Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information for

Phenylene as An Efficient Mediator for Intermetallic Electronic Coupling

Lyndsy A. Miller-Clark, Adharsh Raghavan, Reese A. Clendening and Tong Ren*

* To whom correspondence should be addressed. Email: tren@purdue.edu.

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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1. Experimental details

Materials and instruments. $Ru_2(ap)_4Cl$,[1] $Ru_2(ap)_4(C_6H_5)$[2] and (NC)($Ru_2(ap)_4(C_6H_5)$) (**3**)[3] were prepared according to literature methods. Tetrahydrofuran (THF) was distilled over Na/benzophenone under a N_2 atmosphere. Et_2O was dried and deoxygenated using literature procedures with a Seca solvent purification system.[4] $[Bu_4N][CN]$, $[Bu_4N][PF_6]$ and ^{n}BuLi were purchased from Sigma Aldrich and 1,4-diiodobenzene was purchased from Acros Organics. All reactions were performed under dry N_2 atmosphere using standard Schlenk techniques where noted. UV-Vis-NIR spectra were obtained with a JASCO V-670 spectrophotometer in THF solutions. Infrared spectra were obtained on a JASCO FT-IR 6300 spectrometer equipped with an attenuated total reflectance (ATR) accessory on a diamond crystal. ESI-MS were analyzed on an Advion Mass Spectrometer. ^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300 MHz. Magnetic susceptibility measurements of **3** were taken using a Johnson Matthey Mark-I magnetic susceptibility balance. The room temperature magnetic moments for **1**, **2** and **3** were determined using the Evans method[5] with chemical shifts of ferrocene as the reference. Elemental analyses were performed by Atlantic Microlab, Inc. Cyclic voltammograms were recorded in 0.1 M $[^nBu_4N][PF_6]$ and 1.0 mM analyte solution (THF, Ar degassed) using a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), Pt-wire counter electrode, and an Ag/AgCl reference electrode with ferrocene used as an external reference. Spectroelectrochemical absorption data was taken with a JASCO V-670 spectrophotometer, and IR data was taken on a JASCO FT-IR 6300 spectrometer. Spectroelectrochemical analysis was performed using an optically transparent thin-layer electrochemistry (OTTLE) liquid-sample cell[6] with a 0.2 mm optical path length, 0.3 mL sample volume, and a CaF_2 window. The cell was equipped with a mesh Pt working electrode, mesh Pt

auxiliary electrode, and Ag reference electrode; the analyte concentration was 2.0 mM in 4 mL dry THF at a 0.1 M [^{n}Bu$_4$N][PF$_6$] electrolyte concentration. X-ray diffraction (XRD) data (Table S3) for **2** was obtained on a Bruker Quest diffractometer with Cu Kα radiation (λ = 1.54178 Å) at 150 K. XRD data (Table S3) for **3** was obtained on a Bruker Quest diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 150 K.

[Ru$_2$(*ap*)$_4$]$_2$(μ-1,4-C$_6$H$_4$) (1). 1,4-Diiodobenzene (0.157 g, 0.475 mmol) was dissolved in 10.0 mL Et$_2$O and was treated with 0.6 mL ^{n}BuLi (1.5 mmol) at -78°C for 1 hour. Three half-equivalents (0.6 mL) of the aryllithium solution were added to a 15.0 mL solution of Ru$_2$(*ap*)$_4$Cl in THF (100 mg, 0.109 mmol) every hour. This reaction stirred overnight. The Et$_2$O was then removed and the green-brown solid resuspended in hexanes. The suspension was filtered and the dark solid washed with copious amounts of hexanes and pentane until the wash became colorless (ca. 75 mL total). The solid was then washed with 2 x 10 mL cold MeOH and the final wash with 2 x 10 mL 1:1 Et$_2$O/pentane. The brown solid was dried and either used immediately to make **2** or for characterization. Yield: 62.3 mg, 62%. Data for **1** are as follows. ESI-MS (*m* / *z*, based on ^{101}Ru): [M]$^{2+}$ = 917.6. UV-Vis (in THF) λ / nm (ε / M^{-1} cm^{-1}): 461 (9200), (sh)567 (4900), 761 (5900). μ_{eff} (22°C) (Evans method) = 5.82 μ_B. Electrochemistry (THF, vs Fc$^{+/0}$), $E_{1/2}$ / V, ΔE_p / mV, $i_{backward}/i_{forward}$: -0.131, 79, 0.49; -0.010, 79, 0.72; -1.337, 115, 0.67; -1.566, 136, 0.87.

[(NC)Ru$_2$(*ap*)$_4$]$_2$(μ-1,4-C$_6$H$_4$) (2). A stock solution of **1** was made from 29.8 mg in 90 mL THF (2.42 x 10^{-4} M **1**). To 30.0 mL of the stock solution, [NBu$_4$][CN] (15 mg, 0.06 mmol) in 5.0 mL THF was added. An immediate color change from dark brown-green to deep red was observed. O$_2$ was bubbled through this solution for 2 hours, resulting in a color change from red to a red-purple. The solvent was removed, and the product extracted from CH$_2$Cl$_2$/H$_2$O. The organic layers were combined and dried with Na$_2$SO$_4$. Removal of solvent gave a deep purple

solid, and purification was achieved through a 1:20 (v:v) CH_2Cl_2/hexanes recrystallization at room temperature. Single crystals suitable for X-ray diffraction were grown by layering diethyl ether over a concentrated solution of **2** in THF. Yield: 7 mg, 59%. Elem. Anal. Found (Calcd) for $C_{101.5}H_{87}N_{18}Cl_3O_1Ru4$ (**2**·1.5CH_2Cl_2·THF): C, 58.46 (58.15); H, 4.20 (4.29); N, 12.09 (11.88). ESI-MS (*m / z*, based on ^{101}Ru): $[M - 2\ CN]^{2+}$ = 917.0. UV-Vis (in THF) λ / nm (ε / M^{-1} cm^{-1}): 346 (29400), 552 (8800), (sh)599 (7800), 756 (4700), 1025 (5500). IR $\overline{\nu}$ / cm^{-1}: 2099 $\overline{\nu}$(C≡N). μ_{eff} (21°C) (Evans method) = 2.18 μ_B. Electrochemistry (THF, vs $Fc^{+/0}$), $E_{1/2}$ / V, ΔE_p / mV, $i_{backward}/i_{forward}$: 0.299, 92, 0.63; 0.008, 66, 0.83; -0.913, 62, 0.94; -1.09, 62, 0.61. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 6.4 Hz, 8H, H(a)), 7.22 – 6.99 (m, 32H, H(b,c,f,h)), 6.40 (d, *J* = 9.0 Hz, 8H, H(d)), 6.24 (t, *J* = 6.3 Hz, 12H, H(g,j)), 6.12 (s, 8H, H(i)), 5.62 (s, 8H, H(e)). Isosbestic points for **2** → $\mathbf{2}^+$: ca. 15000 cm^{-1} and ca. 23000 cm^{-1}; isosbestic points for $\mathbf{2}^+$ → $\mathbf{2}^{2+}$: 7500 cm^{-1} and ca. 23000 cm^{-1}.

(NC)Ru_2(*ap*)$_4$(C_6H_5) (3). $Ru_2(ap)_4(C_6H_5)$ (48.9 mg (0.05 mmol)) was dissolved in 20 mL THF, to which 23 mg KCN in 6 mL THF/MeOH (1:1 v/v) was added. An immediate color change from dark green to red was observed. Upon bubbling O_2 for ~10 minutes, the solution darkened to a deep purple. After removing the solvent, the product was extracted with three DCM/H_2O washes and the organic layer dried with Na_2SO_4. Removal of the solvent gave a deep purple solid, and purification achieved with a room temperature 1:20 CH_2Cl_2/hexanes (v/v) recrystallization. Single crystals suitable for X-ray diffraction were grown by layering pentane over a concentrated solution of **3** in ethyl acetate. Yield: 44 mg, 88%. Elem. Anal. Found (Calcd) for $C_{52}H_{44}N_9Cl_2ORu_2$ (**3**·CH_2Cl_2·H_2O): C, 57.57 (57.62); H, 3.99 (4.09); N, 11.25 (11.63). ESI-MS (*m / z*, based on ^{101}Ru): $[M]^+$ = 982.3. UV-Vis (in THF) λ / nm (ε / M^{-1} cm^{-1}): 341 (17500), 553 (6900), (sh)597 (6100), (sh)611 (4200), 958 (4700), (sh)1166 (2600). IR ν / cm^{-1}: 2089

$\overline{\nu}$(C≡N). μ_{eff} (21°C) (Evans method) = 2.26 μ_B. Electrochemistry (THF, vs $Fc^{+/0}$), $E_{1/2}$ / V, ΔE_p /mV, $i_{backward}/i_{forward}$: 0.21, 82, 0.99; -0.916, 82, 0.95. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 1.7 Hz, 4H, H(a)), 7.19 – 6.98 (m, 18H, H(b,c,f,h,k)), 6.92 (t, *J* = 7.0 Hz, 1H, H(m)), 6.63 (d, *J* = 7.8 Hz, 2H, H(j)), 6.40 (d, *J* = 8.8 Hz, 4H, H(d)), 6.20 (t, *J* = 6.5 Hz, 4H, H(g)), 6.09 (s, 4H, H(i)), 5.58 (s, 4H, H(e)). Isosbestic points for **3** → **3**$^+$: ca. 15000 cm^{-1}.

Fig. S1 ESI-MS of the crude reaction mixture of **1** at low fragmentation voltages. Isotopic distribution characteristic of $(Ru_2)_2$ corresponding to $[\mathbf{1}]^{2+}$ (m/z = 1835.04 / 2 = 917.52, left). Protonolysis product $Ru_2(ap)_4(C_6H_5)$ (right).

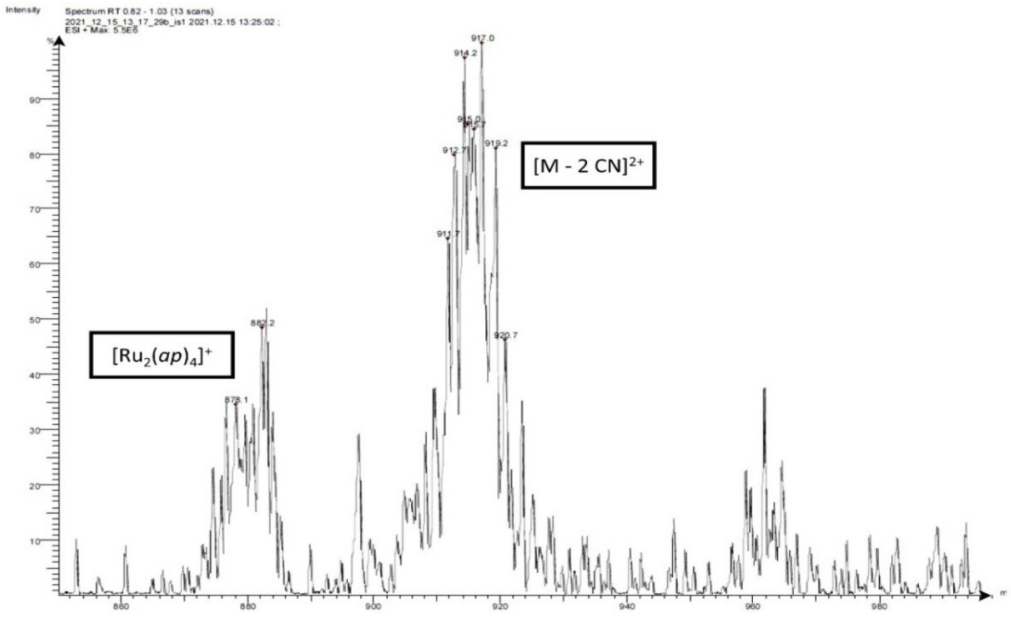


Fig. S2 ESI-MS of **2** at high fragmentation voltages. Isotopic distribution characteristic of $(Ru_2)_2$ corresponding to [**2 – 2 CN**]$^{2+}$ (m/z = (1886.06 – 2(26.02)) / 2 = 917.01, middle). Fragmentation product $[Ru_2(ap)_4]^+$ (left).

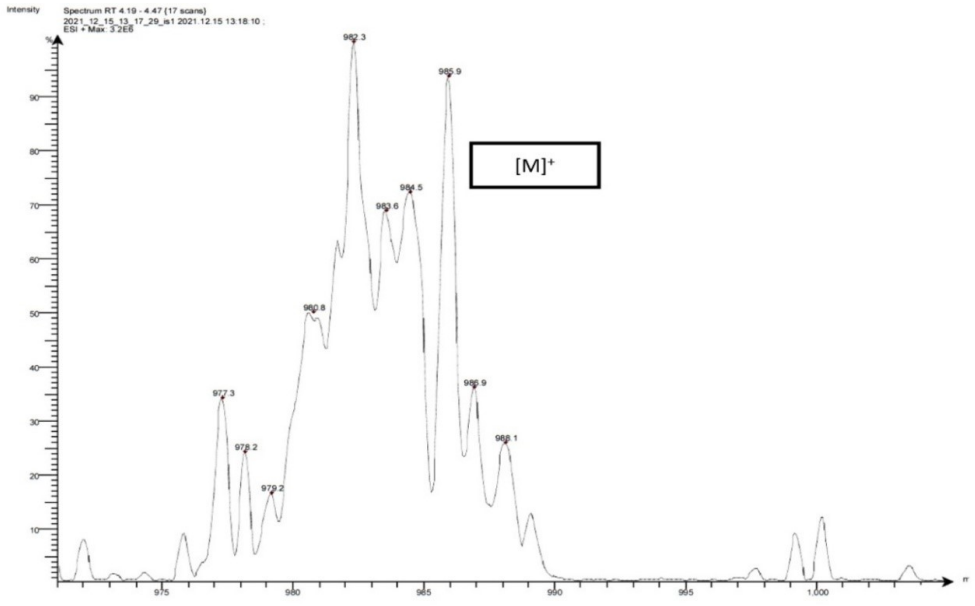


Fig. S3 ESI-MS of **3** at low fragmentation voltages. Isotopic distribution characteristic of Ru_2 corresponding to [**3**]$^+$ (m/z = 982.09).

2. X-ray Structural analysis

Crystals suitable for X-ray diffraction analysis were grown by either layering diethyl ether over a concentrated solution of **2** in THF or layering pentane over a concentrated solution of **3** in ethyl acetate. Single crystals of **2** were coated with paraffin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon-III C14 area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Kα radiation (λ = 1.54178 Å) at 150 K. Single crystals of **3** were coated with paraffin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon II area detector, and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at 150 K. In one of the structures (**2**), only part of the solvent molecules were sufficiently resolved to model, and were included as partially occupied. Based on the XRD data it was not possible to determine whether the remaining volume remained unoccupied, or if additional highly disordered solvate molecules are present. A complete removal of the partially occupied solvent molecules via the Squeeze procedure did not substantially improve the overall quality of the structure, and we thus decided to include the resolved fraction of the void content as partially occupied solvate molecules.

Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3[7] and SADABS.[8] The space groups were assigned using XPREP within the SHELXTL suite of programs[9, 10] and solved by direct methods using ShelXS[10] or dual methods using ShelXT[11] and refined by full matrix least squares against F^2 with all reflections

using Shelxl2018[12, 13] using the graphical interface Shelxle.[14] Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2149734-2149735 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

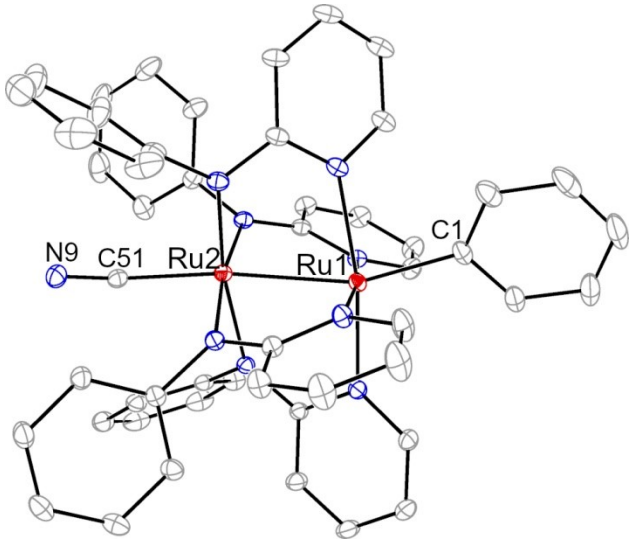


Fig. S4 Molecular structure of **3** at 30% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Full atom labels below.

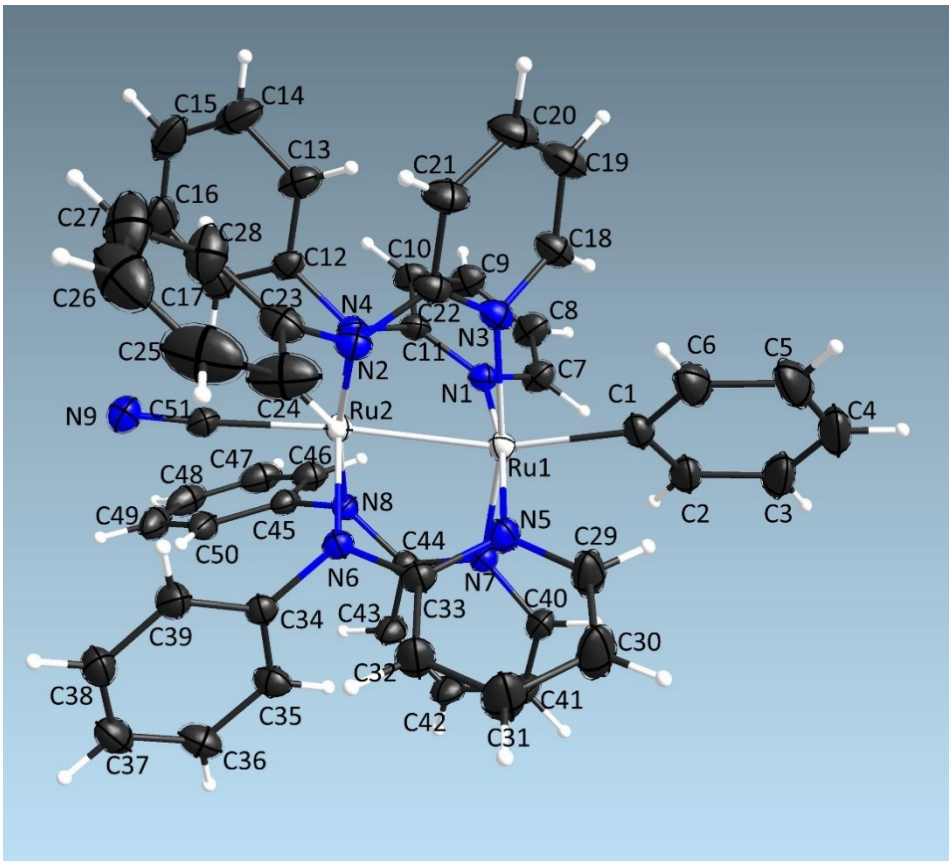
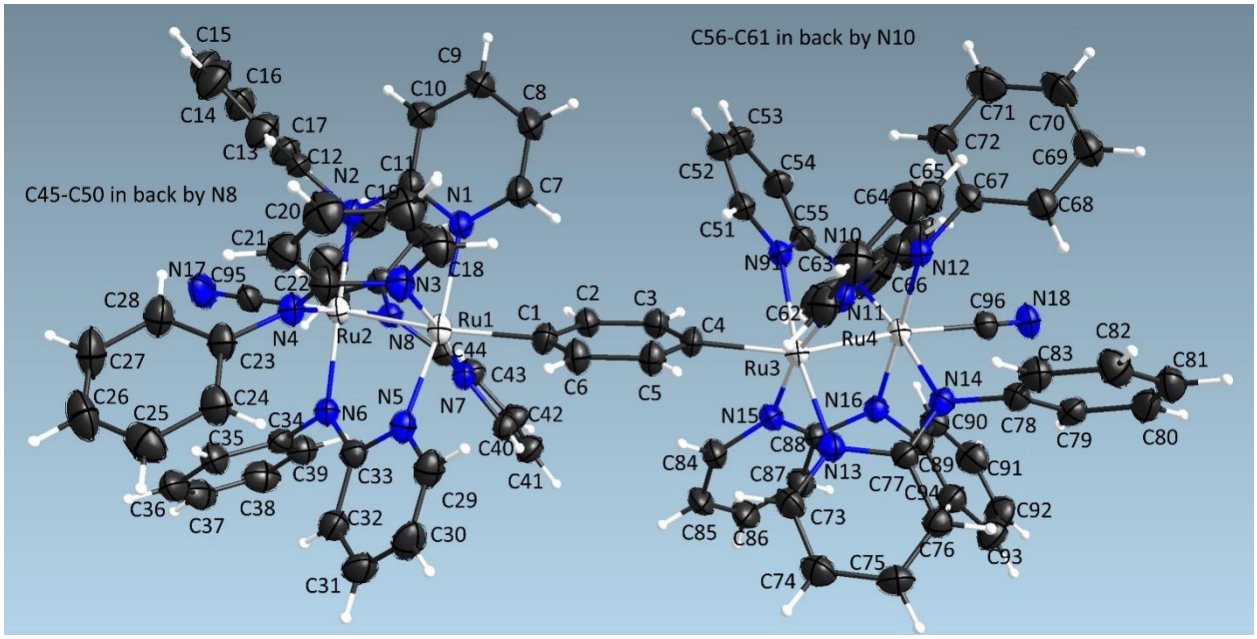


Table S1 Full bond lengths and angles for **3**.

Ru1—N7	2.0293 (13)	C15—C16	1.376 (4)
Ru1—N1	2.0423 (13)	C16—C17	1.389 (3)
Ru1—C1	2.0523 (16)	C18—C19	1.372 (2)
Ru1—N5	2.1331 (13)	C19—C20	1.393 (3)
Ru1—N3	2.1589 (13)	C20—C21	1.371 (3)
Ru1—Ru2	2.5011 (2)	C21—C22	1.423 (2)
Ru2—N4	1.9775 (13)	C23—C24	1.383 (3)
Ru2—N6	1.9963 (12)	C23—C28	1.385 (3)
Ru2—C51	2.0081 (15)	C24—C25	1.400 (3)
Ru2—N2	2.0399 (12)	C25—C26	1.366 (4)
Ru2—N8	2.1462 (12)	C26—C27	1.377 (4)
N1—C7	1.360 (2)	C27—C28	1.392 (3)
N1—C11	1.3817 (19)	C29—C30	1.373 (3)
N2—C11	1.3515 (19)	C30—C31	1.395 (3)
N2—C12	1.4354 (19)	C31—C32	1.361 (2)
N3—C18	1.360 (2)	C32—C33	1.426 (2)
N3—C22	1.371 (2)	C34—C39	1.390 (2)
N4—C22	1.355 (2)	C34—C35	1.397 (2)

N4—C23	1.429 (2)	C35—C36	1.385 (2)
N5—C29	1.365 (2)	C36—C37	1.387 (3)
N5—C33	1.373 (2)	C37—C38	1.380 (3)
N6—C33	1.3581 (19)	C38—C39	1.391 (2)
N6—C34	1.4296 (19)	C40—C41	1.366 (2)
N7—C40	1.3669 (19)	C41—C42	1.399 (3)
N7—C44	1.3750 (19)	C42—C43	1.369 (2)
N8—C44	1.3589 (19)	C43—C44	1.426 (2)
N8—C45	1.4261 (19)	C45—C50	1.393 (2)
N9—C51	1.156 (2)	C45—C46	1.401 (2)
C1—C2	1.402 (3)	C46—C47	1.392 (2)
C1—C6	1.403 (2)	C47—C48	1.382 (3)
C2—C3	1.399 (3)	C48—C49	1.385 (3)
C3—C4	1.382 (4)	C49—C50	1.399 (2)
C4—C5	1.377 (4)		
C5—C6	1.398 (3)		
C7—C8	1.371 (2)		
C8—C9	1.400 (3)		
C9—C10	1.368 (2)		
C10—C11	1.430 (2)		
C12—C13	1.389 (2)		
C12—C17	1.390 (2)		
C13—C14	1.397 (3)		
C14—C15	1.384 (4)		
N7—Ru1—N1	93.24 (5)	C13—C12—N2	118.26 (15)
N7—Ru1—C1	107.46 (6)	C17—C12—N2	121.83 (15)
N1—Ru1—C1	100.30 (6)	C12—C13—C14	119.77 (19)
N7—Ru1—N5	83.83 (5)	C15—C14—C13	120.0 (2)
N1—Ru1—N5	172.15 (5)	C16—C15—C14	120.09 (19)
C1—Ru1—N5	87.54 (6)	C15—C16—C17	120.5 (2)
N7—Ru1—N3	169.38 (5)	C16—C17—C12	119.7 (2)
N1—Ru1—N3	83.06 (5)	N3—C18—C19	124.03 (17)
C1—Ru1—N3	83.03 (6)	C18—C19—C20	118.39 (17)
N5—Ru1—N3	98.53 (5)	C21—C20—C19	119.24 (16)
N7—Ru1—Ru2	93.80 (4)	C20—C21—C22	119.53 (17)
N1—Ru1—Ru2	88.63 (4)	N4—C22—N3	117.21 (13)
C1—Ru1—Ru2	156.27 (5)	N4—C22—C21	122.56 (15)
N5—Ru1—Ru2	84.31 (4)	N3—C22—C21	120.05 (15)
N3—Ru1—Ru2	76.22 (4)	C24—C23—C28	119.55 (18)
N4—Ru2—N6	92.91 (5)	C24—C23—N4	119.78 (18)
N4—Ru2—C51	95.46 (6)	C28—C23—N4	120.67 (15)
N6—Ru2—C51	92.54 (6)	C23—C24—C25	119.5 (2)
N4—Ru2—N2	92.90 (5)	C26—C25—C24	120.9 (2)
N6—Ru2—N2	171.08 (5)	C25—C26—C27	119.6 (2)

C51—Ru2—N2	93.64 (6)	C9—C10—C11	121.27 (15)
N4—Ru2—N8	171.05 (5)	N2—C11—N1	118.37 (13)
N6—Ru2—N8	87.75 (5)	N2—C11—C10	122.71 (14)
C51—Ru2—N8	93.42 (5)	N1—C11—C10	118.90 (14)
N2—Ru2—N8	85.47 (5)	C13—C12—C17	119.91 (16)
N4—Ru2—Ru1	93.55 (4)	C26—C27—C28	120.4 (3)
N6—Ru2—Ru1	88.40 (4)	C23—C28—C27	120.1 (2)
C51—Ru2—Ru1	170.88 (4)	N5—C29—C30	124.60 (17)
N2—Ru2—Ru1	84.48 (4)	C29—C30—C31	118.99 (17)
N8—Ru2—Ru1	77.54 (3)	C32—C31—C30	118.48 (17)
C7—N1—C11	118.23 (13)	C31—C32—C33	120.72 (16)
C7—N1—Ru1	122.87 (11)	N6—C33—N5	118.90 (13)
C11—N1—Ru1	118.66 (10)	N6—C33—C32	120.25 (14)
C11—N2—C12	115.22 (12)	N5—C33—C32	120.81 (14)
C11—N2—Ru2	123.49 (10)	C39—C34—C35	119.41 (15)
C12—N2—Ru2	121.05 (10)	C39—C34—N6	122.07 (14)
C18—N3—C22	116.88 (14)	C35—C34—N6	118.50 (13)
C18—N3—Ru1	119.34 (11)	C36—C35—C34	120.41 (16)
C22—N3—Ru1	123.78 (10)	C35—C36—C37	119.88 (17)
C22—N4—C23	118.32 (13)	C38—C37—C36	119.88 (16)
C22—N4—Ru2	114.63 (10)	C37—C38—C39	120.68 (17)
C23—N4—Ru2	126.56 (10)	C34—C39—C38	119.70 (16)
C29—N5—C33	116.29 (14)	C41—C40—N7	123.15 (15)
C29—N5—Ru1	123.23 (11)	C40—C41—C42	118.23 (15)
C33—N5—Ru1	119.21 (10)	C43—C42—C41	119.95 (16)
C33—N6—C34	115.55 (12)	C42—C43—C44	120.51 (15)
C33—N6—Ru2	121.39 (10)	N8—C44—N7	118.41 (13)
C34—N6—Ru2	122.29 (9)	N8—C44—C43	123.14 (13)
C40—N7—C44	119.37 (13)	N7—C44—C43	118.36 (13)
C40—N7—Ru1	126.78 (11)	C50—C45—C46	119.27 (15)
C44—N7—Ru1	113.77 (10)	C50—C45—N8	122.54 (14)
C44—N8—C45	113.46 (12)	C46—C45—N8	118.16 (14)
C44—N8—Ru2	124.34 (10)	C47—C46—C45	120.49 (18)
C45—N8—Ru2	122.14 (9)	C48—C47—C46	120.00 (18)
C2—C1—C6	116.74 (16)	C47—C48—C49	119.81 (16)
C2—C1—Ru1	114.69 (12)	C48—C49—C50	120.84 (18)
C6—C1—Ru1	128.43 (15)	C45—C50—C49	119.50 (17)
C3—C2—C1	121.74 (19)	N9—C51—Ru2	173.73 (14)
C4—C3—C2	120.3 (2)		
C5—C4—C3	119.06 (19)		
C4—C5—C6	121.1 (2)		
C5—C6—C1	121.1 (2)		
N1—C7—C8	124.05 (16)		
C7—C8—C9	118.81 (16)		
C10—C9—C8	118.71 (15)		



Full list of atom numbers for compound **2**. *ap* ligand numbers:

N1/N2 and C7-C17; N3/N4 and C18-C28; N5/N6 and C29-C39; N7/N8 and C40-C50

N9/N10 and C51-C61; N11/N12 and C62-C72; N13/N14 and C73-C83; N15/N16 and C84-C94

Table S2 Full bond lengths and angles for **2**.

Ru1—N3	2.031 (3)	C36—C37	1.376 (6)
Ru1—N5	2.036 (3)	C37—C38	1.381 (6)
Ru1—C1	2.052 (3)	C38—C39	1.391 (5)
Ru1—N1	2.153 (3)	C40—C41	1.367 (5)
Ru1—N7	2.155 (3)	C41—C42	1.393 (5)
Ru1—Ru2	2.4892 (3)	C42—C43	1.370 (5)
Ru2—N8	1.973 (3)	C43—C44	1.417 (5)
Ru2—N2	1.985 (3)	C45—C50	1.386 (5)
Ru2—C95	2.019 (3)	C45—C46	1.389 (5)
Ru2—N6	2.045 (3)	C46—C47	1.380 (6)
Ru2—N4	2.200 (3)	C47—C48	1.353 (7)
Ru3—N11	2.024 (3)	C48—C49	1.390 (8)
Ru3—N13	2.042 (3)	C49—C50	1.392 (6)
Ru3—C4	2.051 (3)	C51—C52	1.375 (5)
Ru3—N15	2.119 (3)	C52—C53	1.391 (6)
Ru3—N9	2.165 (3)	C53—C54	1.361 (6)
Ru3—Ru4	2.4829 (3)	C5—C6	1.409 (4)
Ru4—N10	1.969 (3)	C7—C8	1.349 (6)

Ru4—N16	1.982 (3)	C8—C9	1.398 (6)
Ru4—C96	2.013 (3)	C9—C10	1.365 (5)
Ru4—N12	2.073 (3)	C10—C11	1.413 (5)
Ru4—N14	2.169 (3)	C12—C13	1.376 (5)
N1—C11	1.368 (4)	C12—C17	1.383 (5)
N1—C7	1.374 (4)	C13—C14	1.394 (6)
N2—C11	1.362 (4)	C14—C15	1.379 (7)
N2—C12	1.444 (4)	C15—C16	1.374 (6)
N3—C18	1.359 (5)	C16—C17	1.387 (5)
N3—C22	1.372 (4)	C18—C19	1.364 (5)
N4—C22	1.357 (4)	C19—C20	1.396 (6)
N4—C23	1.427 (4)	C20—C21	1.363 (6)
N5—C29	1.360 (4)	C21—C22	1.418 (5)
N5—C33	1.378 (4)	C23—C28	1.394 (5)
N6—C33	1.358 (4)	C23—C24	1.399 (5)
N6—C34	1.446 (4)	C24—C25	1.389 (5)
N7—C44	1.362 (4)	C25—C26	1.383 (7)
N7—C40	1.367 (4)	C26—C27	1.370 (7)
N8—C44	1.362 (4)	C27—C28	1.388 (6)
N8—C45	1.425 (4)	C29—C30	1.362 (6)
N9—C51	1.355 (4)	C30—C31	1.392 (6)
N9—C55	1.361 (4)	C31—C32	1.361 (5)
N10—C55	1.355 (4)	C32—C33	1.425 (5)
N10—C56	1.431 (5)	C34—C35	1.382 (5)
N11—C62	1.363 (4)	C34—C39	1.391 (5)
N11—C66	1.380 (4)	C35—C36	1.394 (5)
N12—C66	1.345 (4)	C54—C55	1.418 (5)
N12—C67	1.430 (4)	C56—C57	1.380 (6)
N13—C73	1.357 (4)	C56—C61	1.387 (6)
N13—C77	1.375 (4)	C57—C58	1.408 (7)
N14—C77	1.354 (4)	C58—C59	1.355 (11)
N14—C78	1.430 (4)	C59—C60	1.356 (10)
N15—C88	1.365 (4)	C60—C61	1.390 (7)
N15—C84	1.369 (4)	C62—C63	1.363 (5)
N16—C88	1.357 (4)	C63—C64	1.406 (6)
N16—C89	1.425 (4)	C64—C65	1.360 (5)
N17—C95	1.140 (4)	C65—C66	1.430 (5)
N18—C96	1.143 (4)	C67—C72	1.379 (5)
C1—C6	1.393 (5)	C67—C68	1.387 (5)
C1—C2	1.399 (4)	C68—C69	1.391 (5)
C2—C3	1.389 (4)	C69—C70	1.360 (6)
C3—C4	1.401 (4)	C70—C71	1.381 (7)
C4—C5	1.381 (4)	C71—C72	1.390 (6)
C73—C74	1.369 (5)		
C74—C75	1.405 (5)		

C75—C76	1.366 (5)		
C76—C77	1.424 (4)		
C78—C79	1.388 (5)		
C78—C83	1.402 (5)		
C79—C80	1.389 (5)		
C80—C81	1.387 (5)		
C81—C82	1.380 (5)		
C82—C83	1.391 (5)		
C84—C85	1.359 (5)		
C85—C86	1.390 (6)		
C86—C87	1.362 (5)		
C87—C88	1.426 (5)		
C89—C94	1.387 (5)		
C89—C90	1.392 (5)		
C90—C91	1.390 (5)		
C91—C92	1.378 (6)		
C92—C93	1.386 (6)		
C93—C94	1.385 (5)		
N3—Ru1—N5	93.66 (11)	C5—C4—C3	117.2 (3)
N3—Ru1—C1	107.02 (12)	C5—C4—Ru3	121.4 (2)
N5—Ru1—C1	103.61 (12)	C3—C4—Ru3	121.3 (2)
N3—Ru1—N1	81.04 (11)	C4—C5—C6	121.4 (3)
N5—Ru1—N1	170.96 (10)	C1—C6—C5	121.5 (3)
C1—Ru1—N1	85.01 (12)	C8—C7—N1	125.0 (3)
N3—Ru1—N7	172.22 (11)	C7—C8—C9	119.6 (4)
N5—Ru1—N7	82.96 (10)	C10—C9—C8	117.2 (4)
C1—Ru1—N7	80.64 (11)	C9—C10—C11	121.5 (4)
N1—Ru1—N7	101.36 (10)	N2—C11—N1	118.6 (3)
N3—Ru1—Ru2	96.34 (8)	N2—C11—C10	120.6 (3)
N5—Ru1—Ru2	89.40 (7)	N1—C11—C10	120.8 (3)
C1—Ru1—Ru2	152.21 (9)	C13—C12—C17	120.2 (3)
N1—Ru1—Ru2	83.95 (7)	C13—C12—N2	118.7 (3)
N7—Ru1—Ru2	76.67 (7)	C17—C12—N2	121.0 (3)
N8—Ru2—N2	91.89 (11)	C12—C13—C14	119.8 (4)
N8—Ru2—C95	97.94 (12)	C15—C14—C13	119.9 (4)
N2—Ru2—C95	91.40 (12)	C16—C15—C14	120.1 (4)
N8—Ru2—N6	93.69 (11)	C15—C16—C17	120.2 (4)
N2—Ru2—N6	172.66 (11)	C12—C17—C16	119.8 (4)
C95—Ru2—N6	92.53 (12)	N3—C18—C19	122.7 (3)
N8—Ru2—N4	169.65 (10)	C18—C19—C20	118.1 (4)
N2—Ru2—N4	89.12 (11)	C21—C20—C19	120.4 (3)
C95—Ru2—N4	92.33 (12)	C20—C21—C22	120.3 (4)
N6—Ru2—N4	84.53 (11)	N4—C22—N3	118.4 (3)
N8—Ru2—Ru1	93.84 (8)	N4—C22—C21	123.3 (3)

N2—Ru2—Ru1	90.40 (8)	N3—C22—C21	118.2 (3)
C95—Ru2—Ru1	168.02 (10)	C28—C23—C24	118.2 (3)
N6—Ru2—Ru1	84.48 (7)	C28—C23—N4	122.9 (3)
N4—Ru2—Ru1	75.86 (7)	C24—C23—N4	118.9 (3)
N11—Ru3—N13	90.71 (11)	C25—C24—C23	121.3 (4)
N11—Ru3—C4	106.84 (12)	C26—C25—C24	119.5 (4)
N13—Ru3—C4	111.65 (12)	C27—C26—C25	119.8 (4)
N11—Ru3—N15	168.67 (10)	C26—C27—C28	121.4 (4)
N13—Ru3—N15	80.59 (11)	C27—C28—C23	119.9 (4)
C4—Ru3—N15	83.27 (12)	N5—C29—C30	124.1 (3)
N11—Ru3—N9	83.98 (11)	C29—C30—C31	118.4 (3)
N13—Ru3—N9	170.34 (10)	C32—C31—C30	119.6 (4)
C4—Ru3—N9	77.70 (12)	C31—C32—C33	120.7 (4)
N15—Ru3—N9	103.56 (11)	N6—C33—N5	117.8 (3)
N11—Ru3—Ru4	89.82 (8)	N6—C33—C32	123.3 (3)
N13—Ru3—Ru4	95.84 (8)	N5—C33—C32	118.8 (3)
C4—Ru3—Ru4	147.14 (9)	C35—C34—C39	120.1 (3)
N15—Ru3—Ru4	83.91 (7)	C35—C34—N6	118.3 (3)
N9—Ru3—Ru4	76.13 (7)	C39—C34—N6	121.6 (3)
N10—Ru4—N16	91.98 (11)	C34—C35—C36	119.4 (4)
N10—Ru4—C96	95.31 (12)	C37—C36—C35	120.7 (4)
N16—Ru4—C96	89.61 (12)	C36—C37—C38	119.7 (4)
N10—Ru4—N12	92.39 (11)	C37—C38—C39	120.3 (4)
N16—Ru4—N12	173.11 (11)	C34—C39—C38	119.7 (4)
C96—Ru4—N12	95.28 (11)	C41—C40—N7	124.1 (3)
N10—Ru4—N14	170.83 (11)	C40—C41—C42	118.3 (3)
N16—Ru4—N14	89.18 (10)	C43—C42—C41	119.3 (3)
C96—Ru4—N14	93.80 (11)	C42—C43—C44	119.7 (3)
N12—Ru4—N14	85.66 (10)	N8—C44—N7	117.1 (3)
N10—Ru4—Ru3	94.06 (8)	N8—C44—C43	122.1 (3)
N16—Ru4—Ru3	90.89 (8)	N7—C44—C43	120.6 (3)
C96—Ru4—Ru3	170.60 (9)	C50—C45—C46	120.0 (3)
N12—Ru4—Ru3	83.49 (7)	C50—C45—N8	121.3 (3)
N14—Ru4—Ru3	76.83 (7)	C46—C45—N8	118.8 (3)
C11—N1—C7	115.6 (3)	C47—C46—C45	119.8 (4)
C11—N1—Ru1	120.6 (2)	C48—C47—C46	121.0 (4)
C7—N1—Ru1	121.7 (2)	C47—C48—C49	119.6 (4)
C11—N2—C12	114.7 (3)	C48—C49—C50	120.6 (5)
C11—N2—Ru2	122.0 (2)	C45—C50—C49	118.9 (4)
C12—N2—Ru2	123.2 (2)	N9—C51—C52	123.6 (4)
C18—N3—C22	120.0 (3)	C51—C52—C53	118.4 (4)
C18—N3—Ru1	126.8 (2)	C54—C53—C52	119.4 (4)
C22—N3—Ru1	112.9 (2)	C53—C54—C55	119.5 (4)
C22—N4—C23	114.0 (3)	N10—C55—N9	116.7 (3)
C22—N4—Ru2	124.7 (2)	N10—C55—C54	122.4 (3)

C23—N4—Ru2	121.1 (2)	N9—C55—C54	120.7 (3)
C29—N5—C33	118.2 (3)	C57—C56—C61	120.3 (4)
C29—N5—Ru1	122.6 (2)	C57—C56—N10	120.9 (4)
C33—N5—Ru1	119.1 (2)	C61—C56—N10	118.8 (4)
C33—N6—C34	116.3 (3)	C56—C57—C58	118.4 (5)
C33—N6—Ru2	124.2 (2)	C59—C58—C57	121.0 (6)
C34—N6—Ru2	118.7 (2)	C58—C59—C60	120.3 (5)
C44—N7—C40	117.0 (3)	C59—C60—C61	120.7 (6)
C44—N7—Ru1	123.9 (2)	C56—C61—C60	119.3 (5)
C40—N7—Ru1	119.0 (2)	C63—C62—N11	123.4 (4)
C44—N8—C45	117.6 (3)	C62—C63—C64	118.3 (4)
C44—N8—Ru2	115.0 (2)	C65—C64—C63	119.5 (4)
C45—N8—Ru2	127.2 (2)	C64—C65—C66	120.9 (4)
C51—N9—C55	117.3 (3)	N12—C66—N11	118.3 (3)
C51—N9—Ru3	118.6 (2)	N12—C66—C65	123.6 (3)
C55—N9—Ru3	124.0 (2)	N11—C66—C65	118.0 (3)
C55—N10—C56	118.5 (3)	C72—C67—C68	119.4 (3)
C55—N10—Ru4	115.0 (2)	C72—C67—N12	118.6 (3)
C56—N10—Ru4	126.3 (2)	C68—C67—N12	121.9 (3)
C62—N11—C66	119.0 (3)	C67—C68—C69	120.1 (4)
C62—N11—Ru3	122.6 (2)	C70—C69—C68	120.4 (4)
C66—N11—Ru3	118.3 (2)	C69—C70—C71	120.0 (4)
C66—N12—C67	114.8 (3)	C70—C71—C72	120.2 (4)
C66—N12—Ru4	123.2 (2)	C67—C72—C71	120.0 (4)
C67—N12—Ru4	121.5 (2)	N13—C73—C74	123.1 (3)
C73—N13—C77	120.1 (3)	C73—C74—C75	118.0 (3)
C73—N13—Ru3	126.8 (2)	C76—C75—C74	119.7 (3)
C77—N13—Ru3	113.1 (2)	C75—C76—C77	120.9 (3)
C77—N14—C78	114.4 (3)	N14—C77—N13	118.3 (3)
C77—N14—Ru4	125.3 (2)	N14—C77—C76	123.6 (3)
C78—N14—Ru4	120.3 (2)	N13—C77—C76	118.0 (3)
C88—N15—C84	116.1 (3)	C79—C78—C83	119.1 (3)
C88—N15—Ru3	121.9 (2)	C79—C78—N14	123.1 (3)
C84—N15—Ru3	119.6 (2)	C83—C78—N14	117.8 (3)
C88—N16—C89	114.6 (3)	C78—C79—C80	119.9 (3)
C88—N16—Ru4	121.2 (2)	C81—C80—C79	120.8 (3)
C89—N16—Ru4	123.7 (2)	C82—C81—C80	119.7 (3)
C6—C1—C2	116.6 (3)	C81—C82—C83	120.1 (3)
C6—C1—Ru1	120.1 (2)	C82—C83—C78	120.4 (3)
C2—C1—Ru1	123.0 (2)	C85—C84—N15	125.3 (3)
C3—C2—C1	121.8 (3)	C84—C85—C86	118.2 (3)
C2—C3—C4	121.4 (3)	C87—C86—C85	119.2 (3)
		C86—C87—C88	120.2 (3)
		N16—C88—N15	118.7 (3)
		N16—C88—C87	120.8 (3)

		N15—C88—C87	120.5 (3)
		C94—C89—C90	119.7 (3)
		C94—C89—N16	119.0 (3)
		C90—C89—N16	121.2 (3)
		C91—C90—C89	119.4 (4)
		C92—C91—C90	120.5 (4)
		C91—C92—C93	120.3 (4)
		C94—C93—C92	119.4 (4)
		C93—C94—C89	120.6 (4)
		N17—C95—Ru2	175.8 (3)
		N18—C96—Ru4	170.8 (3)

Table S3 Crystal data for complexes **2** and **3**.

	2	**3**
Chemical Formula	$C_{96}H_{76}N_{18}Ru_4$· 2.337(OC_4H_{10})·0.824(OC_4H_8)	2($C_{51}H_{41}N_9Ru_2$)· C_5H_{12}·$C_4H_8O_2$
Fw, g/mol	2118.64	2124.38
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	22.2621(10)	11.8877(5)
b, Å	22.2426(9)	20.4352(9)
c, Å	20.7463(9)	19.6259(9)
α °	90	90
β °	109.053(2)	101.0991(18)
γ °	90	90
V, Å^3	9710.1(7)	4678.5(4)
Z	4	2
T, K	150	150
λ, Å	1.54178	0.71073
ρ_{calcd}, g/cm^3	1.449	1.508
μ (mm^{-1})	5.43	0.70
F(000)	4340	2172
Crystal size (mm^3)	0.29 x 0.20 x 0.17	0.62 x 0.22 x 0.18
Radiation	CuKα	MoKα
2θ range (°)	2.1 to 74.7	2.3 to 33.2
Index ranges	-25 < *h* < 27; -27 < *k* < 27; -25 < *l* < 25	-18 < *h* < 18; -31 < *k* < 31; -30 < *l* < 30
Reflections collected	132368	233241
Independent reflections	19838	17892
Data/restraints/parameters	19838/786/1427	17892/312/765
R	0.0397	0.0292
$R_w(F^2)$	0.1063	0.0744
Largest diff. peak/hole e Å^{-3}	0.71, -1.16	0.89, -0.82

3. Electrochemistry details

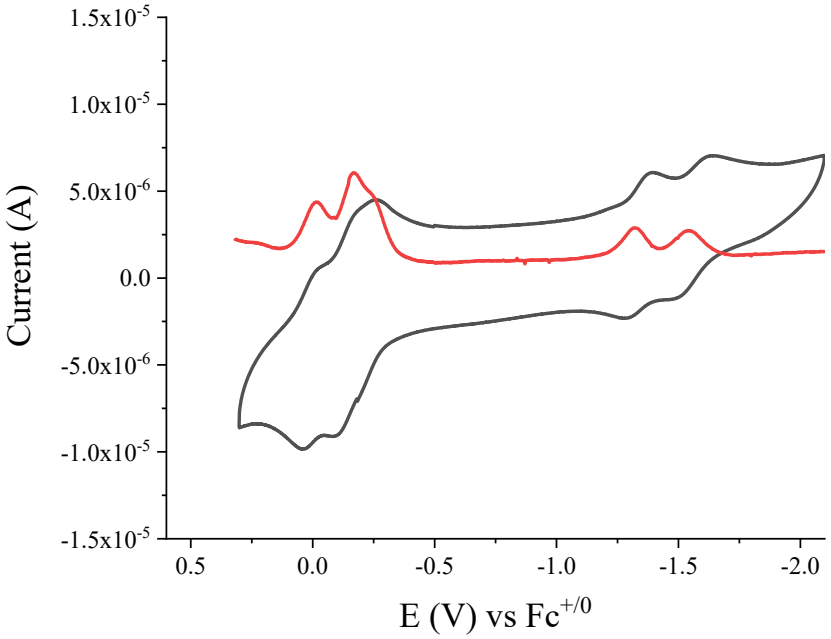


Fig. S5 Cyclic (black) and differential pulse (red) voltammograms of compound **1** (<1.0 mM) recorded in 0.1 M Bu_4NPF_6 in THF at a scan rate of 100 mV/s.

Table S4 Electrochemical data from CV (in V vs. Ag/AgCl).

Compound	+2/+1	+1/0	0/-1	-1/-2
1	-0.010	-0.131	-0.839	-1.068
2	0.838	0.547	-0.374	-0.551
3	----	0.741	-0.385	----
***$Ru_2(ap)_4Cl$**[1]	1.430	0.457	-0.834	----
***$Ru_2(ap)_4(C_6H_5)$**[2]	----	0.100	-1.160	----

*Measurements run in DCM. Compounds **1** – **3** run in THF.

Table S5 Electrochemical data for **1** and **2**.

Compound	$\Delta E_{1/2}$ (+1) (mV)	K_c[a]	$\Delta E_{1/2}$ (-1) (mV)	K_c[a]
1	133	179	221	5568
2	291	85,546	174	889

[a] $K_c = 10^{\Delta E(mV)/59}$

Table S6 Summary of optical & electrochemical data of **2** vs $[Ru_2(ap)_4]_2(\mu\text{-}(C{\equiv}C)_n)$ (n = 1, 2).

	2	$[Ru_2(ap)_4]_2(\mu\text{-}C{\equiv}C)$[15]	$[Ru_2(ap)_4]_2(\mu\text{-}(C{\equiv}C)_2)$[15]
$\Delta E_{1/2}$ (+1) (mV)	291	280	170
$\Delta E_{1/2}$ (-1) (mV)	174	660	380
λ IVCT (cm^{-1}) (ox.)	4,050	----	7,700
ε (M^{-1} cm^{-1}) (ox.)	6,860	----	11,000
$\overline{\nu}_{1/2}$ (cm^{-1}) (ox.)	1,716	----	1,820
Hab (cm^{-1}) (ox.)	647	----	1,022
λ IVCT (cm^{-1}) (red.)	----	----	8,450; 5,670
ε (M^{-1} cm^{-1}) (red.)	----	----	27,000; 7,700
$\overline{\nu}_{1/2}$ (cm^{-1}) (red.)	----	----	1,820; 1,630
Hab (cm^{-1}) (red.)	----	----	1,678; 694
Ru–Ru (Å) Avg.	2.486[4]	----	2.332[2]

4. Absorption Details

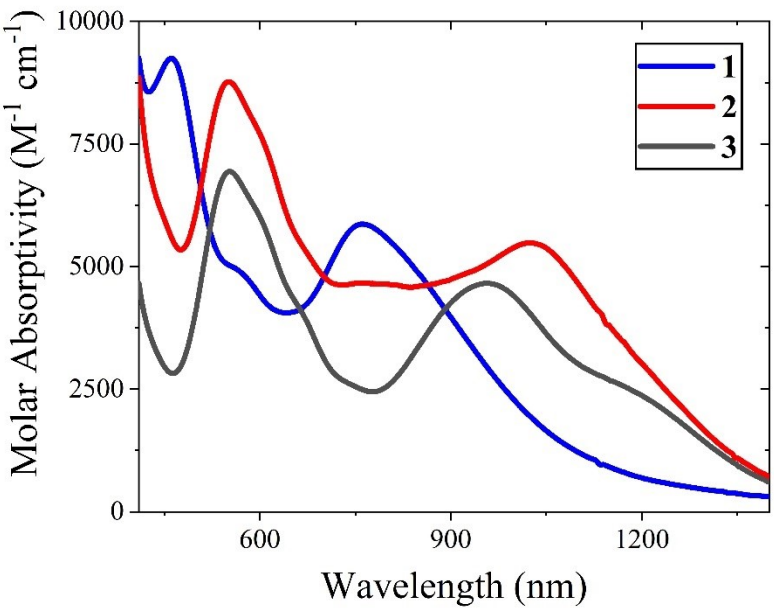


Fig. S6 Vis-NIR absorption of **1**, **2** and **3** in THF.

5. Spectroelectrochemical Vis-NIR spectra of 2

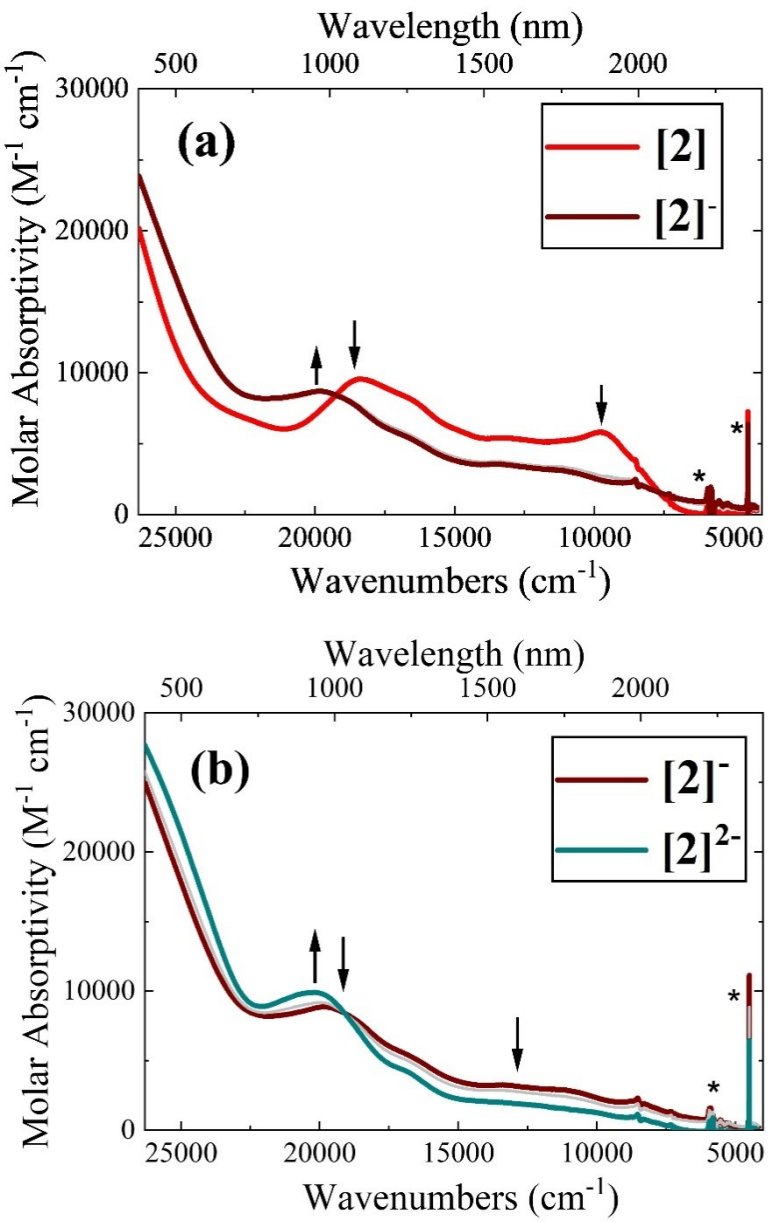


Fig. S7 Full spectroelectrochemical UV-Vis-NIR changes of **2** at −1.1 V (a) and −1.2 V (b) vs Ag wire. 2 mM analyte with 0.1 M $[Bu_4N][PF_6]$ in THF in all cases. Instrument artifacts/solvent overtones noted as *. Isosbestic point located at 1000 nm.

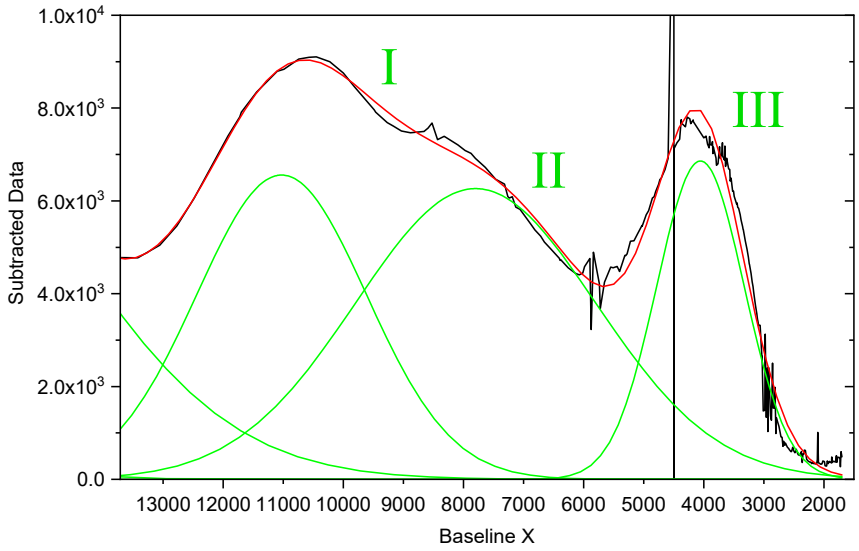
Peak Analysis

Data Set:[Book3]Sheet1!B"Molar Absorptivity" Date:3/2/2022

BaseLine:Constant

Chi^2=2.74712E+05 Adj. R-Square=9.82814E-01 # of Data Points=4487

SS=1.22851E+09 Degrees of Freedom=4472



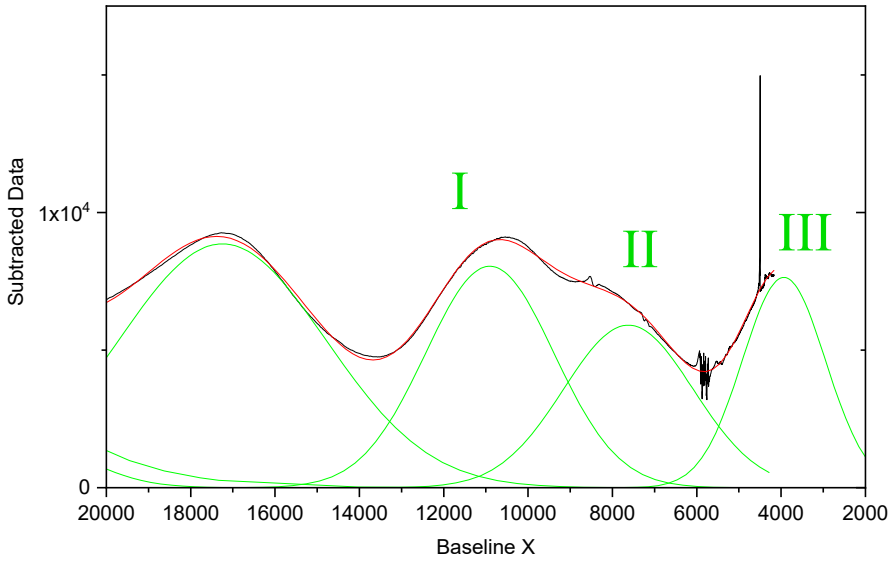
Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	1.25249E7	1716.54256	6859.20063	4054.84527	3.57105
2	Gaussian	3.13663E7	4709.33319	6264.3359	7797.50275	8.94303
3	Gaussian	2.32336E7	3329.01494	6556.44433	11027.33262	6.62426
4	Gaussian	5.98842E7	6506.66669	8646.12887	17385.32735	17.07393
5	Gaussian	2.23726E8	11164.51916	29305.22258	31603.296	63.78774

Fig. S8 Visible-NIR absorption spectrum (black line) of the mixed-valence complex [**2**]$^{+}$ in 0.1 M [NBu_4][PF_6] with additional IR data. Multiple Gaussian bands (green lines) and their sum (red line) to fit the absorption band of [**2**]$^{+}$. IVCT peak of interest is III; labeled as #1 in peak index.

Peak Analysis

Data Set:[Secondoxidati]"Second oxidation"!I"Molar Absorptivity" Date:3/2/2022
BaseLine:Constant
Chi^2=9.42554E+04 Adj. R-Square=9.93965E-01 # of Data Points=2100
SS=1.96240E+08 Degrees of Freedom=2082



Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	7649134.2051	2317.60999	7639.44078	3933.43888	2.23147
2	Gaussian	5.44574E7	5775.62881	8857.78331	17247.37563	15.88678
3	Gaussian	5276508.33156	3260.90507	1520.11436	21759.89636	1.53931
4	Gaussian	2.22196E8	10895.05736	29346.09978	31514.51255	64.82113
5	Gaussian	2.24435E7	3615.54866	5904.16467	7622.5666	6.54741
6	Gaussian	3.07611E7	3592.26903	8044.56733	10906.8928	8.97389

Fig. S9 Visible-NIR absorption spectrum (black line) of the mixed-valence complex $[\mathbf{2}]^{+}$ in 0.1 M $[NBu_4][PF_6]$ without IR data. Multiple Gaussian bands (green lines) and their sum (red line) to fit the absorption band of $[\mathbf{2}]^{+}$. IVCT peak of interest is peak III; labeled as #1 in peak index.

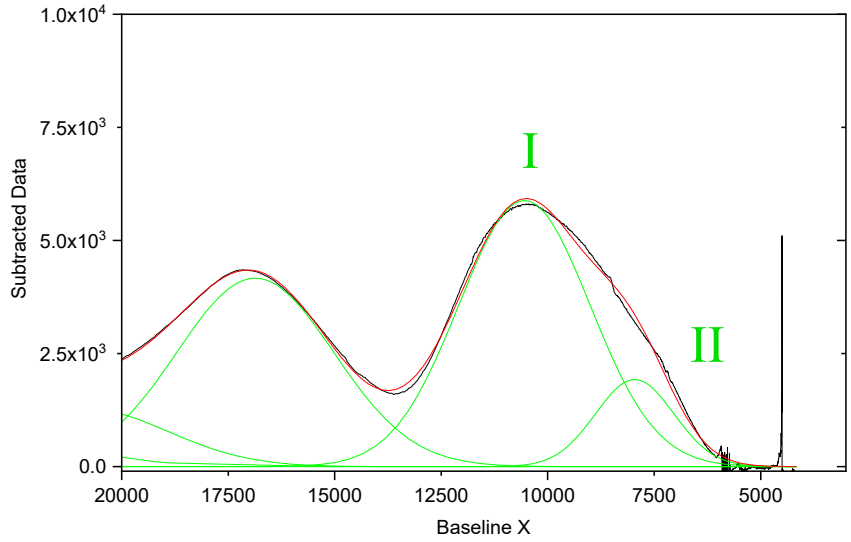
Peak Analysis

Data Set:[Book1]Sheet1!C Date:3/2/2022

BaseLine:Constant

Chi^2=1.22173E+05 Adj. R-Square=9.89738E-01 # of Data Points=2101

SS=2.54853E+08 Degrees of Freedom=2086



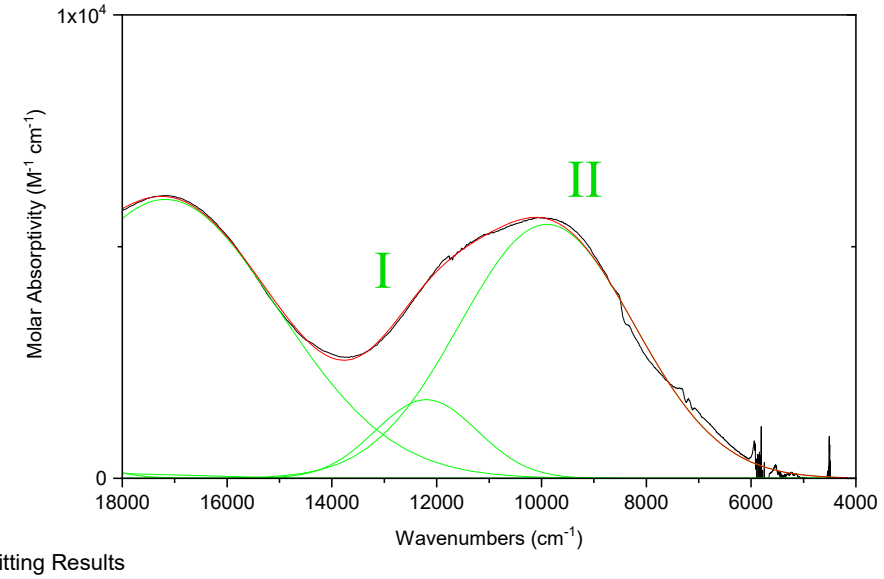
Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	2.27488E7	3634.95995	5879.42081	10546.35519	12.3543
2	Gaussian	1.92391E7	4339.28727	4165.1891	16865.42965	10.44828
3	Gaussian	1.31526E8	9016.53353	20258.84783	31580.36096	71.42849
4	Gaussian	6172690.21362	4549.64608	1274.57283	20832.26971	3.35223
5	Gaussian	4450037.63696	2172.38725	1924.43502	7957.32799	2.4167

Fig. S10 Visible-NIR absorption spectrum (black line) of the complex $[\mathbf{2}]^{2+}$ in 0.1 M NBu_4PF_6 in THF with IR data. Multiple Gaussian bands (green lines) and their sum (red line) to fit the absorption band of $[\mathbf{2}]^{2+}$.

Peak Analysis

Data Set:[Book3]Sheet1!C Date:3/2/2022
BaseLine:Constant
Chi^2=8.42836E+04 Adj. R-Square=9.91461E-01 # of Data Points=2101
SS=1.75563E+08 Degrees of Freedom=2083



Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	3.25388E7	5079.67338	6017.74166	17181.0568	18.03364
2	Gaussian	1864891.37246	2191.95213	799.26402	19806.93192	1.03356
3	Gaussian	1.14512E8	10295.91782	17285.43174	32174.87881	63.46498
4	Gaussian	4551875.41621	2732.91999	1564.70056	22008.92185	2.52274
5	Gaussian	4127909.24167	2285.65541	1696.63012	12196.9372	2.28777
6	Gaussian	2.28381E7	3916.55669	5479.59108	9897.30462	12.65732

Fig. S11 Visible-NIR absorption spectrum (black line) of the complex $[\mathbf{3}]^+$ in 0.1 M NBu_4PF_6 in THF with IR data. Multiple Gaussian bands (green lines) and their sum (red line) to fit the absorption band of $[\mathbf{3}]^+$.

Hush Model Analysis (with IR data):

$$\Delta\overline{\nu}_{1/2theor} = (2310^{*}\ \overline{\nu}_{IVCT})^{0.5}$$

$$\Delta\overline{\nu}_{1/2theor} = (2310^{*}4054)^{0.5} \rightarrow \Delta\overline{\nu}_{1/2theor} = 3{,}060\ cm^{-1}\ (experimental:\ 1{,}716\ cm^{-1})$$

$$H_{ab} = (0.0206 / r)^{*}(\overline{\nu}_{IVCT}\ ^{*}\ \Delta\overline{\nu}_{1/2exp}\ ^{*}\ \varepsilon)^{0.5}\ (\ r = \text{geometric distance or number of bonds})$$

$$H_{ab} = (0.0206 / 6.954)^{*}(4054^{*}1716^{*}6859)^{0.5} \rightarrow H_{ab} = 647.1$$

Hush Model Analysis (w/o IR data):

$$\Delta\overline{\nu}_{1/2theor} = (2310^{*}\ \overline{\nu}_{IVCT})^{0.5}$$

$$\Delta\overline{\nu}_{1/2theor} = (2310^{*}3933)^{0.5} \rightarrow \Delta\overline{\nu}_{1/2theor} = 3{,}014\ cm^{-1}\ (experimental:\ 2{,}316\ cm^{-1})$$

$$H_{ab} = (0.0206 / r)^{*}(\overline{\nu}_{IVCT}\ ^{*}\Delta\overline{\nu}_{1/2exp}\ ^{*}\ \varepsilon)^{0.5}$$

$$H_{ab} = (0.0206 / 6.954)^{*}(3933^{*}2316^{*}7638)^{0.5} \rightarrow H_{ab} = 781.6$$

6. Spectroelectrochemical IR changes of 2

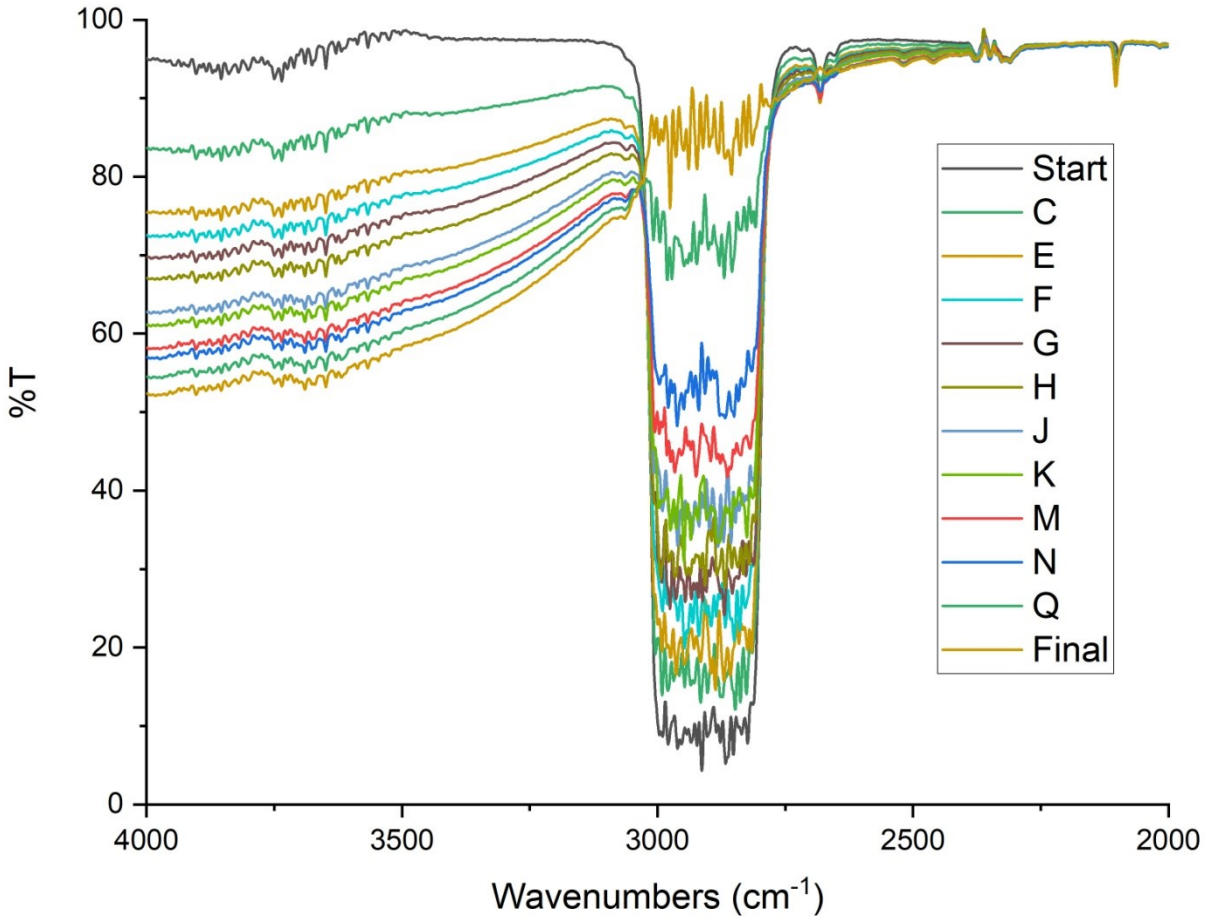


Fig. S12 Full FT-IR spectroelectrochemistry of **2** at 0.1 V vs Ag wire. 2 mM analyte with 0.1 M $[Bu_4N][PF_6]$ in THF in all cases. Upon application of the potential, general absorption from 4,000 cm^{-1} to *ca.* 2,500 cm^{-1} is observed. This was determined not to be shifting of the baseline absorption as the area around $\overline{\nu}$(C≡N) does not experience the same large shifts (see Fig. S13 below). Conversion from %T to absorbance then absorbance values to molar absorptivity values was done to generate the 'missing' half of the IVCT band in the spectra of $[\mathbf{2}]^+$.

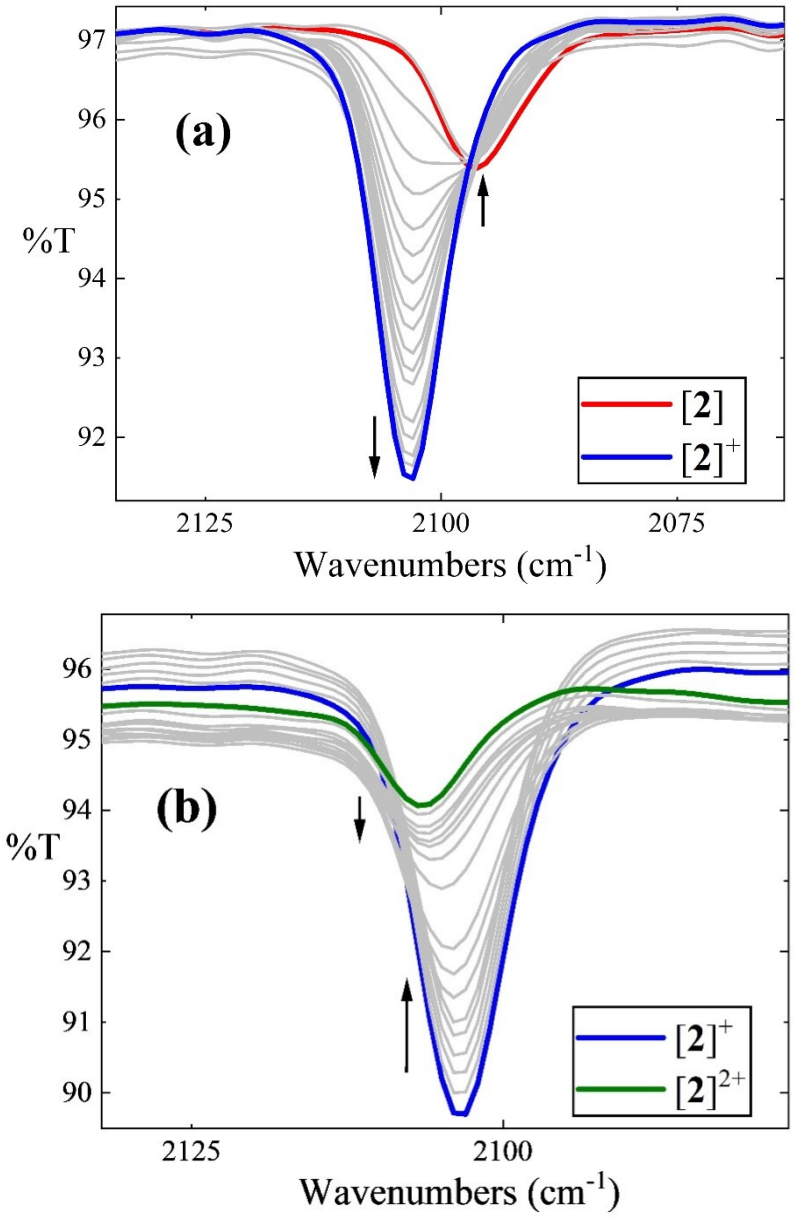


Fig. S13 FT-IR spectroelectrochemistry of **2** at 0.1 V (a) and 0.3-0.4 V (b) vs Ag wire. 2 mM analyte with 0.1 M $[Bu_4N][PF_6]$ in THF in all cases.

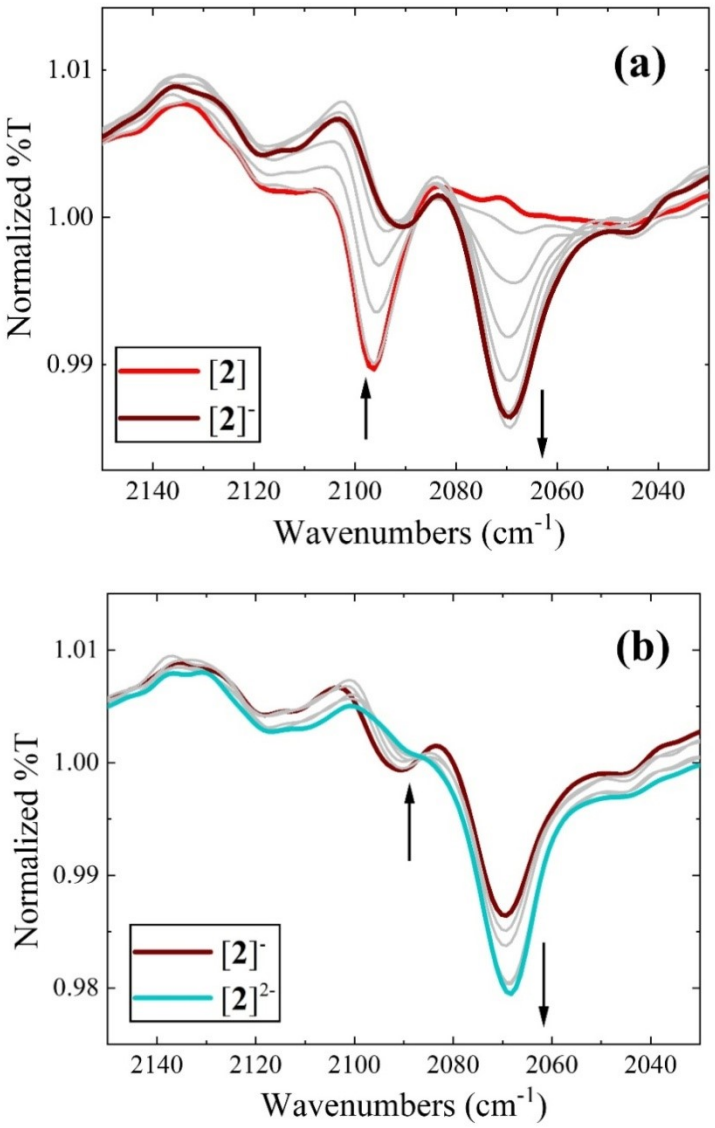


Fig. S14 FT-IR spectroelectrochemistry of **2** at −1.1 V (a) and −1.35 V (b) vs Ag wire. 2 mM analyte with 0.1 M $[Bu_4N][PF_6]$ in THF in all cases.

Table S7 $\overline{\nu}$ (C≡N) of $[\mathbf{2}]^{n-}/[\mathbf{2}]^{n+}$ (n = 1,2) and $[\mathbf{3}]^{+/-}$.

(cm^{-1})	$[\mathbf{2}]^{2+}$	$[\mathbf{2}]^{+}$	**2**	$[\mathbf{2}]^{-}$	$[\mathbf{2}]^{2-}$	$[\mathbf{3}]^{+}$	**3**	$[\mathbf{3}]^{-}$
$\overline{\nu}$ (C≡N)	2107	2103	2096	2092, 2069	2068	2119	2096	2070

7. **Spectroelectrochemical UV-Vis-NIR spectra of [3]$^-$**

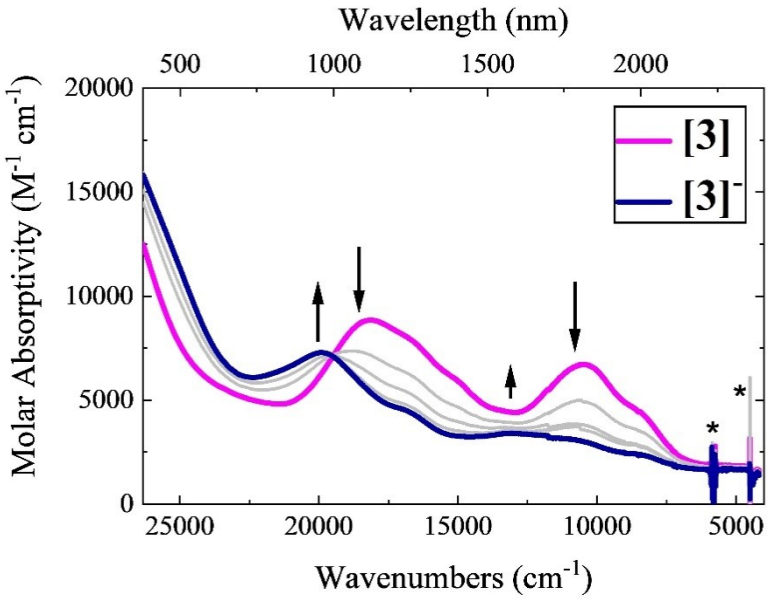


Fig. S15 Spectroelectrochemistry Vis-NIR of **3** at –1.15 V in THF vs Ag wire. 2 mM analyte with 0.1 M [Bu_4N][PF_6] in THF. Instrument artifacts/solvent overtones noted as *.

8. Spectroelectrochemical IR changes of 3

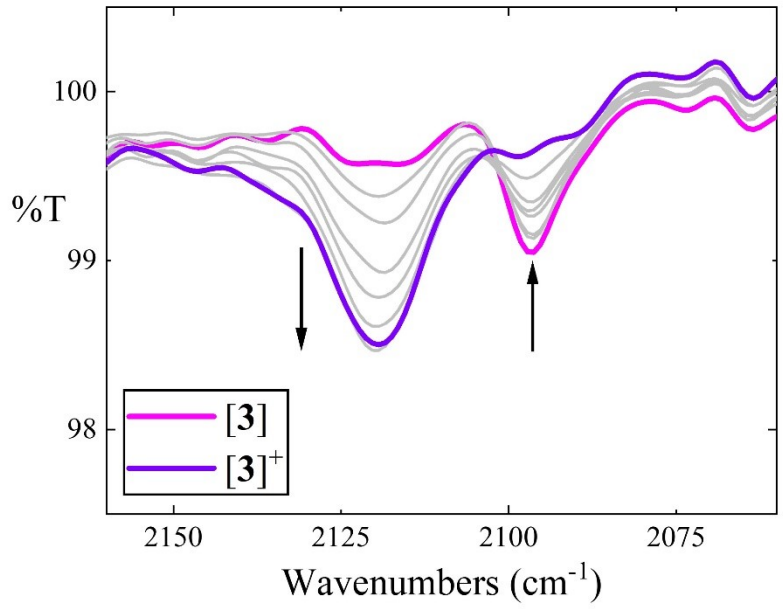


Fig. S16 FT-IR spectroelectrochemistry of **3** at 0.4 V vs Ag wire. 2 mM analyte with 0.1 M $[Bu_4N][PF_6]$ in THF.

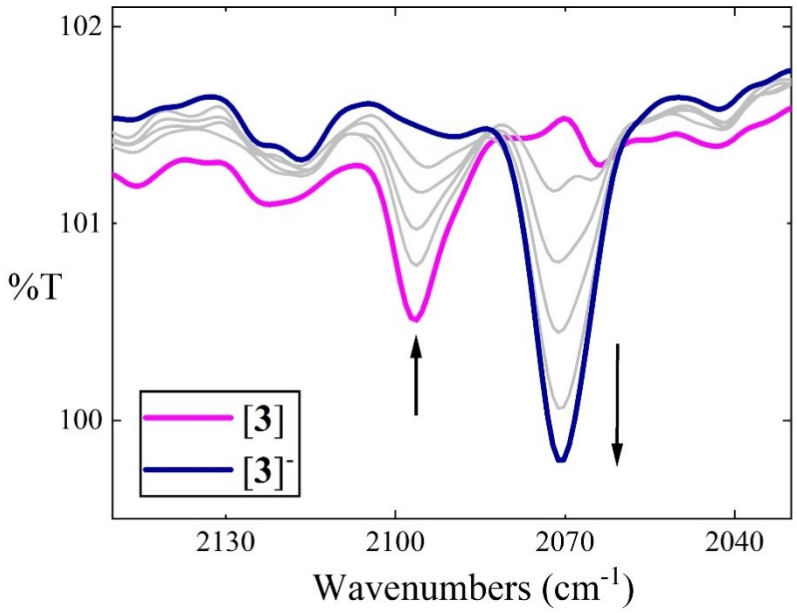


Fig. S17 FT-IR spectroelectrochemistry of **3** at −1.15 V vs Ag wire. 2 mM analyte with 0.1 M $[Bu_4N][PF_6]$ in THF.

9. ^{1}H NMR of 2 and 3

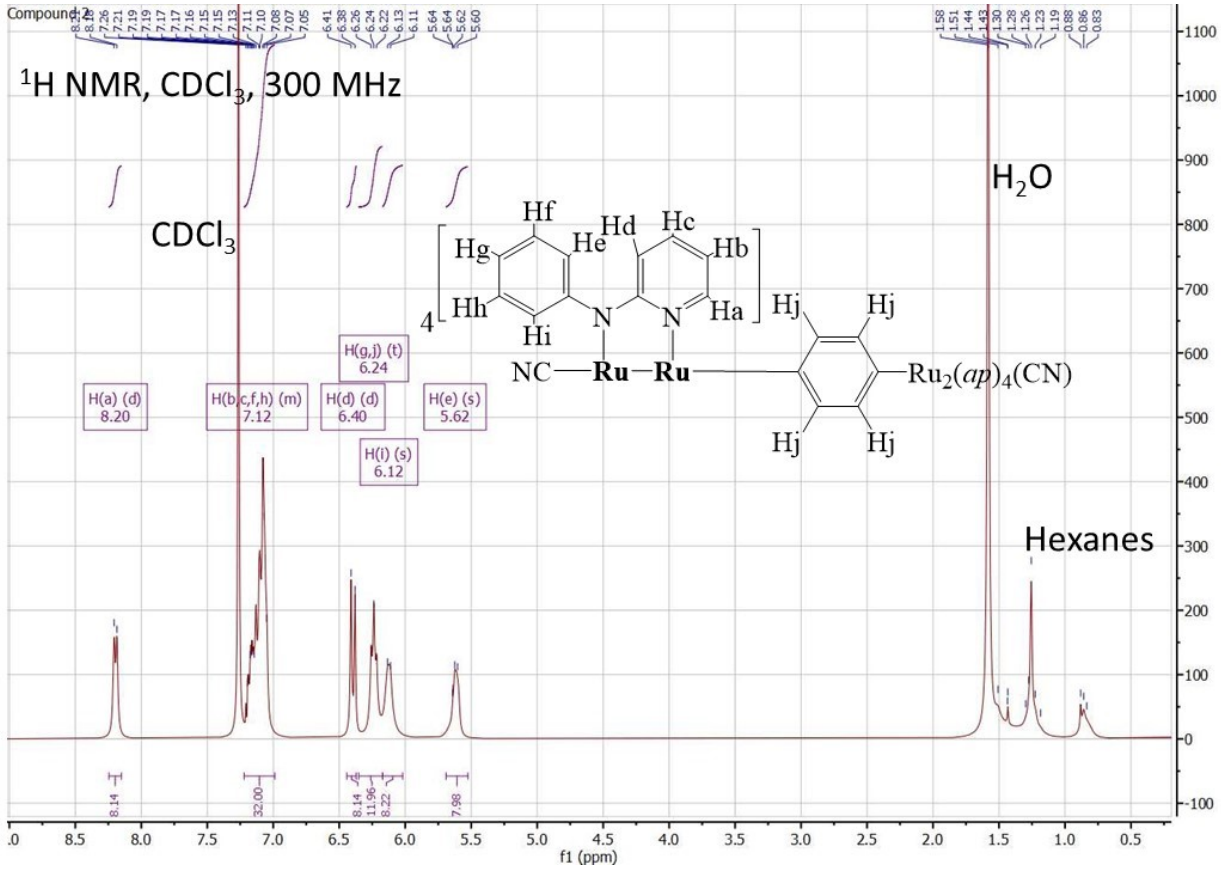


Fig. S18 ^{1}H NMR of **2** in $CDCl_3$ at 293 K. The phenyl protons Hj are assigned to the triplet at 6.24 ppm as we are unable to determine if the expected singlet for Hj is overlapped by the expected triplet for Hg. These protons are shifted from **3**, but since all four protons of the phenyl are near Ru_2 atoms, all would be shifted to lower ppm. The remaining *ap*-based peaks match well with the assignments for **3** in **Fig. S19**.

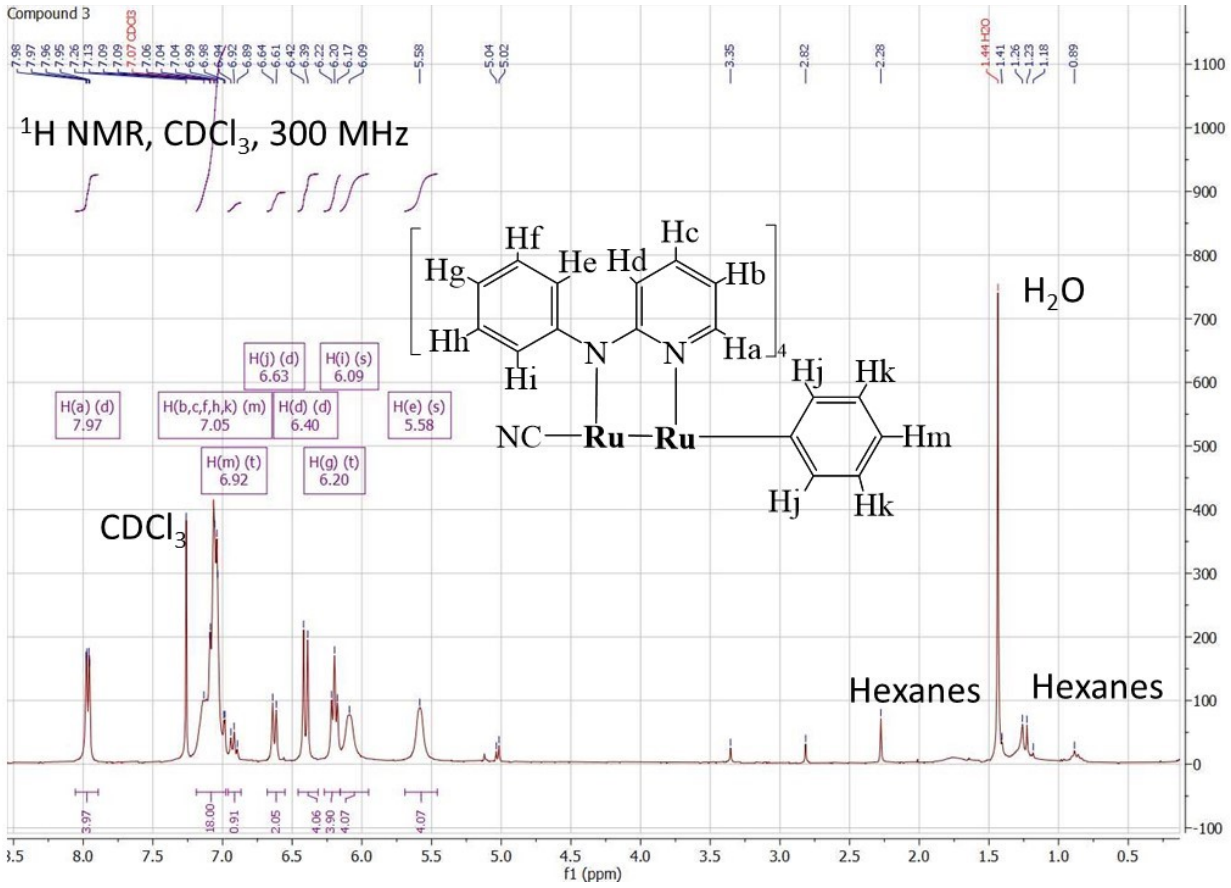


Fig. S19 ^{1}H NMR of **3** in $CDCl_3$ at 293 K. For the phenyl proton assignments, the peak Hm is almost overlapping with the multiplet, suggesting that Hk would be nearby. Hj would be shifted upfield due to closeness to the Ru_2 atoms. The remaining *ap*-based protons are assigned due to expected symmetry and comparisons to the base molecules, pyridine and aniline.

10. Room Temperature Magnetism Measurements of 1 – 3

Table S8 Room temperature magnetism data reported as per compound (Evans method[5]). Solvent: $CDCl_3$, Reference: Ferrocene

Compound	Δδ (Hz)	[Ru_2] (mM)	χ_m (emu/mol)	μ_{eff} (B.M.) (per compound)
1	36.6	2.18×10^{-3}	0.01336	5.81
2	2.04	1.59×10^{-3}	0.00105	2.18
3	9	4.25×10^{-3}	0.00218	2.26

Compound **1** was predicted to contain 6 unpaired electrons (two Ru_2(II,III) centers). The experimentally determined μ_{eff} is slightly lower than expected and is attributed to some degradation of **1** back to either $Ru_2(ap)_4Cl$ or $Ru_2(ap)_4(C_6H_5)$ in the presence of $CDCl_3$ during prep and running of the spectra. Both $Ru_2(ap)_4Cl$ and $Ru_2(ap)_4(C_6H_5)$ have a μ_{eff} *ca.* 3.8 (3 unpaired electrons).[1,2]

Table S9 Solid state magnetism of **3** with diamagnetic corrections.

Avg. χ_g (emu/mol)	Avg. χ_m (emu/mol)	Avg. μ_{eff} (B.M.)
9.41×10^{-7}	9.25×10^{-3}	1.83

11. Computational details

Ground state DFT calculations were performed using Gaussian 16 version A.03.[16] The B97D3[17,18] and B3LYP[19-22] functionals were found suitable for geometry optimizations, single point energy calculations and frequency analyses. While B97D3 accurately reproduced the crystal structure metrical parameters and vibrational frequencies, B3LYP was found to be better for energies. The xyz coordinates for the initial geometries were obtained from the respective crystal structures of the compounds. Minima at the optimized geometries were confirmed through vibrational frequency analyses. For **3**, The def2tzvp basis set was employed for Ru (with ECP), N, $C_{phenylene}$ and C_{CN} atoms and the def2svp for all others.[23,24] For **2**, de2tzvp was employed for Ru (with ECP) and N and def2svp for all other atoms. Grimme's D3 dispersion correction was used with the B3LYP functional. In both cases, geometry optimizations were carried out for both the S = 0 and S = 1 states. Wavefunction stability analysis was carried out for the closed-shell and open shell singlet calculations, by mixing the HOMO and LUMO orbitals, and using the stable=opt keyword as implemented in Gaussian16 rev A.03. A broken symmetry singlet was not encountered. For **3**, both B97D3 and B3LYP predict the singlet to be lower in energy than the triplet by 4.9 kcal/mol and 2.0 kcal/mol respectively. For **2**, the singlet was found to be more stable by 2.5 kcal/mol and 0.87 kcal/mol using the B97D3 and B3LYP functional, respectively. These low energy barriers are scaled easily at room temperature, which could be the reason for non-zero magnetic moments. DFT methods are known to carry intrinsic errors for energies, so we acknowledge that for these molecules whose energy differences appear to be < 3 – 5 kcal/mol, the ground state may have multireference character. However, such calculations are outside the scope of this communication. Looking forward, variable temperature

NMR can be utilized to experimentally determine this value, providing a reference point for future studies.

For the oxidized species [**2**]$^+$, we hypothesize that it may not matter whether we start from a singlet or triplet state of **2**, for we end up with a doublet for [**2**]$^+$ in either case. DFT calculations carried out (see below) with a spin of S = ½ for [**2**]$^+$ agree well with spectroelectrochemical observations. For [**2**]$^+$, the optimized geometry of $\mathbf{2}_{S=0}$ was taken as the input geometry, and a geometry optimization and frequency analysis was carried out at the B97D3 level in the doublet state. TDDFT[25-29] calculations were done using the B3LYP functional, CPCM solvation model[30] (THF) and Grimme's D3 dispersion correction. 50 excited states were calculated, but an intense low-energy transition was observed as the 5th excited state. So, 'functional screening' was done with 7 excited states in the interest of saving computational cost and time. Other functionals like CAM-B3LYP,[31] M06,[32] and M06L[33] gave comparable or much worse accuracy compared to B3LYP. Natural transition orbital analysis was done using the method of Martin.[34]

Table S10 Selected bond metrics for the DFT-optimized structure of **2**, vs experimental values.*

Bond metrics, Å/°	**Expt, 2**	**2 B97D3**		**2 B3LYP**	
		S = 0	**S = 1**	**S = 0**	**S = 1**
Ru-Ru	2.4892(7), 2.4829(5)	2.49444	2.46186	2.52986	2.5306, 2.4362
Ru-C_{aryl}	2.052(3), 2.051(3)	2.020915	2.00454	2.06045	2.0488, 2.0639
Ru-C_{CN}	2.019(4), 2.013(3)	1.977115	1.97057	1.99883	2.0008
C≡N	1.140(5), 1.143(4)	1.17343	1.17945	1.16177	1.16151
Ru-Ru-C_{aryl}	152.2(1), 147.1(1)	153.2346	154.4704	154.5895	154.249, 157.049
Ru-Ru-C_{CN}	168.0(1), 170.6(1)	167.2827	167.1395	166.7488	166.0565

ν(C≡N)	2096	2101.43	DNC	2204.34	2201.26, 2205.78

**All values are averages, unless there is a significant discrepancy in the two 'halves' of the molecule, in which case two values are reported. DNC = Calculation did not converge.*

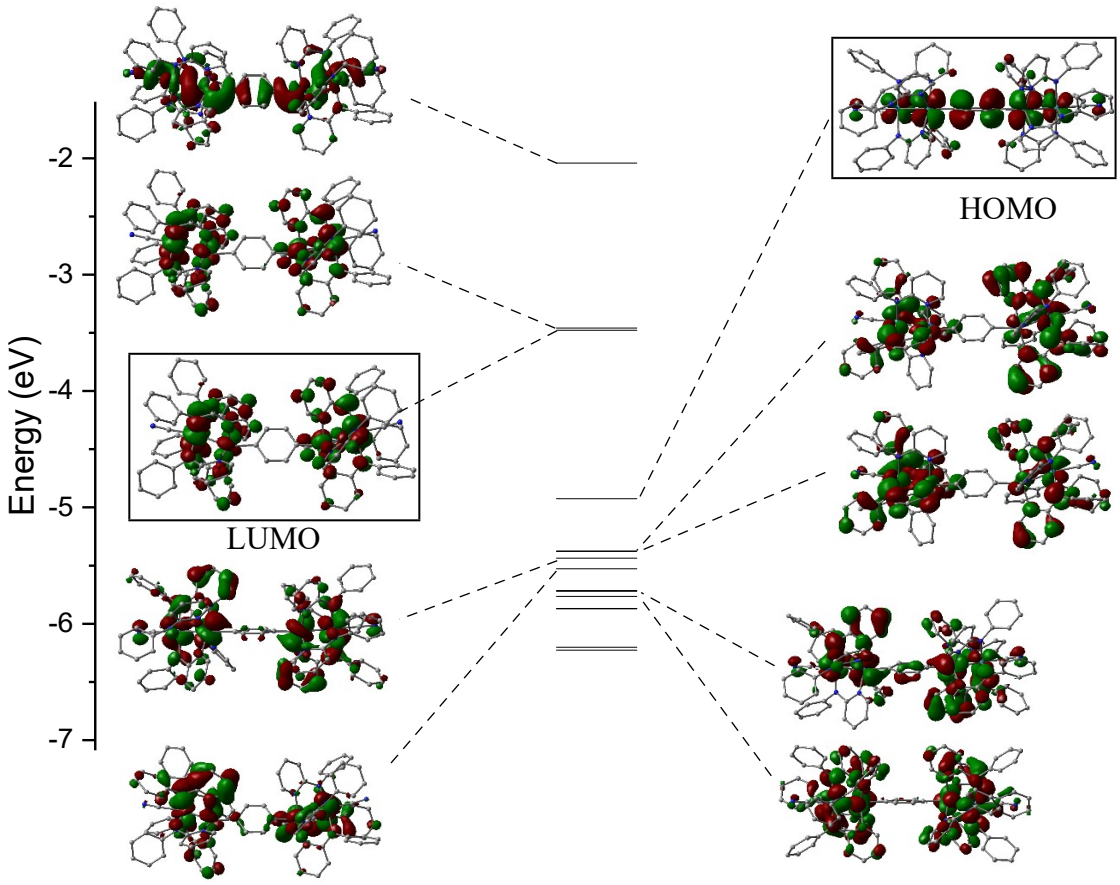


Fig. S20 Frontier α-spin molecular orbitals of **2**, S = 0, plotted |Isovalue| = 0.025.

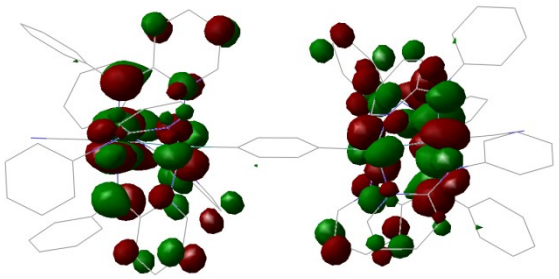
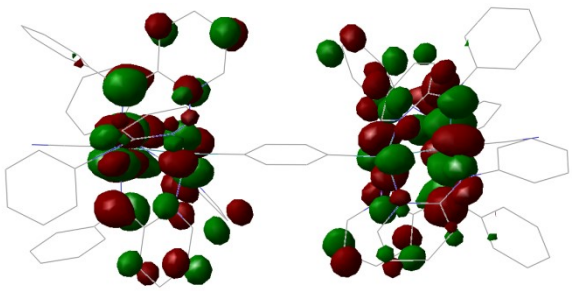
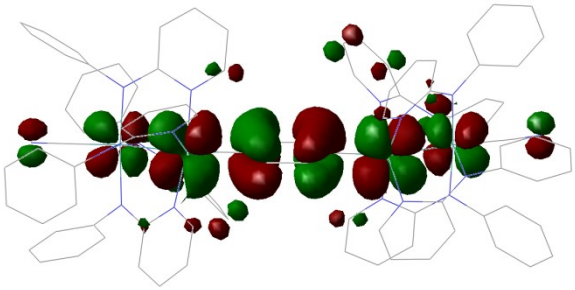
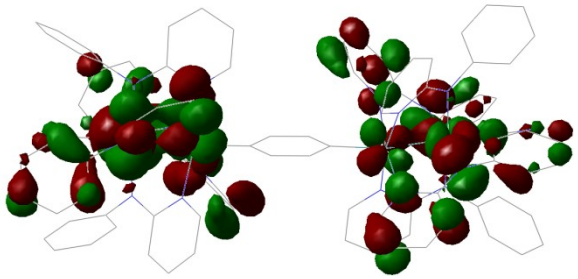
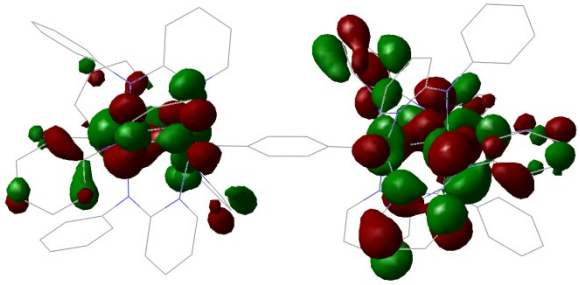
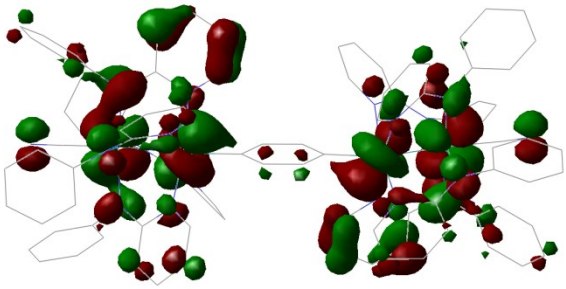
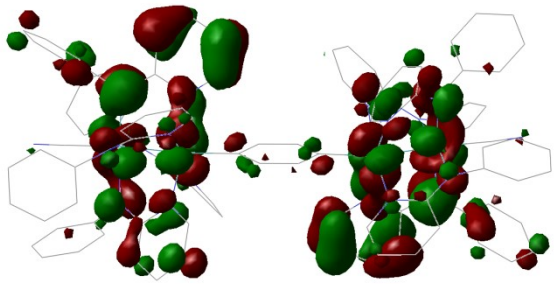
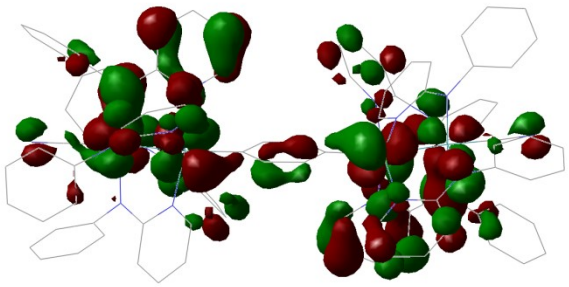
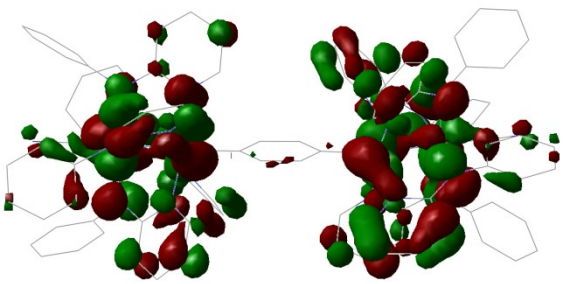
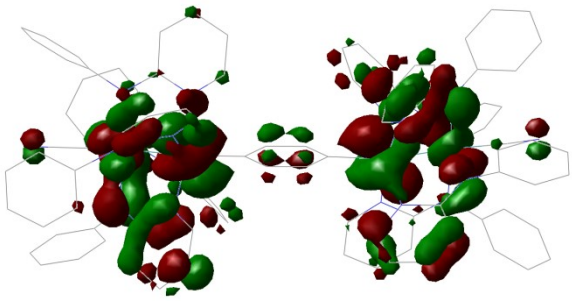
Note about electronic configurations:

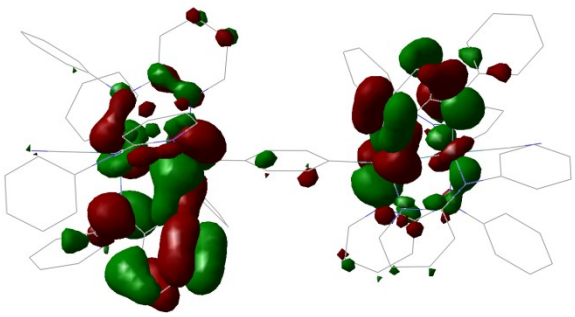
Note that for simplicity, the electronic configuration of (Y)$Ru_2(ap)_4(C_6H_4$-4-$NMe_2)$ (Y = CN, CO) is denoted as **"$\pi^4\delta^2(\pi^*)^4$"** (CN) or "$\pi^4\delta^2(\pi^*)^4\delta^*$" (CO). This does not reflect the true energetic ordering of the MOs. It is easy to see that the π/π*(Ru-Ru) orbitals are not identical. One set is perpendicular to the plane of the axial aryl, thereby interacting with its π/π* set. The other set of π/π*(Ru-Ru) orbitals, being parallel to the plane of the aryl ligand, does not interact in this fashion.

When all the orbital contributions are summed up, we can indeed condense the representation of the valence d-manifold of the Ru-Ru motif in this way for convenience and d-electron counting purposes.

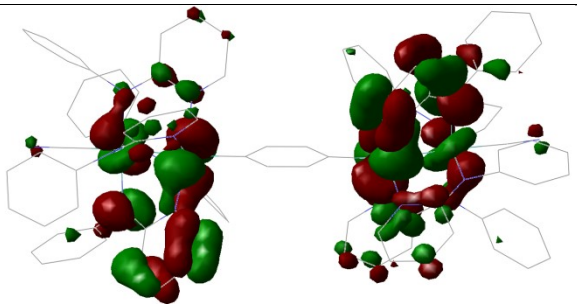
Unfortunately, assignments of individual MOs are further complicated by the large structural deviations from idealized mono-axial/bis-axial paddlewheel structures observed in **2** and **3**, which result in extensive mixing among the fragment orbitals (see **Table S13**).

Table S11 Selected molecular orbitals of **2** (S = 0 state) (see **Fig S20** for orbital energies)

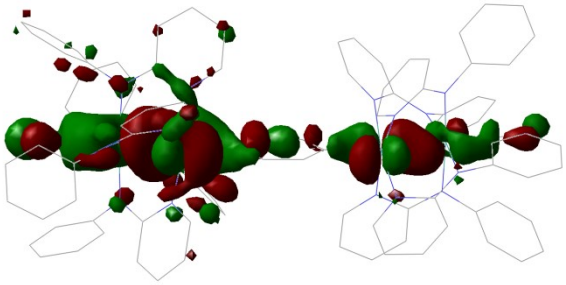
 LUMO + 1	 LUMO
 HOMO	 HOMO – 1
 HOMO – 2	 HOMO – 3
 HOMO – 4	 HOMO – 5
 HOMO – 6	 HOMO – 7



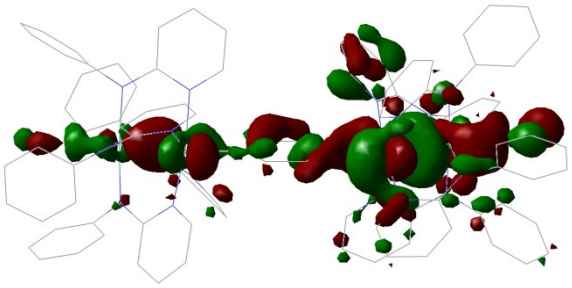
HOMO – 8



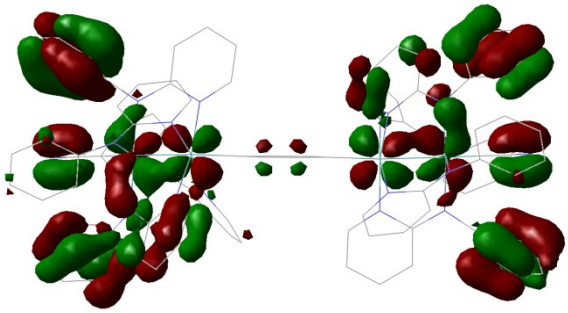
HOMO - 9



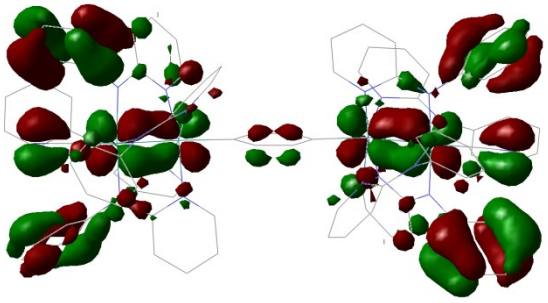
HOMO – 10



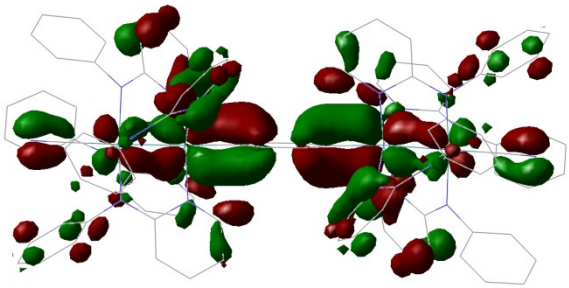
HOMO – 11



HOMO – 20



HOMO – 30



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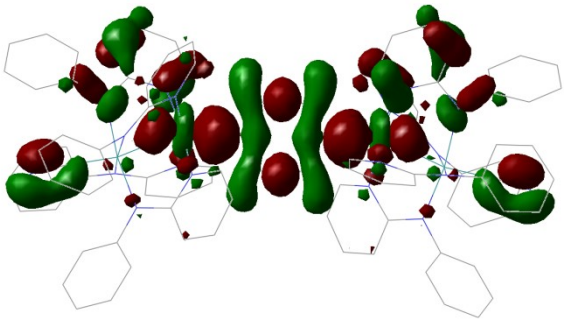

HOMO – 36

Table S12 Frontier molecular orbitals for **2** with respective orbital compositions (minor contributions < 5% not included).*†

Molecular orbital	Assignment	% Contribution
HOMO	$\pi^*(Ru_2) + \pi(C_6H_4)$ or $\pi^*(Ru\text{-}C_{aryl})$	d_{yz}(Ru1 + Ru3) 44.3 p_π (C_6H_4) 25.3 d_{yz} (Ru2 + Ru4) 11.2
LUMO	$\delta^*(Ru_2)$	d_{xy}(Ru2 + Ru4) 27.9 p_N 13.1 Minor (Ru1 + Ru3) 6.8

**Atom labels are according to Figure 1. † The phenylene moiety lies on the xz plane. $_Z$ axis and Ru-Ru bond are collinear*

Table S13 Some frontier molecular orbitals and % atomic/fragment orbital contributions.

MO	% Ru contribution (Ru-Ru fragment orbitals) †	% phenylene contribution
LUMO + 1	49.64 ($\delta^*(Ru_2)$)	1.13
LUMO	48.75 ($\delta^*(Ru_2)$)	0.49
HOMO	62.10 ($\pi_{yz}^*(Ru_2)$)	25.86 (only $2p_y$)
HOMO – 1	21.36 (mix, Ru1 and Ru3: $d_{yz}+d_{xz}$; Ru2 and Ru4: $d_{z2} + d_{xz}$)	0.74
HOMO – 2	23.27 (mix, Ru1 and Ru3: $d_{x2-y2}+d_{xz}$; Ru2 and Ru4: $d_{z2} + d_{xz}$)	0.95
HOMO – 3	53.06 ($\pi_{yz}^*(Ru_2)$)	1.54
HOMO – 4	24.27 (Mix; major d_{x2-y2})	2.43
HOMO – 5	29.98 (mix, Ru1 and Ru3: $d_{yz}+d_{xz}$; Ru2 and Ru4: $d_{z2} + d_{xy}$)	2.81
HOMO – 6	23.48 (mix, Ru1 and Ru3: $d_{x2-y2}+d_{z2}+d_{xz}$; Ru2 and Ru4: $d_{yz} + d_{xy}$)	0.93
HOMO – 7	50.54 ($\pi_{yz}^*(Ru_2)$)	2.64
HOMO – 8	41.91 ($\delta(Ru_2)$)	1.26
HOMO – 9	49.05 ($\delta(Ru_2)$)	0.82
HOMO – 10	56.94 ($\pi_{xz}^*(Ru_2)$)	4.29
HOMO – 11	55.37 ($\pi_{xz}^*(Ru_2)$)	5.98
HOMO – 20	18.89 ($\pi_{yz}(Ru_2) - \pi(CN)$)	0.20
HOMO – 30	30.72 ($\pi_{yz}(Ru_2) - \pi(CN)$)	2.4
HOMO – 35	29.10 (π_{yz}(Ru-C))	26.1
HOMO – 36	23.30 (σ(Ru-C))	26.2

†Where assignments of the Ru-Ru d-manifold could not be discerned due to extensive mixing, the component d-orbitals are listed.

Among the frontier MOs listed above, the one with significant phenylene contribution is the HOMO (and LUMO + 2, but LUMO + 2 consists only of $C_{phenylene}$ 2*s* and $2p_z$ orbitals whereas

HOMO consists only of $C_{phenylene}$ $2p_y$ orbitals). The phenylene ring is parallel to the xz plane. This, along with the large energy gap (>3 eV) between HOMO and LUMO + 2 of **2** strengthens our argument that the SOMO of [**2**]$^+$ (aka HOMO of **2**) is involved in the low-energy IVCT transition.

Table S14 Selected bond metrics for the DFT-optimized structure of **3**, vs experimental values.

	Expt, 3	**3 B97D3**		**3 B3LYP**	
		S = 0	**S = 1**	**S = 0**	**S = 1**
Ru-Ru	2.5011(6)	2.50495	2.41004	2.52001	2.42176
Ru-C_{aryl}	2.052(2)	2.02367	2.04369	2.03573	2.04837
Ru-C_{CN}	2.008(2)	1.97202	2.00320	1.99359	2.00495
C≡N	1.156(2)	1.17310	1.17129	1.16908	1.16809
Ru-Ru-C_{aryl}	156.26(5)	152.36105	153.08416	153.23693	155.12857
Ru-Ru-C_{CN}	170.88(5)	168.01125	167.38325	167.99598	167.18985
ν(C≡N)	2089	2090.36	DNC	2224.79	2223.50

DNC = Calculation did not converge

Table S15 Selected bond metrics for the DFT-optimized structure of [**2**]$^+$.

	B97D3	**B3LYP**
Ru-Ru	2.46636	2.51132
Ru-C_{aryl}	2.00740	1.97618
Ru-C_{CN}	1.97741	1.99719
C≡N	1.17227	1.16171

Ru-Ru-C_{aryl}	153.85443	153.16124
Ru-Ru-C_{CN}	174.17953	167.9283

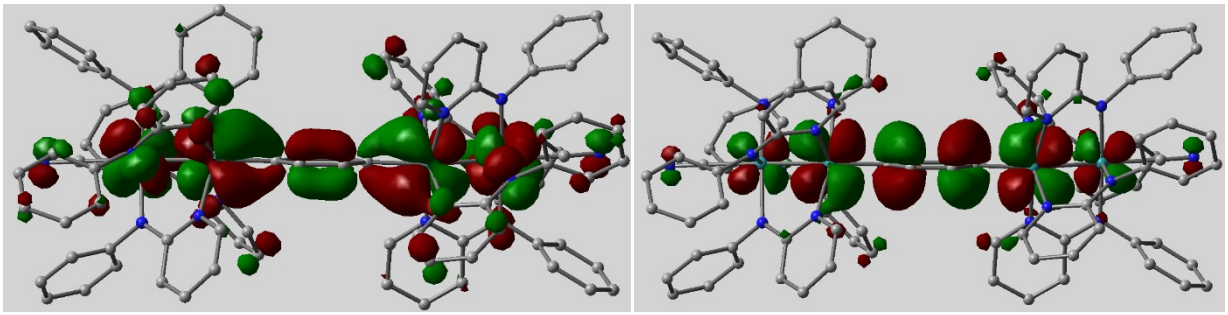

Fig. S21 Natural transition donor (left) and acceptor (right) orbitals corresponding to the IVCT band, extracted from excited state #5 of [**2**]$^{+}$. Experimental (Figs. 3a and S7) *ca*. 4000 cm^{-1}, Calculated (Fig. S22) 4647.1 cm^{-1}. |Isovalue| = 0.025.

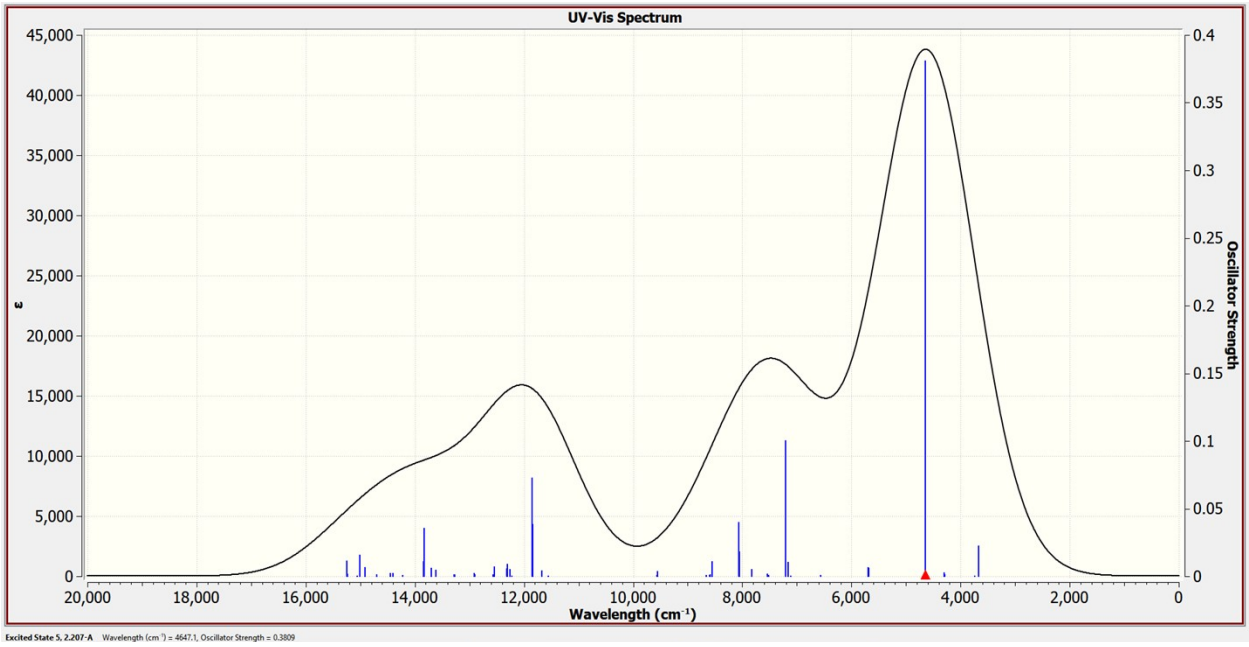

Fig. S22 TD-DFT calculated electronic absorption spectrum of [**2**]$^{+}$.

Table S16 xyz coordinates for **2**, S=0, B97D3

Ru 3.46416320 -0.70150710 -0.08499282
Ru 5.74942995 0.29597953 -0.01261492
Ru -3.46368952 -0.70440762 0.06324954
Ru -5.74912774 0.29410794 0.02398292
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N 5.71449441 -0.33884970 1.94671506
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C -7.68983159 0.66734613 -0.03343484

Table S17 xyz coordinates for **2**, S=1, B97D3

Ru 3.44320846 0.11642212 -0.63365898
Ru 5.73637462 -0.01677395 0.26476695
Ru -3.44860325 -0.01177076 -0.64155147
Ru -5.73316246 -0.03019783 0.26313759
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H 8.68108181 -0.65728381 5.00134198
C 7.02735612 -0.71179279 3.61229858
H 7.47709964 -1.46340933 2.95937982
C -2.35763697 2.19657715 1.22888819
H -1.88507986 2.45453323 0.27734581
C -2.00738668 2.85318517 2.40293158
H -1.27360363 3.66378122 2.37913126
C -2.59324253 2.41317146 3.61063162
H -2.30785027 2.86724950 4.56703980
C -3.57114807 1.43074171 3.57397610
H -4.10231688 1.11301023 4.47476453
C -3.97647736 0.88693795 2.31585213
C -5.76648269 -0.42602779 3.25775387
C -7.02064182 0.04602577 3.68683163
H -7.46654382 0.90651887 3.18245394
C -7.69098530 -0.61520095 4.72425222
H -8.67469062 -0.25259402 5.04423025
C -7.11823983 -1.73917688 5.34193198
H -7.65262127 -2.25713526 6.14703183

C -5.86012965 -2.20057012 4.92133003
H -5.40931144 -3.08143966 5.39411156
C -5.18415415 -1.54831309 3.88189477
H -4.21510912 -1.91097768 3.52202255
C -3.17173115 2.28479003 -2.58285158
H -2.44605831 1.59923171 -3.02306819
C -3.33660780 3.56561495 -3.08960605
H -2.74615587 3.89240282 -3.95062992
C -4.26545265 4.41931723 -2.45020702
H -4.40669629 5.44941064 -2.79827431
C -5.01661367 3.93741978 -1.39367277
H -5.77081861 4.55652860 -0.90333984
C -4.86388936 2.58269957 -0.95118344
C -6.60900537 2.83925223 0.65234551
C -7.91082776 3.03055667 0.15599940
H -8.19788334 2.55737965 -0.78565342
C -8.82697910 3.79768568 0.88604478
H -9.84493763 3.92734476 0.50069261
C -8.45550815 4.37764056 2.10931106
H -9.18064132 4.96788023 2.68206250
C -7.15200848 4.19629322 2.59689965
H -6.85047455 4.64828695 3.54968583
C -6.22777364 3.43228725 1.87022312
H -5.20948787 3.28664392 2.24124268
C -3.09260796 -1.79975438 -3.06340802
H -2.09481433 -1.94672997 -2.63925001
C -3.45971380 -2.36536274 -4.27520689
H -2.74924023 -2.98543169 -4.82975300
C -4.76545879 -2.10734405 -4.75933519
H -5.09133732 -2.52393299 -5.72002606
C -5.64590685 -1.35252019 -4.00381674
H -6.67118301 -1.17398251 -4.33623120
C -5.24755946 -0.83658246 -2.72539876
C -7.27000861 0.33573530 -2.42660516
C -8.53554653 -0.24940880 -2.23949496
H -8.61436975 -1.18015160 -1.67440633
C -9.67766650 0.37489117 -2.75874381
H -10.66004575 -0.08113455 -2.58961938
C -9.57220899 1.57713449 -3.47540866
H -10.47140269 2.06491058 -3.87016884
C -8.30732497 2.14941845 -3.68671597
H -8.21067853 3.08674204 -4.24815616
C -7.16207640 1.53079020 -3.16917659
H -6.17240334 1.97211933 -3.32216093
C -2.15231749 -2.71844371 0.19151228
H -1.25513613 -2.16025464 -0.07323589
C -2.04998626 -4.06970883 0.49341021
H -1.06924146 -4.55442450 0.46726058
C -3.22687525 -4.77309599 0.82462846
H -3.19598650 -5.83688612 1.08847704
C -4.42935889 -4.09272600 0.80966897
H -5.36779854 -4.59222085 1.05877895
C -4.47928344 -2.69919927 0.47414170
C -6.85610876 -2.80675056 0.36019323
C -7.69929174 -2.94213944 1.47579227
H -7.42051641 -2.46575634 2.41735598
C -8.89633656 -3.65911060 1.35851117
H -9.55673908 -3.74643291 2.22904184
C -9.25957695 -4.24484616 0.13581104
H -10.20334605 -4.79587953 0.04776063
C -8.41140710 -4.11734671 -0.97560634
H -8.68826438 -4.56834348 -1.93629471
C -7.21104154 -3.40270469 -0.86549728
H -6.54546478 -3.28246964 -1.72662896
C 7.68223440 -0.10014810 0.55810949
C -7.68113223 0.00801258 0.56463893

Table S18 xyz coordinates for **3**, S=0, B97D3

Ru -1.72273300 -0.19533400 -0.18688200
Ru 0.74668300 0.12833600 0.08145300
N -1.49157900 -2.14079300 0.37195900
N 0.61638300 -1.56359200 1.24059400
N -1.50923500 0.18685400 1.93670600
N 0.52379300 1.30061200 1.66399500
N -1.67218700 1.80168700 -0.99266800
N 0.68118500 1.69870700 -1.13915000
N -1.63000400 -0.70319700 -2.14135200
N 0.61585900 -1.19748700 -1.63359300
N 3.88897100 0.07537100 0.09078000
C -3.64645500 0.20776400 0.29482700
C -4.64125300 -0.59214800 -0.29058800
H -4.38372700 -1.39180500 -0.97780800
C -5.99821600 -0.36872000 -0.03306800
H -6.74014100 -1.00908100 -0.50756300
C -6.39855300 0.66181200 0.81819200
H -7.45326000 0.83347800 1.01990900
C -5.42131000 1.47410000 1.39891300
H -5.71095100 2.29327100 2.05528800
C -4.06893000 1.24985200 1.14418000
H -3.33624500 1.91588200 1.58981900
C -2.38070800 -3.11394600 0.04721200
H -3.18867800 -2.80942600 -0.61705700
C -2.30693300 -4.41116700 0.52810700
H -3.06318800 -5.14430500 0.23360500
C -1.25667500 -4.73508600 1.41792300
H -1.18273700 -5.73760700 1.85376700
C -0.30323300 -3.77758000 1.71479400
H 0.54120100 -4.01063900 2.36593300
C -0.37480700 -2.47362800 1.12979800
C 1.72016600 -1.88001800 2.09351300
C 1.74262300 -1.36460200 3.40143000
H 0.90039000 -0.76592400 3.75821900
C 2.84167400 -1.61930800 4.23561400
H 2.85500900 -1.20896200 5.25237900
C 3.91566700 -2.39670000 3.77324600
H 4.77500200 -2.59285400 4.42512900
C 3.88074900 -2.92402900 2.47158400
H 4.71390900 -3.53336000 2.10154300
C 2.78941900 -2.66766000 1.63163300
H 2.75906300 -3.05893800 0.61237200
C -2.38413600 -0.38610900 2.79964400
H -3.06488800 -1.11748200 2.36291400
C -2.45041000 -0.06910100 4.15092600
H -3.17135800 -0.58052200 4.79498800
C -1.59614100 0.93978600 4.64284100
H -1.64522200 1.25493900 5.69121800
C -0.65282700 1.49770200 3.79139700
H 0.07761900 2.22707600 4.14942000
C -0.55644000 1.03713800 2.44577500
C 1.36472100 2.39983900 1.96776600
C 0.88156500 3.70691500 1.75610100
H -0.14470500 3.84204300 1.39804900
C 1.72175900 4.80725200 1.97533300
H 1.34611000 5.82155800 1.79641800
C 3.04373700 4.60917400 2.40791500
H 3.70370700 5.46908700 2.57070800
C 3.51634200 3.30482100 2.63187900
H 4.54511000 3.14553000 2.97563100
C 2.68167300 2.19961000 2.41653500
H 3.03714400 1.17877200 2.57375200

C -2.81286100 2.43078900 -1.38615200
H -3.74250300 1.94757600 -1.09608000
C -2.85792400 3.61370300 -2.11028300
H -3.82798900 4.04909700 -2.36782400
C -1.64193300 4.21774500 -2.48760500
H -1.62448900 5.16398100 -3.03983600
C -0.46212000 3.57966400 -2.15239800
H 0.50411500 4.00355000 -2.43112700
C -0.47618600 2.34889400 -1.42197500
C 1.85286300 2.10198800 -1.85198500
C 2.04714500 1.61361400 -3.15701800
H 1.28701000 0.96162700 -3.59883800
C 3.21067900 1.94919600 -3.86386000
H 3.36278600 1.55591000 -4.87606000
C 4.17657500 2.78350800 -3.27721900
H 5.08663700 3.04527600 -3.82958400
C 3.96898500 3.28250500 -1.98062800
H 4.71625200 3.93719000 -1.51661400
C 2.81232600 2.94344000 -1.26568800
H 2.64776600 3.31719600 -0.25337600
C -2.62754300 -0.55656700 -3.04659100
H -3.53272500 -0.07163900 -2.67471700
C -2.52952600 -1.00960200 -4.35295100
H -3.36854100 -0.87867300 -5.04223100
C -1.32641800 -1.64041100 -4.74938000
H -1.20824300 -2.01687400 -5.77191600
C -0.28163300 -1.75452000 -3.84712100
H 0.67018600 -2.20180000 -4.14250300
C -0.40689100 -1.23324400 -2.51919400
C 1.63681200 -2.16781600 -1.83746100
C 1.33834900 -3.52449700 -1.58618700
H 0.32664100 -3.79441800 -1.26764300
C 2.32646300 -4.50776800 -1.72794500
H 2.08386300 -5.55545100 -1.51315400
C 3.62353500 -4.14928500 -2.13202500
H 4.40086600 -4.91518000 -2.23711800
C 3.91449800 -2.80317300 -2.40801900
H 4.92033900 -2.51564900 -2.73691400
C 2.92880700 -1.81580800 -2.26716400
H 3.14809600 -0.76846000 -2.48144200
C 2.71703700 0.05781300 0.04147900

Table S19 xyz coordinates for **3**, S=1

Ru -1.64462900 -0.24946900 -0.22647500
Ru 0.71153900 0.13202500 0.10705500
N -1.33097200 -2.23912500 0.27994500
N 0.69041300 -1.58688800 1.26433800
N -1.50576300 0.04156800 1.94440900
N 0.39759400 1.33430800 1.69501000
N -1.73025900 1.80897500 -0.90259100
N 0.60368600 1.74896200 -1.11900200
N -1.50620400 -0.64655200 -2.21082300
N 0.69472600 -1.19311300 -1.63987500
N 3.88074700 0.21863500 0.14512500
C -3.61459600 -0.02986800 0.27117300
C -4.51079200 -0.81344200 -0.47067000
H -4.15645500 -1.51073700 -1.22298400
C -5.89335400 -0.69765200 -0.28798300
H -6.56250800 -1.31937600 -0.87978500
C -6.40699300 0.20721400 0.63990000
H -7.48108300 0.29647600 0.78449200
C -5.52518000 1.00710400 1.37297200
H -5.91037300 1.73231100 2.08735700
C -4.14886100 0.88985400 1.19282500
H -3.48975300 1.54548500 1.75194300
C -2.18290200 -3.22471000 -0.08499000
H -2.97798300 -2.93364700 -0.77071400
C -2.08693200 -4.53200500 0.37274100
H -2.80976600 -5.28107200 0.03803200
C -1.05488800 -4.83877700 1.28651300
H -0.96178100 -5.84702900 1.70576600
C -0.14002100 -3.85842300 1.63364100
H 0.68812300 -4.07734000 2.31043200
C -0.23392900 -2.54635500 1.07356200
C 1.79368600 -1.84458500 2.12950500
C 1.82488000 -1.25761500 3.40689900
H 0.97920400 -0.65051500 3.74004500
C 2.93840900 -1.44883500 4.23909300
H 2.95864000 -0.98201100 5.23113400
C 4.01900800 -2.23410500 3.80669800
H 4.88937200 -2.38003600 4.45718300
C 3.97789200 -2.83307900 2.53611200
H 4.81765400 -3.44707100 2.18921000
C 2.87301300 -2.63844800 1.69767100
H 2.83993900 -3.08020600 0.69828000
C -2.32202400 -0.63731300 2.78117300
H -2.90887800 -1.43611700 2.32475400
C -2.45444500 -0.33111400 4.13025100
H -3.12547900 -0.91991600 4.76179300
C -1.73384800 0.77492100 4.63370300
H -1.84846800 1.08618700 5.67845600
C -0.83974600 1.43997800 3.80665300
H -0.21372600 2.25542600 4.17755700
C -0.65340600 0.98271100 2.46747900
C 1.13074300 2.51270200 1.96126800
C 0.52475600 3.76969300 1.75881900
H -0.51897200 3.80778900 1.42897700
C 1.26468200 4.94459800 1.94926200
H 0.79179600 5.91844900 1.77541300
C 2.61172800 4.87411700 2.34354800
H 3.19323300 5.79292900 2.48217900
C 3.20994100 3.62078700 2.55812200
H 4.25906800 3.55986000 2.87066000
C 2.47469100 2.44207800 2.37184000
H 2.92907200 1.45981800 2.52292700

C -2.89735700 2.43894000 -1.18832100
H -3.80385900 1.92445700 -0.87717200
C -2.99584800 3.66004000 -1.84312700
H -3.98185100 4.09895900 -2.02056400
C -1.80640300 4.28919200 -2.26174000
H -1.82918300 5.25764400 -2.77444600
C -0.59932100 3.65888900 -2.01620800
H 0.34472100 4.11239800 -2.32378100
C -0.55676400 2.39960500 -1.33740500
C 1.76896600 2.18969700 -1.81440600
C 2.04471400 1.66026600 -3.08798900
H 1.34679000 0.94061600 -3.52630000
C 3.21095100 2.04090400 -3.76765400
H 3.42723300 1.61507100 -4.75475700
C 4.09856800 2.96099200 -3.18580400
H 5.01166200 3.25583600 -3.71618300
C 3.80851300 3.50459300 -1.92311200
H 4.49354000 4.22772800 -1.46451400
C 2.64817000 3.12191000 -1.23683200
H 2.41917100 3.52936300 -0.24996300
C -2.46235500 -0.41855000 -3.14223300
H -3.36201300 0.08750300 -2.78418900
C -2.33200800 -0.82607700 -4.46117300
H -3.13842300 -0.63750000 -5.17530100
C -1.14055500 -1.49346500 -4.83454200
H -1.00249900 -1.84357700 -5.86409200
C -0.13054400 -1.67679600 -3.90377700
H 0.81368800 -2.15179500 -4.18057600
C -0.28330300 -1.19044900 -2.56561300
C 1.72780000 -2.15368900 -1.81439900
C 1.43526000 -3.51710800 -1.59529800
H 0.41364600 -3.80480500 -1.32990700
C 2.44062800 -4.48705000 -1.70453700
H 2.20106200 -5.54005000 -1.51336600
C 3.75021300 -4.10939600 -2.04578900
H 4.54067800 -4.86507900 -2.12362000
C 4.03625200 -2.75742700 -2.29703500
H 5.05135800 -2.45498200 -2.58120000
C 3.03262100 -1.78402700 -2.18943500
H 3.24781300 -0.73280400 -2.38894700
C 2.71425500 0.14815900 0.06607300

Table S20 xyz coordinates for [**2**]$^{+}$, S=1/2, B97D3, gas phase.

Ru 3.44794274 -0.66110362 -0.11341936
Ru 5.72304544 0.28386730 0.01099542
Ru -3.44793672 -0.67186861 0.03498465
Ru -5.72226093 0.28220690 0.02508171
N 3.30083994 0.49115464 -1.93630536
N 5.63996869 0.78460461 -1.91638996
N 3.94952437 -2.15669043 -1.37727054
N 6.11761883 -1.76110523 -0.56154971
N 3.89516230 -1.82381371 1.51360120
N 5.69369060 -0.38081078 1.94910878
N 3.24082121 0.92410776 1.37273129
N 5.08321932 2.08142054 0.54273605
N -3.23870385 1.08352486 -1.24525196
N -5.08243444 2.13130929 -0.28315654
N -3.89216740 -1.62627680 -1.72234912
N -5.69017935 -0.14054854 -1.98032497
N -3.95082964 -2.31202128 1.10379990
N -6.11845462 -1.81712371 0.34210521
N -3.30307138 0.24643045 1.98658019
N -5.64178789 0.54308359 1.99921371
N 8.79823355 0.91952637 0.20142031
N -8.79739523 0.93577972 -0.08894041
C 1.44488358 -0.55400121 -0.03640369
C 0.69569410 0.65235733 0.04139373
H 1.21339337 1.61541562 0.07359518
C -0.69633323 0.65143106 0.04873276
H -1.21446999 1.61071987 0.13740944
C -1.44458443 -0.55569991 -0.02505734
C -0.70149611 -1.75634977 -0.10299756
H -1.20344980 -2.72865157 -0.13827688
C 0.70269551 -1.75561029 -0.10773776
H 1.20539041 -2.72442803 -0.19321060
C 2.14617561 0.56229242 -2.65133016
H 1.25888200 0.17232684 -2.15745983
C 2.04058500 1.08712982 -3.93122313
H 1.06446213 1.10661022 -4.42493488
C 3.20321183 1.58073654 -4.55657650
H 3.16530034 2.02552470 -5.55721880
C 4.40290957 1.48612189 -3.87699993
H 5.33328777 1.85166681 -4.31544331
C 4.45761042 0.91366436 -2.56704307
C 6.83609411 0.88904287 -2.69614110
C 7.18937782 -0.19136225 -3.52567873
H 6.53092823 -1.06492071 -3.57587981
C 8.38419866 -0.14539464 -4.25661163
H 8.66456470 -0.99304960 -4.89275727
C 9.22035242 0.97868518 -4.16744691
H 10.15771012 1.01228970 -4.73423294
C 8.85376033 2.05823938 -3.34863192
H 9.50428909 2.93646714 -3.27115938
C 7.66416575 2.01876574 -2.61094759
H 7.38102020 2.84578132 -1.95752194
C 3.11612586 -2.77072744 -2.25221300
H 2.10477891 -2.36094186 -2.30460679
C 3.50308075 -3.85745466 -3.01885700
H 2.79155460 -4.32550057 -3.70512657
C 4.83013403 -4.33151383 -2.88091956
H 5.17332084 -5.19444392 -3.46287430
C 5.70719288 -3.68164392 -2.03060596
H 6.74700447 -4.00229860 -1.93625576
C 5.28389929 -2.52729700 -1.29444764
C 7.32714075 -2.39063289 -0.13422032
C 7.25024426 -3.35372012 0.89253094

H 6.27108727 -3.61442814 1.30656904
C 8.41581864 -3.95860743 1.38069496
H 8.34747185 -4.69704997 2.18824238
C 9.66525423 -3.61232605 0.84151717
H 10.57954906 -4.07758427 1.22729650
C 9.73683894 -2.67338102 -0.19916072
H 10.70701537 -2.40226775 -0.63025914
C 8.57440057 -2.06597655 -0.69321020
H 8.62618337 -1.33553100 -1.50274259
C 3.23224460 -2.97006625 1.80619706
H 2.50270437 -3.29331391 1.06433972
C 3.43318232 -3.69402750 2.97064131
H 2.86295679 -4.61070745 3.14683827
C 4.37003934 -3.20522136 3.90996370
H 4.53799653 -3.73099104 4.85650543
C 5.09722523 -2.06758281 3.60998047
H 5.85873580 -1.68480163 4.29225077
C 4.90662582 -1.39337996 2.36315549
C 6.65526588 0.14501263 2.87471398
C 6.30192529 1.26072704 3.65267763
H 5.29363731 1.67660314 3.57390934
C 7.24453915 1.82910338 4.52177378
H 6.96803853 2.70187768 5.12492105
C 8.53387417 1.28351399 4.61781477
H 9.27259312 1.73368842 5.29068322
C 8.87415530 0.15980725 3.84869704
H 9.88064747 -0.26840147 3.91316626
C 7.93947916 -0.41392238 2.97807774
H 8.20212962 -1.27423717 2.35871941
C 2.34451795 0.78757128 2.37890337
H 1.87937158 -0.19652504 2.46388974
C 1.99638735 1.82128077 3.23886052
H 1.27213922 1.64594388 4.03913524
C 2.57551319 3.09124549 3.02727362
H 2.29433339 3.94591309 3.65293998
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