **Ru-2**$^{+}$.

wavelength / nm	oscillator strength (f)	excitation
935.23	0.0913	94β → 98β, 96β → 97β
907.66	0.0274	94β → 97β , 96β → 98β
728.56	0.0564	93β → 97β, 94β → 98β, 96β → 97β
658.06	0.0607	93β → 98β, 94β → 97β, 95β → 97β, 96β → 98β
654.70	0.0815	93β → 97β, 94β → 98β
610.11	0.0078	97α → 100α, 98α → 99α, 93β → 98β, 94β → 97β

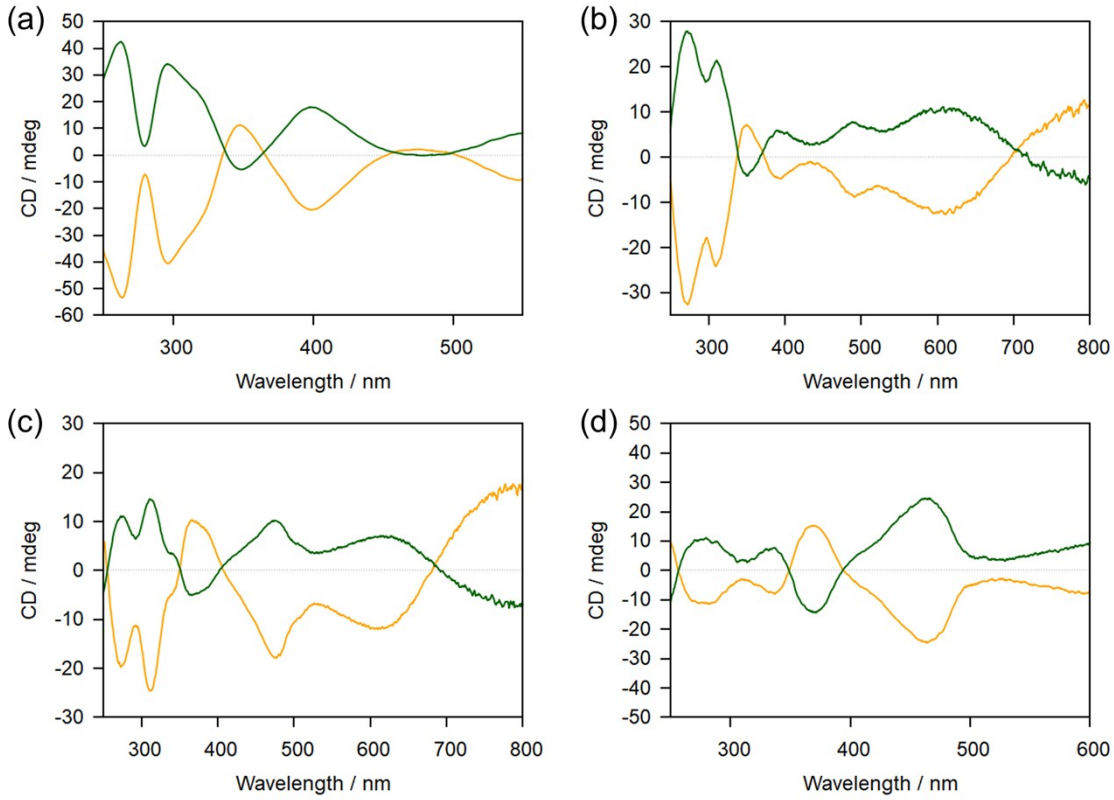


Figure S11 ECD spectra of (a) **Ru-0**$^{+}$, (b) **Ru-1**$^{+}$, (c) **Ru-2**$^{+}$, and (d) **Ru-3**$^{+}$, which were in-situ oxidized by the addition of 1.0~2.5 equiv. of CAN. Orange and green lines correspond to Λ and Δ isomers, respectively.

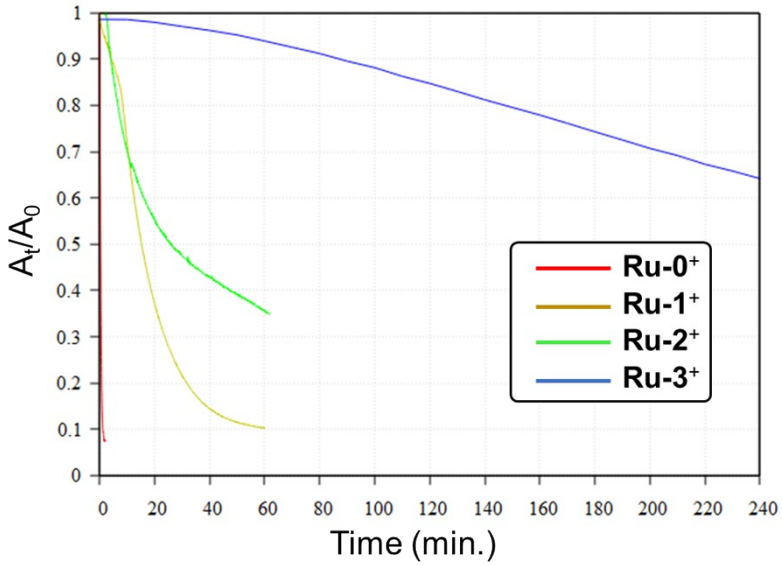


Figure S12 Time-dependent absorption changes of oxidized complexes **Ru-0**$^+$, **Ru-1**$^+$, **Ru-2**$^+$**,** and **Ru-3**$^+$, which were in-situ prepared by adding an acetonitrile solution of CAN to the acetonitrile solution of each complex. The data of **Ru-0**$^+$, **Ru-1**$^+$, and **Ru-3**$^+$ were previously reported.[1] The relative absorption intensities at 800 nm (A_t/A_0, where A_t is the observed absorption at an arbitrary time and A_0 refers to the absorption in the initial state) are plotted against the time after the addition of CAN.

References

[1] J. Yoshida, K. Tateyama, H. Yuge, *Dalton Trans.* **2020**, *49*, 2102–2111.