Supporting Information

Noninnocence of deprotonated 1,2-bis((1H-pyrrol-2-yl)methylene) hydrazine bridge in diruthenium frameworks-a function of co-ligands

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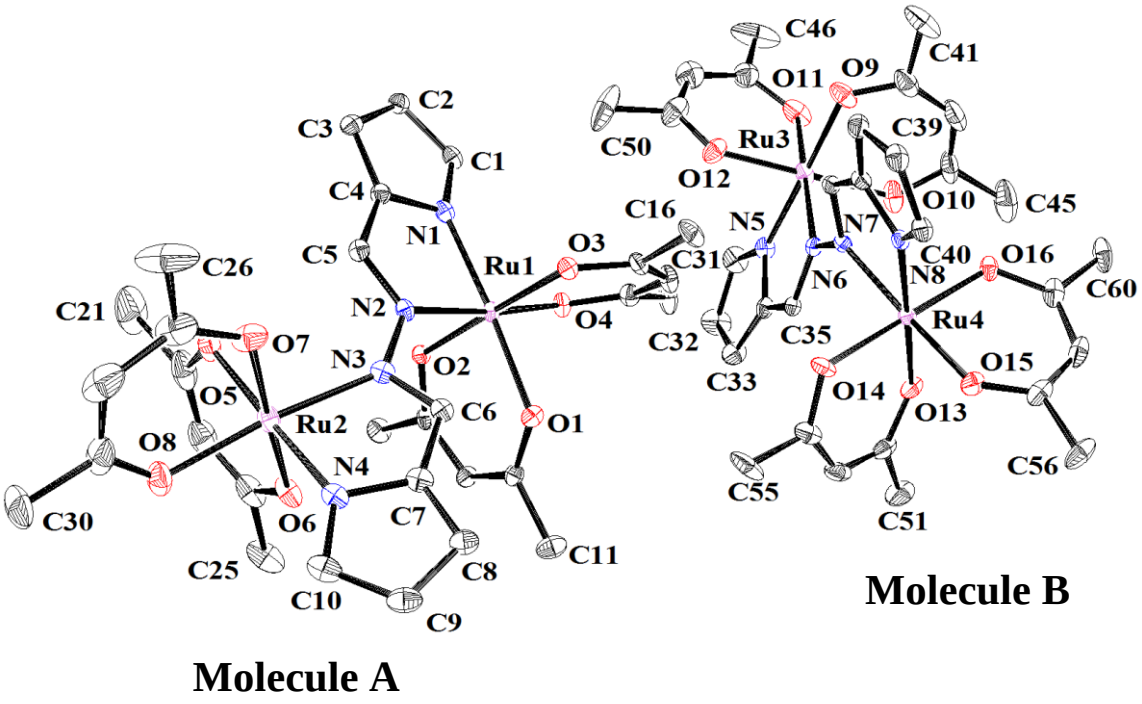


Fig. S1 ORTEP of the asymmetric unit of **1a** consisting of two independent molecules. Ellipsoids are drawn at 20% probability level. Hydrogen atoms are omitted for clarity.

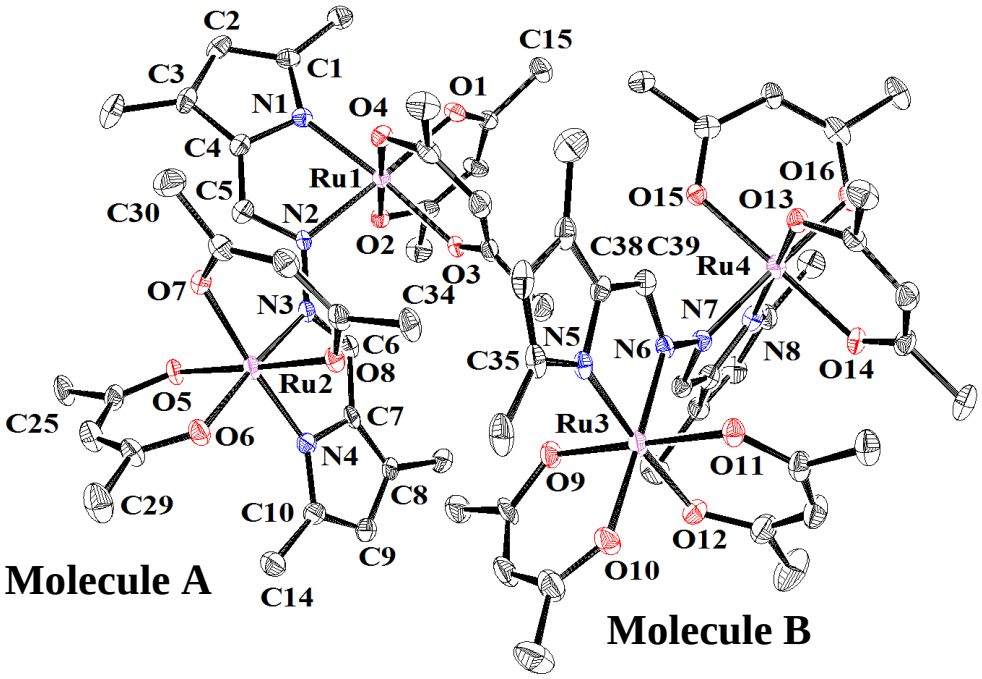


Fig. S2 ORTEP of the asymmetric unit of **1b** consisting of two independent molecules. Ellipsoids are drawn at 20% probability level. Hydrogen atoms are omitted for clarity.

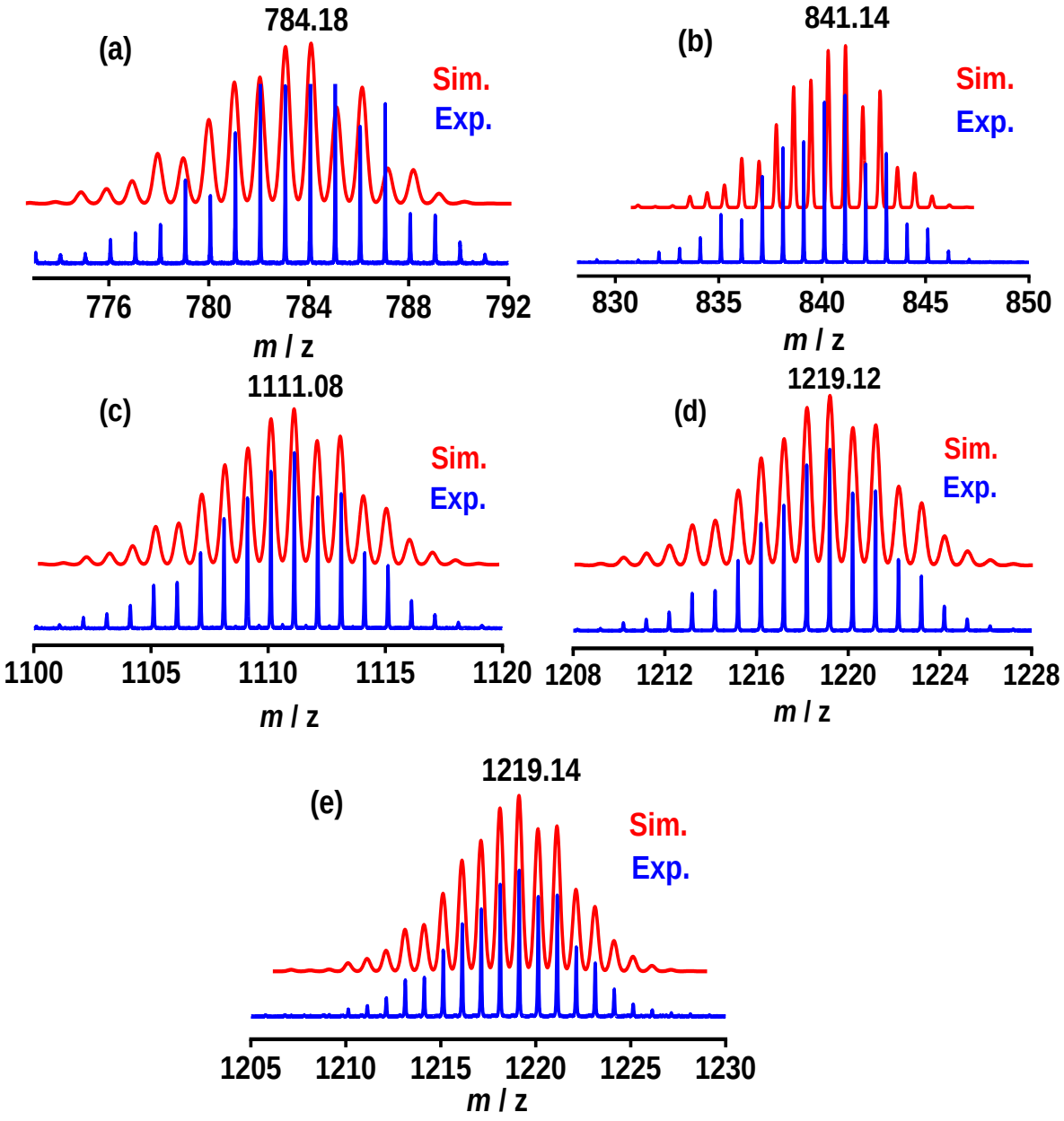


Fig. S3 ESI(+) mass spectra of (a) {**1a**+H}$^+$**,** (b) {**1b**+H}$^+$, (c) {[**2**]$(ClO_4)_2$-ClO_4}$^+$, (d) {[**3a**]$(ClO_4)_2$-ClO_4}$^+$ and (e) {[**3b**]$(ClO_4)_2$-ClO_4}$^+$ in CH_3CN.

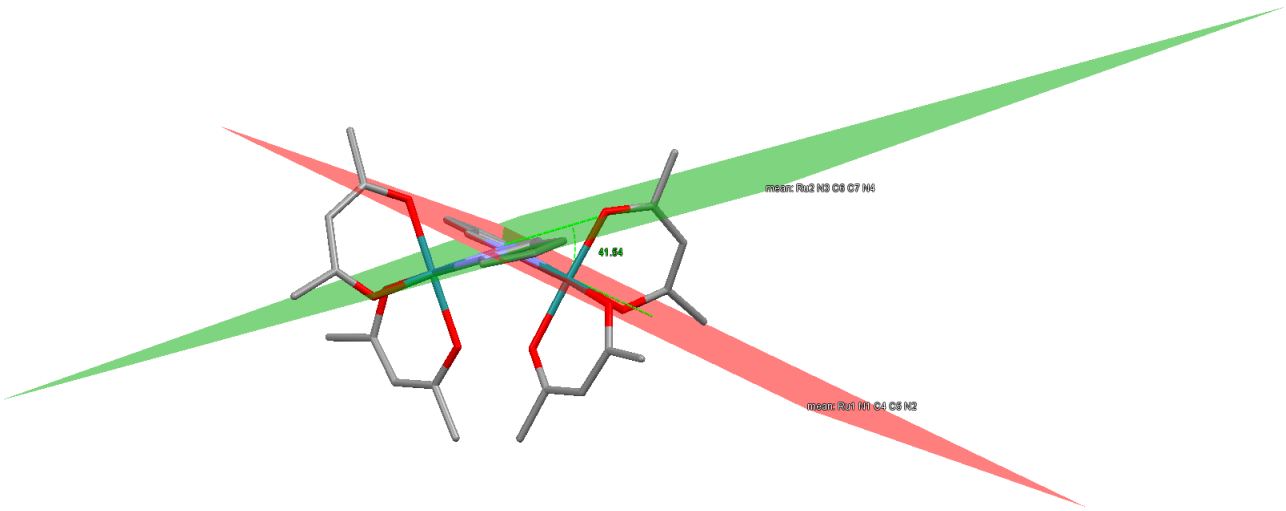


Fig. S4 Torsional angle (deg) between the planes for **1a**.

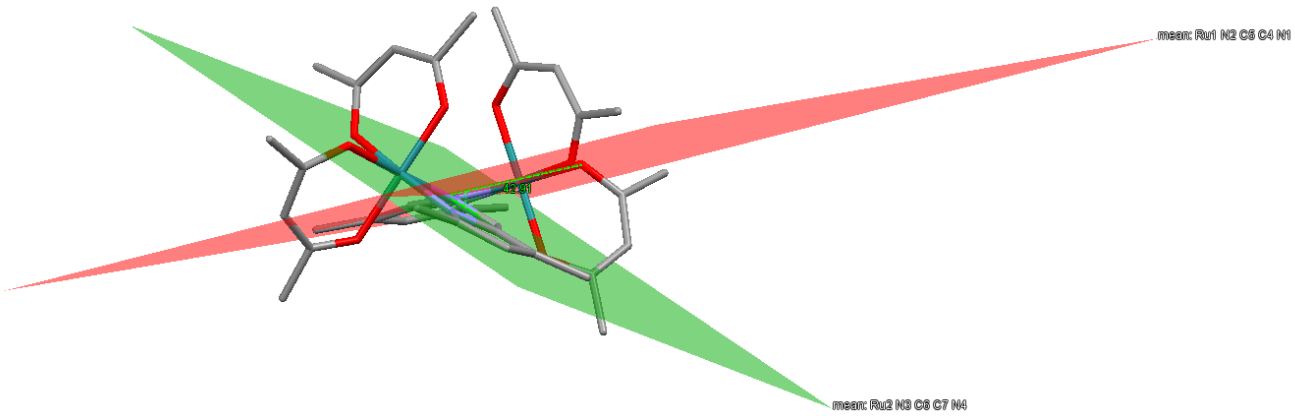


Fig. S5 Torsional angle (deg) between the planes for **1b**.

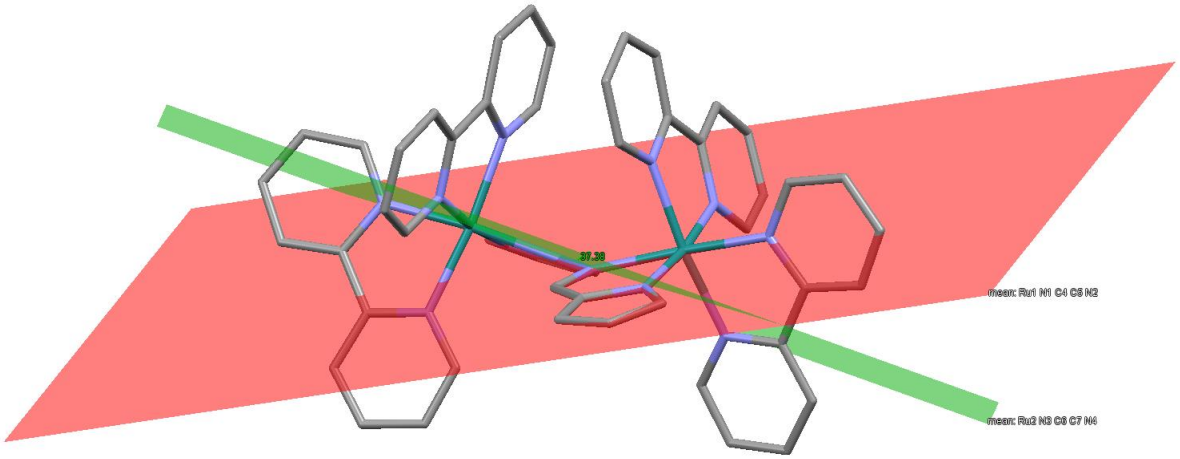


Fig. S6 Torsional angle (deg) between the planes for [**2**]$^{2+}$.

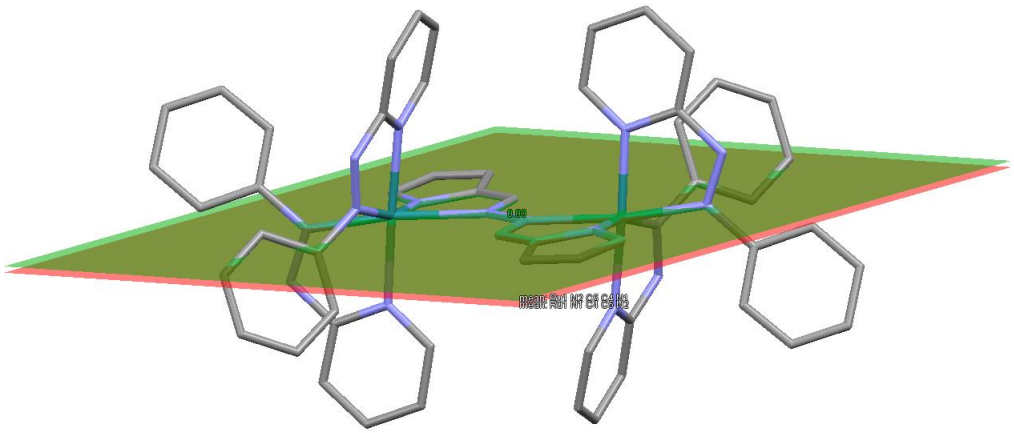


Fig. S7 Torsional angle (deg) between the planes for [**3a**]$^{2+}$.

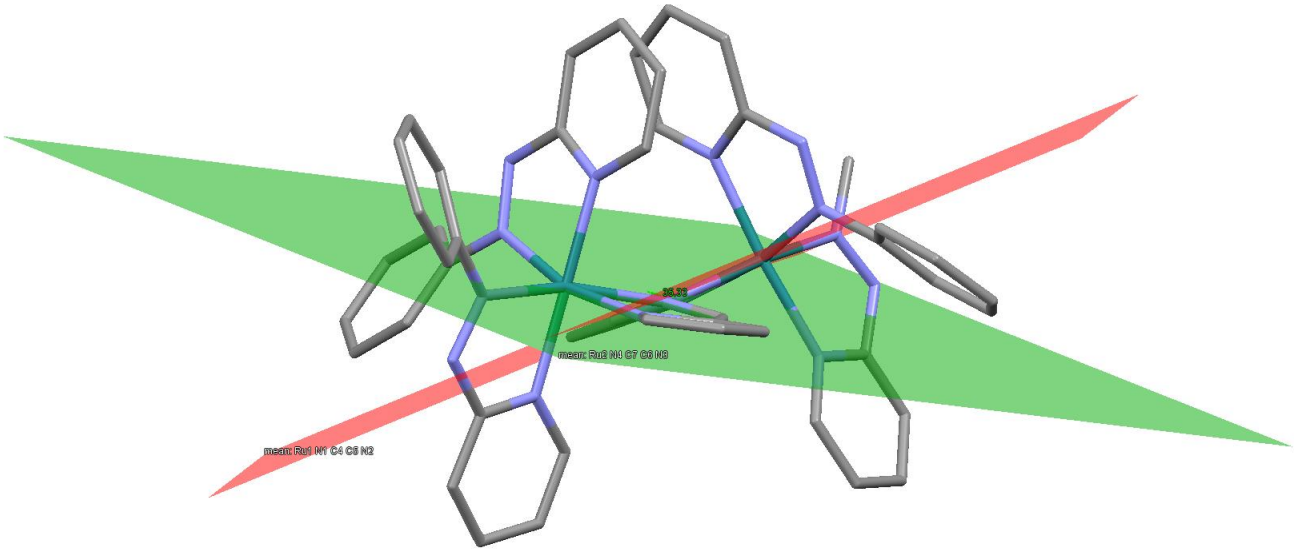


Fig. S8 Torsional angle (deg) between the planes for [**3b**]$^{2+}$.

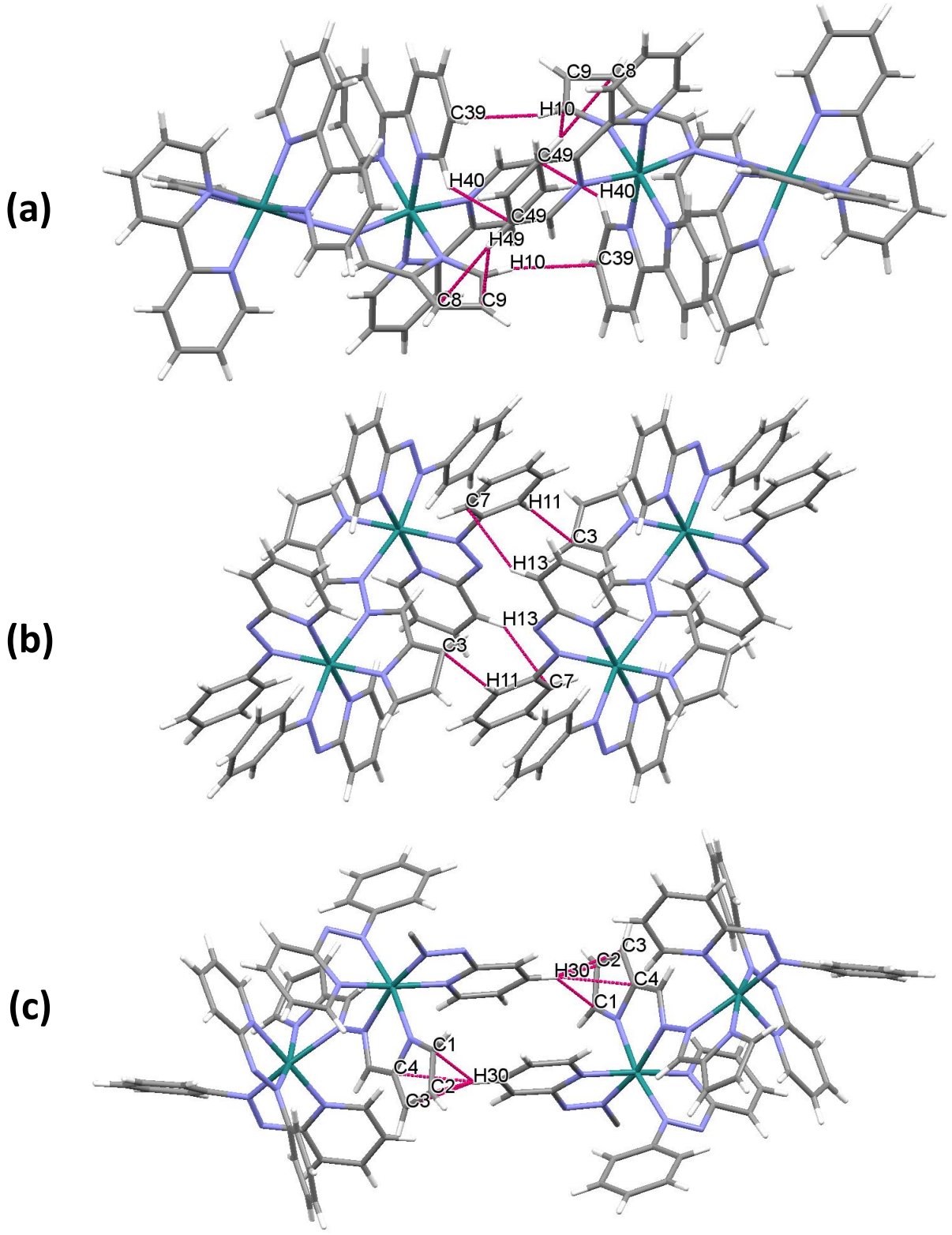


Fig. S9 C-H---π interactions in the crystals of (a) [**2**]$(ClO_4)_2$, (b) [**3a**]$(ClO_4)_2$ and (c) [**3b**] $(ClO_4)_2$.

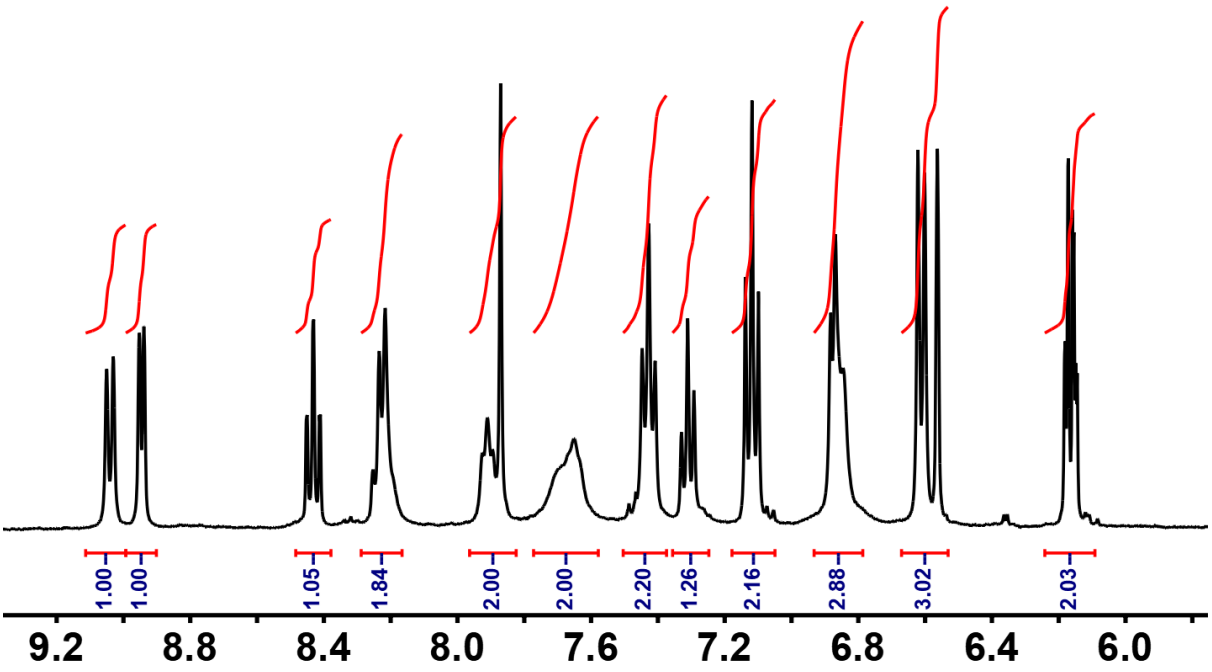


Fig. S10 Integrated ^{1}H NMR spectrum of [**3a**]$(ClO_4)_2$ in $(CD_3)_2SO_3$ with TMS (δ = 0 ppm) as an internal standard.

Table S1 Selected crystallographic parameters

Complex	**1a** (molecule A)	**1b** (molecule A)	**[2]**$(ClO_4)_2$ •CH_2Cl_2	[**3a**]$(ClO_4)_2$	[**3b**]$(ClO_4)_2$ •CH_3OH
empirical formula	$2(C_{30}H_{36}N_4O_8Ru_2)$	$2(C_{34}H_{45}N_4O_8Ru_2)$	$C_{51}H_{42}Cl_4N_{12}O_8Ru_2$	$C_{27}H_{22}ClN_8O_4Ru$	$C_{53.7}H_{46.7}Cl_2N_{16}O_9Ru_2$
formula weight	1563.57	1676.73	1294.90	659.04	1333.86
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*P* ī	*P* ī	*P* ī	*P* ī	*P* ī
a (Å)	9.6955(5)	12.6118(9)	13.8250(3)	9.3715(7)	11.3064(2)
b (Å)	19.0317(9)	15.1919(12)	14.1090(3)	12.8604(10)	12.8799(3)
c (Å)	19.4285(6)	22.0273(17)	14.5097(3)	14.0731(10)	20.0088(4)
α (deg)	100.6410(10)	88.880(6)	82.406(2)	65.971(7)	82.3750(18)
β (deg)	91.2890(10)	78.068(6)	87.564(2)	75.515(6)	80.6850(18)
γ (deg)	104.4110(10)	84.835(6)	73.395(2)	85.018(6)	85.8215(18)
V (Å^3)	3403.6(3)	4112.4(5)	2688.37(10)	1499.7(2)	2846.00(11)
Z	2	2	2	2	2
μ (mm^{-1})	0.937	0.782	0.826	0.657	0.695
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
ρ_{calcd} (g cm^{-3})	1.526	1.354	1.600	1.459	1.557
F (000)	1582	1710	1304	666	1350.0
θ range (deg)	2.176 to 25	1.645 to 24.999	2.095, 24.999	1.630 to 31.209	2.382 to 25
data/restraints/ parameters	11114/ 24/809	14450/0/889	9481/30/785	8746/0/370	10012/79/761
R1, *w*R2 [$I > 2\sigma(I)$]	0.0668, 0.1743	0.0668, 0.1419	0.0331, 0.0758	0.0487, 0.1201	0.0624, 0.1608
R1, *w*R2(all data)	0.0823, 0.1872	0.1318, 0.1713	0.0396, 0.0803	0.0650, 0.1302	0.0702, 0.1682
GOF on F^2	1.022	0.947	1.066	1.049	1.042
largest difference in peak/hole, (e Å^{-3})	1.989 / -1.848	0.916 / -0.882	0.575 / -1.074	0.94 / -1.24	2.84/-1.26

Table S2 Selected bond distances (Å)

Bond (Å)	**1a** (molecule A)		**1b** (molecule A)	
	X-ray	DFT	X-ray	DFT
Ru1-N1	2.014(5)	2.031	2.015(6)	2.049
Ru1-N2	2.056(5)	2.099	2.017(6)	2.090
Ru1-O1	2.030(4)	2.085	2.035(5)	2.084
Ru1-O2	2.004(4)	2.045	1.988(5)	2.046
Ru1-O3	2.010(4)	2.075	2.037(5)	2.080
Ru1-O4	2.009(4)	2.042	1.997(5)	2.045
Ru2-N3	2.054(6)	2.100	2.035(6)	2.092
Ru2-N4	2.000(6)	2.030	2.016(6)	2.047
Ru2-O5	2.037(6)	2.075	1.981(5)	2.080
Ru2-O6	1.991(5)	2.042	2.031(5)	2.044
Ru2-O7	2.005(5)	2.083	2.030(5)	2.085
Ru2-O8	2.029(5)	2.046	1.997(5)	2.046
N2-N3	1.423(7)	1.383	1.405(8)	1.382
N2-C5	1.296(8)	1.317	1.307(9)	1.320
N3-C6	1.300(8)	1.317	1.311(8)	1.320
C4-C5	1.417(9)	1.409	1.380(10)	1.402
C6-C7	1.425(9)	1.409	1.397(10)	1.320
Ru1⋯Ru2	4.935	5.004	4.934	4.975

Table S3 Selected bond distances (Å)

Bond distances (Å)	**1a** (molecule B)		**1b** (molecule B)	
	X-ray	DFT	X-ray	DFT
Ru3-N5	1.980(6)	2.001	2.007(6)	2.039
Ru3-N6	2.050(5)	2.199	2.024(6)	2.076
Ru4-N7	2.067(5)	2.105	2.023(6)	2.081
Ru4-N8	1.995(5)	2.005	2.011(6)	2.046
Ru3-O9	2.045(6)	2.085	1.996(5)	2.001
Ru3-O10	1.986(6)	2.002	2.019(5)	2.055
Ru3-O11	2.038(5)	2.120	2.004(5)	2.019
Ru3-O12	2.002(6)	2.080	2.027(5)	2.077
Ru4-O13	2.043(5)	2.071	2.040(5)	2.100
Ru4-O14	1.996(5)	2.002	2.008(5)	2.014
Ru4-O15	2.012(5)	2.093	2.000(5)	2.005
Ru4-O16	1.999(5)	2.000	2.024(5)	2.086
N6-N7	1.405(7)	1.393	1.413(7)	1.389
N5-C34	1.399(9)	1.410	-	-
N5-C38	-	-	1.380(9)	1.410
N6-C35	1.316(8)	1.345	-	-
N6-C39	-	-	1.314(9)	1.398
N7-C36	1.308(8)	1.305	-	-
N7-C40	-	-	1.287(9)	1.297
C34-C35	1.423(9)	1.413	-	-
C36- C37	1.422(9)	1.401	-	-
C38-C39	-	-	1.410(10)	1.419
C40-C41	-	-	1.385(10)	1.401
Ru3···Ru4	5.005	5.215	4.920	4.975

Table S4 Selected bond distances (Å)

Bond (Å)	[**2**](ClO4)2		[**3a**](ClO4)2		[**3b**](ClO4)2	
	X-ray	DFT	X-ray	DFT	X-ray	DFT
Ru1-N1	2.051(2)	2.085	2.042(2)	2.074	2.059(5)	2.086
Ru1-N2	2.119(2)	2.136	2.164(2)	2.147	2.152(4)	2.133
Ru1-N3	-	-	2.032(2)	2.136	-	-
Ru1-N5	2.056(2)	2.138	2.061(2)	2.093	2.043(5)	2.120
Ru1-N6	2.051(2)	2.100	2.013(2)	2.069	-	-
Ru1-N7	2.058(2)	2.093	-	-	2.048(4)	2.080
Ru1-N8	2.050(2)	2.098	2.027(2)	2.087	1.981(5)	2.063
Ru1-N10	-	-	-	-	2.051(4)	2.096
Ru2-N3	2.120(2)	2.136	-	-	2.123(4)	2.127
Ru2-N4	2.077(2)	2.085	-	-	2.041(4)	2.075
Ru2-N9	2.077(2)	2.093	-	-	-	-
Ru2-N10	2.055(2)	2.098	-	-	-	-
Ru2-N11	2.058(2)	2.138	-	-	2.052(4)	2.065
Ru2-N12	2.054(2)	2.100	-	-	-	
Ru2-N13	-	-	-	-	2.052(4)	2.095
Ru2-N14	-	-	-	-	2.016(4)	2.152
Ru2-N16	-	-	-	-	2.043(4)	2.089
N2-N3	1.412(3)	1.395	-	-	1.411(6)	1.394
N2-N2^{i}	-	-	1.400(4)	1.391	-	-
N3-N4	-	-	1.288(3)	1.298	-	-
N5-N6	-	-	-	-	1.282(6)	1.283
N6-N7	-	-	1.286(3)	1.292	-	-
N8-N9	-	-	-	-	1.279(6)	1.281
N11-N12	-	-	-	-	1.291(6)	1.279
N14-N15	-	-	-	-	1.286(6)	1.279
N2-C5	1.309(3)	1.319	1.310(4)	1.320	1.307(7)	1.319
N2^{i}-C5^{i}	-	-	1.439(4)	1.420	-	-
N3-C6	1.305(4)	1.319	-	-	1.310(7)	1.319
C4-C5	1.405(4)	1.406	1.402(4)	1.404	1.403(7)	1.403
C4^{i}-C5^{i}	-	-	1.386(4)	1.404	-	-
C6-C7	1.410(4)	1.406	-	-	1.405(7)	1.405
Ru1⋯Ru2	5.141	5.497	5.351	5.537	5.201	5.467

Table S5 Selected bond angles (deg)

Bond angles (deg)	**1a** (molecule A)		**1b** (molecule A)	
	X-ray	DFT	X-ray	DFT
N1-Ru1-N2	79.00(2)	78.66	79.90(2)	79.03
N1-Ru1-O1	175.57(19)	174.64	97.50(2)	97.91
N1-Ru1-O2	88.24(18)	88.01	93.00(2)	94.05
N1-Ru1-O3	93.03(19)	94.14	174.60(2)	174.06
N1-Ru1-O4	94.7(2)	95.92	87.30(2)	87.69
N2-Ru1-O1	96.71(19)	96.85	177.00(2)	176.93
N2-Ru1-O2	90.23(18)	91.22	89.10(2)	88.52
N2-Ru1-O3	90.67(18)	88.12	94.70(2)	95.84
N2-Ru1-O4	173.00(19)	174.51	90.10(2)	91.42
O1-Ru1-O2	90.91(17)	89.16	92.60(2)	91.39
O1-Ru1-O3	87.87(17)	88.59	87.80(2)	88.74
O1-Ru1-O4	89.60(18)	88.59	88.20(2)	89.44
O2-Ru1-O3	178.57(17)	177.57	87.50(2)	87.21
O2-Ru1-O4	86.64(17)	89.44	179.10(2)	178.20
O3-Ru1-O4	92.60(17)	91.42	92.20(2)	89.78
N3-Ru2-N4	78.90(2)	78.69	78.67(2)	78.96
N3-Ru2-O5	99.10(2)	96.52	88.40(2)	88.27
N3-Ru2-O6	90.30(2)	91.19	176.40(2)	176.93
N3-Ru2-O7	88.40(2)	88.14	96.10(2)	95.94
N3-Ru2-O8	173.30(2)	174. 59	90.00(2)	91.58
N4-Ru2-O5	177.10(2)	174.25	93.00(2)	93.94
N4-Ru2-O6	87.30(2)	87.72	97.50(2)	98.00
N4-Ru2-O7	93.00(2)	94.43	175.20(2)	173.98
N4-Ru2-O8	94.70(2)	95.95	87.80(2)	87.64
O5-Ru2-O6	90.60(3)	91.50	93.50(2)	91.49
O5-Ru2-O7	89.10(3)	89.36	88.10(2)	87.11
O5-Ru2-O8	87.30(2)	88.86	178.00(2)	178.35
O6-Ru2-O7	178.60(2)	177.56	87.00(2)	88.73
O6-Ru2-O8	87.50(2)	88.54	88.20(2)	89.06

Table S6 Selected bond angles (deg)

Bond angles (deg)	**1a** (molecule B)		**1b** (molecule B)	
	X-ray	DFT	X-ray	DFT
N5-Ru3-N6	79.80(2)	78.59	79.40(2)	79.02
N5-Ru3-O9	175.30(2)	174.03	94.00(2)	93.89
N5-Ru3-O10	92.20(3)	91.29	96.60(2)	95.78
N5-Ru3-O11	95.10(2)	93.99	87.80(2)	87.09
N5-Ru3-O12	88.90(2)	87.98	175.00(2)	174.98
N6-Ru3-O9	96.90(2)	95.91	89.00(2)	88.69
N6-Ru3-O10	89.30(2)	90.00	175.90(2)	174.76
N6-Ru3-O11	174.10(2)	173.01	89.80(2)	87.84
N6-Ru3-O12	88.90(2)	88.04	95.60(2)	96.01
O9-Ru3-O10	91.10(3)	90.87	92.50(2)	91.59
O9-Ru3-O11	88.40(2)	87.99	177.60(2)	176.82
O9-Ru3-O12	87.80(2)	87.89	86.90(2)	85.91
O10-Ru3-O11	88.00(3)	87.09	88.80(2)	87.98
O10-Ru3-O12	177.70(2)	176.71	88.30(2)	87.00
O11-Ru3-O12	94.00(3)	93.09	91.20(2)	92.00
N7-Ru4-N8	78.80(2)	77.98	79.00(3)	77.99
N7-Ru4-O13	99.38(19)	98. 99	95.00(2)	95.09
N7-Ru4-O14	92.46(19)	91.69	90.00(2)	90.10
N7-Ru4-O15	173.40(2)	173.00	89.00(2)	88.95
N7-Ru4-O16	87.83(19)	86.78	97.00(2)	96.89
N8-Ru4-O13	178.10(2)	177.88	173.60(2)	174.69
N8-Ru4-O14	88.20(2)	87.77	85.40(2)	84.89
N8-Ru4-O15	94.70(2)	93.89	95.10(2)	95.00
N8-Ru4-O16	92.70(2)	90.99	97.00(2)	96.09
O13-Ru4-O14	91.60(2)	92.00	92.40(2)	92.01
O13-Ru4-O15	87.18(19)	86.45	86.94(19)	87.04
O13-Ru4-O16	87.50(2)	86.67	88.90(2)	88.89
O14-Ru4-O15	86.60(2)	87.09	178.85(19)	177.91
O14-Ru4-O16	179.10(2)	178.78	88.80(2)	89.00
O15-Ru4-O16	93.20(2)	94.00	92.10(2)	93.01

Table S7 Selected bond angles (deg)

Bond angles (deg)	[**2**](ClO$_4$)$_2$	
	X-ray	DFT
N1-Ru1-N2	77.78(9)	77.14
N3-Ru2-N4	77.32(9)	77.14
N1-Ru1-N5	172.96(9)	172.06
N1-Ru1-N6	94.79(9)	94.72
N1-Ru1-N7	87.05(9)	88.62
N1-Ru1-N8	93.52(9)	91.75
N2-Ru1-N5	98.99(9)	96.25
N2-Ru1-N6	85.45(9)	88.72
N2-Ru1-N7	100.69(9)	103.12
N2-Ru1-N8	171.30(9)	167.71
N5-Ru1-N6	78.64(9)	77.99
N5-Ru1-N7	99.75(9)	99.19
N5-Ru1-N8	89.64(9)	88.59
N6-Ru1-N7	173.84(9)	174.52
N6-Ru1-N8	95.23(9)	97.54
N7-Ru1-N8	78.77(10)	77.37
N3-Ru2-N9	101.69(9)	103.13
N3-Ru2-N10	89.66(9)	88.73
N3-Ru2-N11	96.04(9)	96.24
N3-Ru2-N12	170.79(9)	167.71
N4-Ru2-N9	173.15(9)	172.06
N4-Ru2-N10	94.92(9)	94.72
N4-Ru2-N11	88.47(9)	88.62
N4-Ru2-N12	94.89(9)	91.75
N9-Ru2-N10	78.26(9)	77.37
N9-Ru2-N11	98.38(9)	97.55
N9-Ru2-N12	86.62(9)	88.58
N10-Ru2-N11	173.89(9)	174.52
N10-Ru2-N12	95.97(9)	99.19
N11-Ru2-N12	78.66(9)	77.99

Table S8 Selected bond angles (deg)

Bond angles (deg)	[**3a**](ClO4)2	
	X-ray	DFT
N1-Ru1-N2	76.77(9)	77.13
N1-Ru1-N3	166.77(9)	168.12
N1-Ru1-N5	93.36(10)	93.51
N1-Ru1-N6	91.06(10)	93.89
N1-Ru1-N8	89.67(10)	86.98
N2-Ru1-N3	108.25(9)	105.01
N2-Ru1-N5	83.11(9)	86.93
N2-Ru1-N6	165.01(10)	167.29
N3-Ru1-N5	75.46(10)	75.07
N3-Ru1-N6	85.54(10)	85.62
N3-Ru1-N8	101.91(10)	104.35
N5-Ru1-N6	106.63(10)	102.77
N5-Ru1-N8	175.59(9)	178.63
N6-Ru1-N8	76.49(10)	75.92

Table S9 Selected bond angles (deg)

Bond angles (deg)	[**3b**]$(ClO_4)_2$	
	X-ray	DFT
N1-Ru1-N2	77.44(17)	77.05
N3-Ru2-N4	77.78(16)	77.16
N1-Ru1-N5	169.22(17)	166.39
N1-Ru1-N7	93.80(18)	91.58
N1-Ru1-N8	90.81(19)	89.20
N1-Ru1-N10	87.33(17)	86.93
N2-Ru1-N5	97.05(17)	97.40
N2-Ru1-N7	87.26(17)	87.43
N2-Ru1-N8	167.54(18)	163.87
N2-Ru1-N10	98.45(16)	94.39
N5-Ru1-N7	76.54(19)	75.63
N5-Ru1-N8	95.21(18)	97.80
N5-Ru1-N10	102.75(17)	106.02
N7-Ru1-N8	97.76(18)	101.52
N7-Ru1-N10	174.29(18)	177.33
N8-Ru1-N10	76.62(17)	76.25
N3-Ru2-N11	98.11(16)	99.83
N3-Ru2-N13	88.09(16)	87.56
N3-Ru2-N14	165.46(17)	166.95
N3-Ru2-N16	93.47(17)	94.19
N4-Ru2-N11	166.15(17)	166.98
N4-Ru2-N13	90.56(17)	91.87
N4-Ru2-N14	91.12(17)	93.46
N4-Ru2-N16	88.50(17)	86.58
N11-Ru2-N13	76.01(18)	75.28
N11-Ru2-N14	94.81(17)	91.28
N11-Ru2-N16	105.04(17)	106.33
N13-Ru2-N14	101.54(17)	101.97
N13-Ru2-N16	177.97(17)	177.34
N14-Ru2-N16	76.68(17)	75.98

Table S10 Intermolecular C-H---π interactions

Interaction C-H---π (Å)	[**2**]$(ClO_4)_2$	[**3a**]$(ClO_4)_2$	[**3b**]$(ClO_4)_2$
C8---H49	2.836	-	-
C9---H49	2.744	-	-
C49---H40	2.893	-	-
C39---H10	2.792	-	-
C3---H11	-	2.655	-
C7---H13	-	2.766	-
C1---H30	-	-	2.759
C2---H30	-	-	2.758
C3---H30	-	-	2.752
C4---H30	-	-	2.727

Table S11 Energies of DFT (B3LYP/LanL2DZ/6-31G*) calculated optimised structures

Complex	*E* (Hartrees)				$\Delta E_{(HE\text{-}LE)}$ [a]
	S = 0	*S* = 1/2	*S* = 1	*S* = 3/2	
1b^{+}	-	–2330.6658737	-	–2330.6648219	0.0010518 Hartrees 290.84341583 cm^{-1}
1b^{0}	–2330.8396338	-	–2330.8593586	-	0.0197248 Hartrees 4329.0931818 cm^{-1}
1b^{-}	-	–2330.9293102	-	–2330.8663904	0.0629198 Hartrees 13809.299825 cm^{-1}
2^{4+}	–2773.213059	-	–2773.2084285	-	0.0046305 Hartrees 1016.277274 cm^{-1}
2^{0}	–2774.3493344	-	–2774.3626048	-	0.0132704 Hartrees 2912.51613 cm^{-1}
3a^{0}	–3148.084729	-	–3148.1016969	-	0.019224 Hartrees 4219.18029 cm^{-1}
3b^{0}	–3148.0802045	-	–3148.0981333	-	0.0179255 Hartrees 3934.19248 cm−1

[a] HE = Spin state in higher in energy and LE = Spin state in lower in energy.

Table S12 DFT calculated selected MO compositions

Complex	MO	Fragments	% Contribution
1b^{+} (*S*=1/2)	β-LUMO	Ru/acac/L	69/22/09
1b (*S*=1)	SOMO	L/Ru /acac	85/12/03
	β-LUMO	Ru/acac/L	68/20/12
1b^{-} (*S*=1/2)	HOMO	Ru/L/acac	55/36/09
2^{4+} (*S*=0)	LUMO	L/Ru/bpy	66/30/04
2^{3+} (*S*=1/2)	SOMO	L/Ru/bpy	84/13/03
	β-LUMO	L/Ru/bpy	84/14/02
2^{2+} (*S*=0)	HOMO	L/Ru/bpy	83/14/03
	LUMO	bpy/Ru/L	90/07/03
2^{+} (*S*=1/2)	SOMO	bpy/Ru/L	94/05/01
	β-LUMO	bpy/Ru/L	93/06/01
2^{0} (*S*=1)	SOMO	bpy/Ru/L	94/05/01
3a^{3+} (*S*=1/2)	LUMO	L/Ru/pap	90/08/02
3a^{2+} (*S*=0)	HOMO	L/Ru/pap	92/06/02
	LUMO	pap/Ru/L	83/14/02
3a^{+} (*S*=1/2)	SOMO	pap/Ru/L	89/09/02
	β-LUMO	pap/Ru/L	87/11/02
3a^{0} (*S*=1)	SOMO	pap/Ru/L	90/08/02
3b^{3+} (*S*=1/2)	LUMO	L/Ru/pap	88/09/03
3b^{2+} (*S*=0)	HOMO	L/Ru/pap	87/08/05
	LUMO	pap/Ru/L	88/09/03
3b^{+} (*S*=1/2)	SOMO	pap/Ru/L	89/09/02
	β-LUMO	pap/Ru/L	86/12/02
3b^{0} (*S*=1)	SOMO	pap/Ru/L	90/08/02

Table S13 DFT calculated MO composition for **1b**$^{+}$ in *S* = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	$acac^{-}$
		α-MO		
LUMO+5	–3.324	07	28	65
LUMO+4	–3.401	07	20	73
LUMO+3	–3.426	03	02	95
LUMO+2	–3.627	05	09	86
LUMO+1	–4.156	05	92	03
LUMO	–6.583	13	84	03
SOMO	–7.894	38	41	21
HOMO–1	–8.176	36	48	16
HOMO–2	–8.283	32	13	55
HOMO–3	–8.350	36	22	42
HOMO–4	–8.501	20	42	38
HOMO–5	–8.720	11	28	61
		β-MO		
LUMO+5	–3.399	05	04	91
LUMO+4	–3.473	06	39	55
LUMO+3	–3.625	05	38	57
LUMO+2	–4.291	06	91	03
LUMO+1	–5.642	67	11	22
LUMO	–5.648	69	09	22
HOMO	–7.809	41	46	13
HOMO–1	–7.954	51	24	25
HOMO–2	–8.163	26	46	28
HOMO–3	–8.462	45	14	41
HOMO–4	–8.622	37	15	48
HOMO–5	–8.729	34	28	38

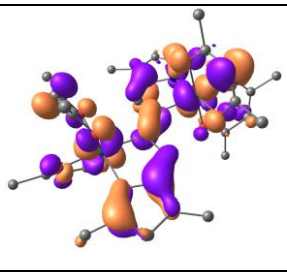
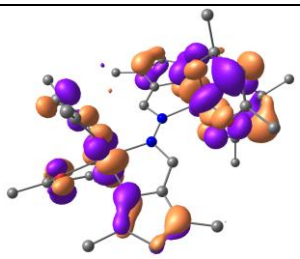
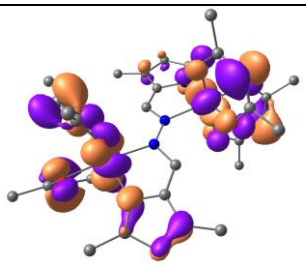
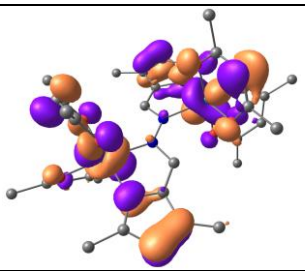
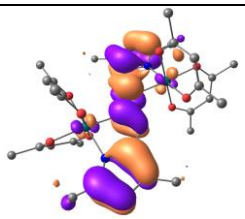
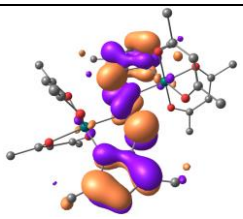
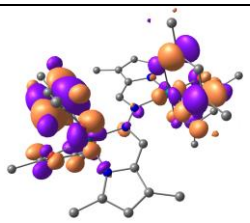
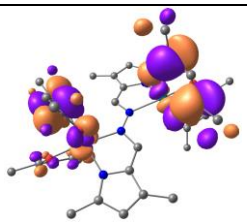
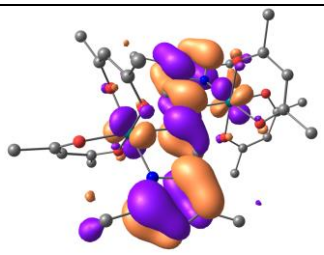
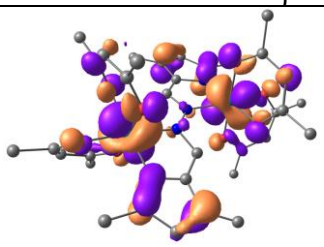
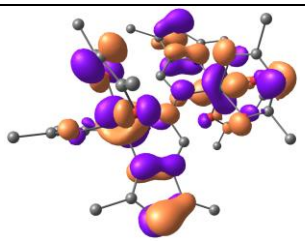
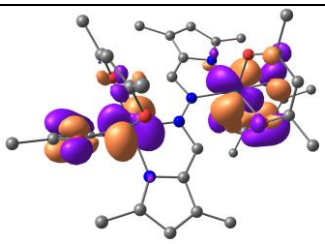
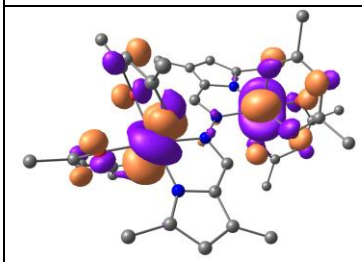
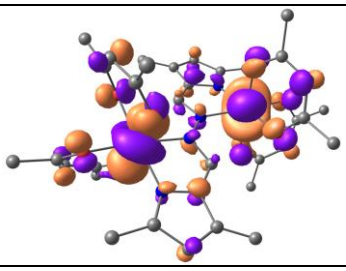
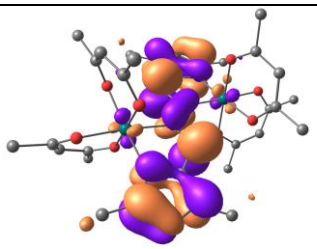
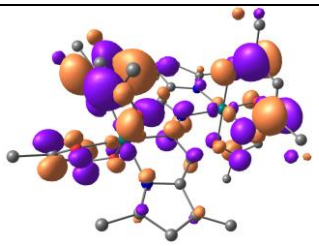
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 DFT calculated MO composition for **1b** in *S* = 1 state

MO	Energy (eV)	% Composition		
		Ru	L^-	$acac^-$
		α-MO		
LUMO+5	–0.133	23	61	16
LUMO+4	–0.552	03	07	90
LUMO+3	–0.707	05	05	90
LUMO+2	–0.767	03	03	94
LUMO+1	–0.902	06	57	37
LUMO	–0.944	03	32	65
SOMO1	–4.324	12	85	03
SOMO2	–4.951	42	45	13
HOMO–2	–5.051	35	56	09
HOMO–3	–5.216	27	55	18
HOMO–4	–5.481	37	07	56
HOMO–5	–5.561	34	23	43
		β-MO		
LUMO+5	–0.651	07	05	88
LUMO+4	–0.735	03	02	95
LUMO+3	–0.868	07	45	48
LUMO+2	–0.908	04	44	52
LUMO+1	–2.506	65	16	19
LUMO	–2.625	68	12	20
HOMO	–4.304	21	72	07
HOMO–1	–4.763	49	35	16
HOMO–2	–4.901	37	46	17
HOMO–3	–5.268	19	67	14
HOMO–4	– 5.476	67	14	19
HOMO–5	–5.556	64	13	23

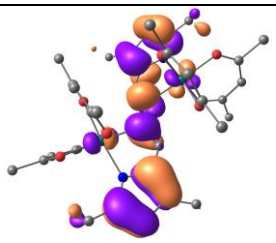
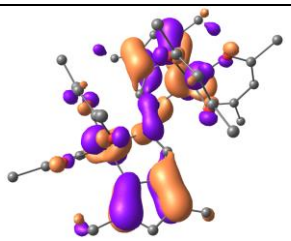
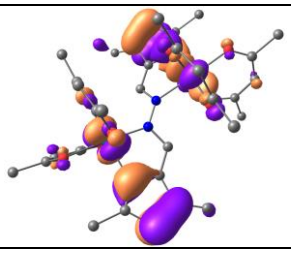
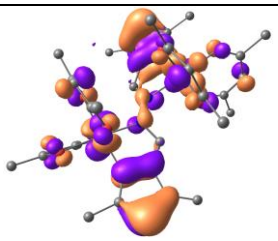
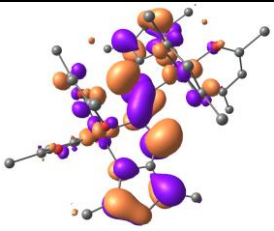
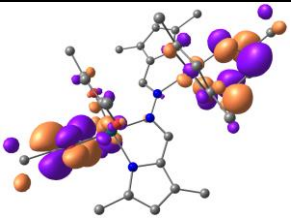
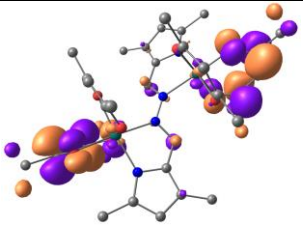
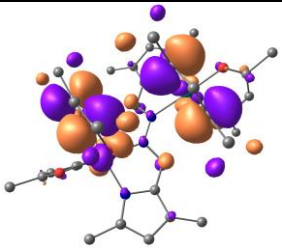
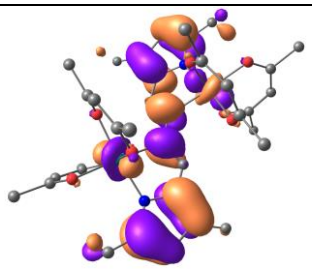
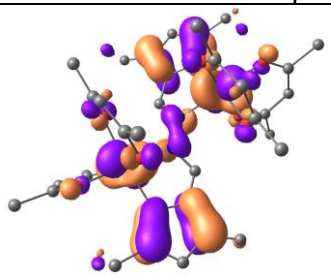
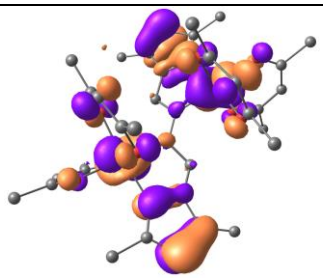
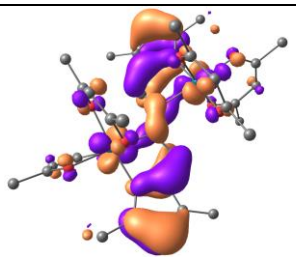
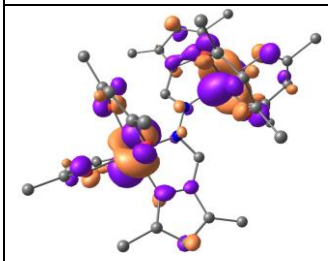
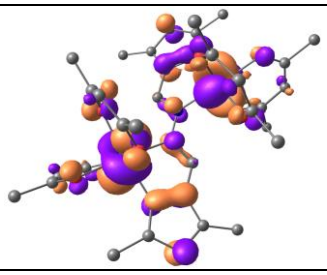
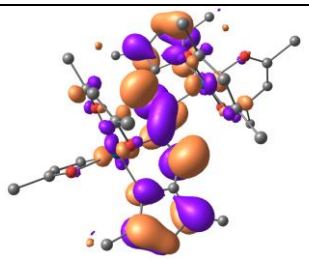
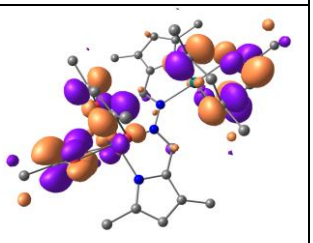
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 DFT calculated MO composition for **1b**$^{-}$ in *S* = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	$acac^{-}$
		α-MO		
LUMO+5	3.008	13	74	13
LUMO+4	2.556	05	08	87
LUMO+3	2.365	05	05	90
LUMO+2	2.302	05	02	93
LUMO+1	2.053	08	79	13
LUMO	1.876	04	11	85
SOMO	−1.222	36	55	09
HOMO−1	−1.308	60	22	18
HOMO−2	−1.573	54	23	23
HOMO−3	−1.718	61	23	16
HOMO−4	−1.898	62	17	21
HOMO−5	−2.100	52	23	25
		β-MO		
LUMO+5	2.578	07	09	85
LUMO+4	2.379	05	06	89
LUMO+3	2.324	06	02	92
LUMO+2	2.109	09	81	10
LUMO+1	1.896	05	09	86
LUMO	0.133	59	23	17
HOMO	−0.536	69	11	21
HOMO−1	−1.176	55	32	14
HOMO−2	−1.448	51	34	15
HOMO−3	−1.661	58	23	19
HOMO−4	−1.850	52	32	16
HOMO−5	−2.150	70	13	17

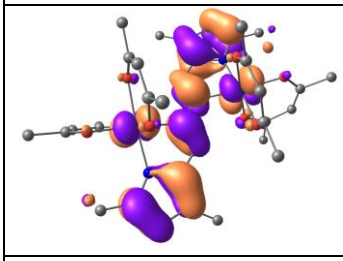
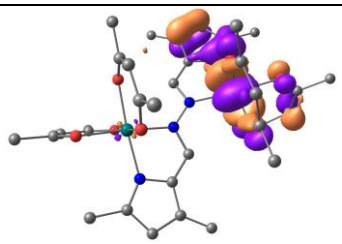
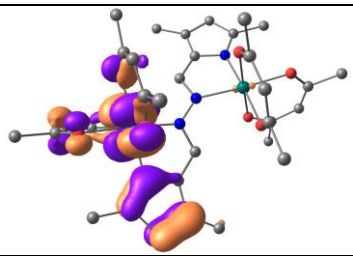
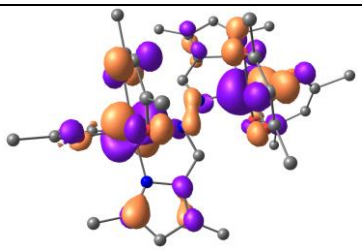
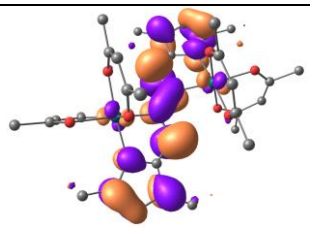
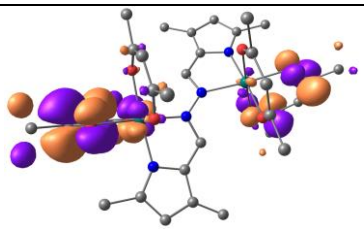
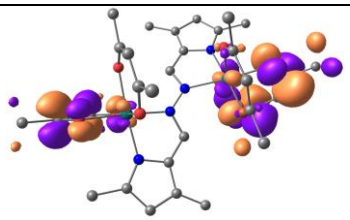
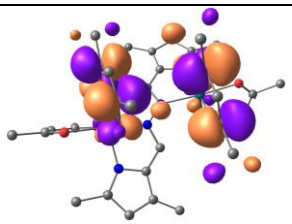
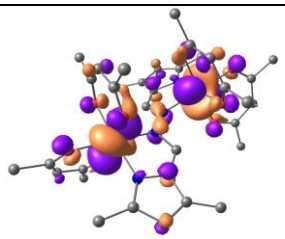
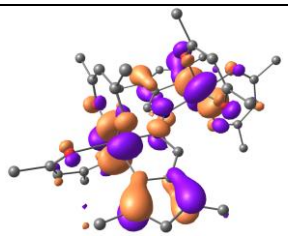
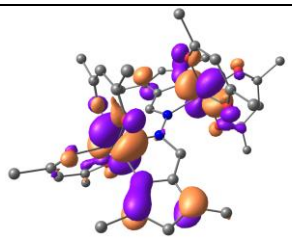
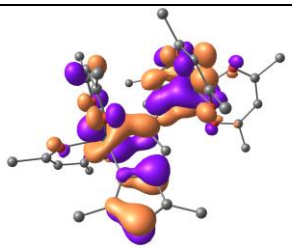
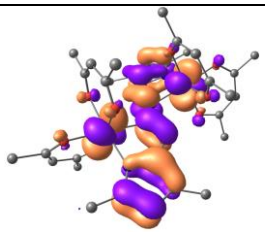
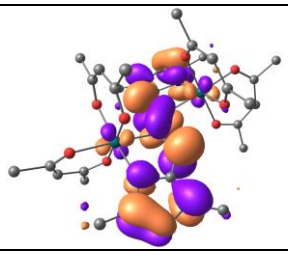
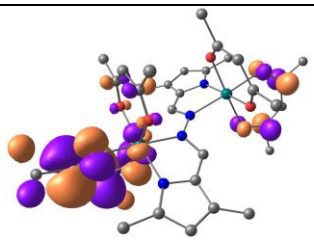
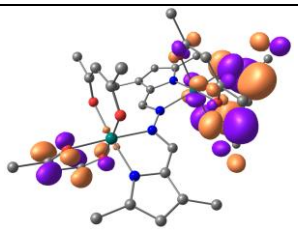
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 DFT calculated MO composition for $\mathbf{2}^{4+}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	bpy
LUMO+5	−11.047	05	01	94
LUMO+4	−11.055	05	01	94
LUMO+3	−11.307	06	03	91
LUMO+2	−11.314	05	02	93
LUMO+1	−11.713	03	92	05
LUMO	−14.213	30	66	04
HOMO	−15.133	71	18	11
HOMO−1	−15.218	63	25	12
HOMO−2	−15.460	78	08	14
HOMO−3	−15.466	74	07	19
HOMO−4	−15.559	73	07	20
HOMO−5	−15.773	63	19	18

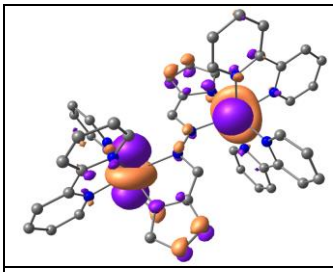
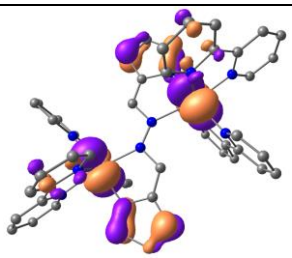
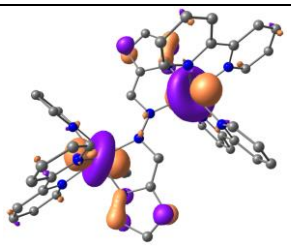
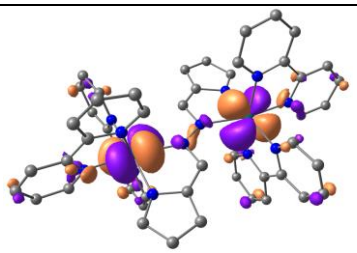
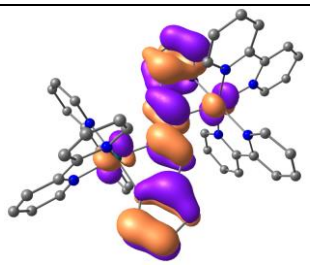
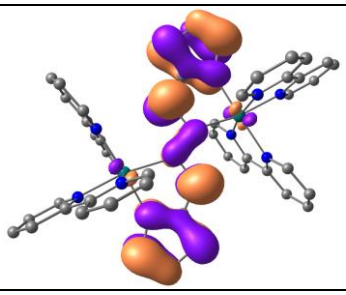
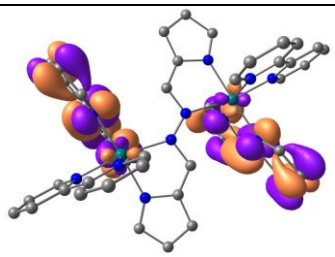
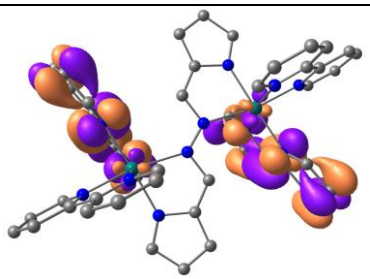
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 DFT calculated MO composition for $\mathbf{2}^{3+}$ in $S = 1/2$ state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	bpy
		α-MO		
LUMO+5	–7.967	06	04	90
LUMO+4	–8.641	07	22	71
LUMO+3	–8.661	06	01	93
LUMO+2	–8.684	04	62	34
LUMO+1	–8.847	05	01	94
LUMO	–8.848	05	09	86
SOMO	–12.156	45	50	05
HOMO–1	–12.224	69	21	10
HOMO–2	–12.263	55	36	09
HOMO–3	–12.514	80	05	15
HOMO–4	–12.619	80	06	14
HOMO–5	–12.632	82	05	13
		β-MO		
LUMO+5	–8.538	05	85	10
LUMO+4	–8.653	06	02	92
LUMO+3	–8.659	06	01	93
LUMO+2	–8.837	06	04	90
LUMO+1	–8.844	05	01	94
LUMO	–10.809	14	84	02
HOMO	–12.127	70	20	10
HOMO–1	–12.176	67	23	10
HOMO–2	–12.386	70	19	11
HOMO–3	–12.482	79	06	15
HOMO–4	–12.569	79	08	13
HOMO–5	–12.708	76	09	15

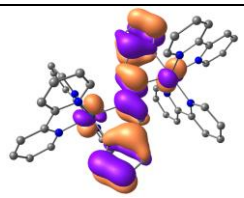
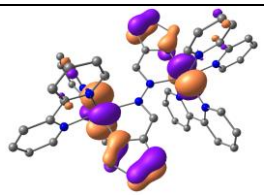
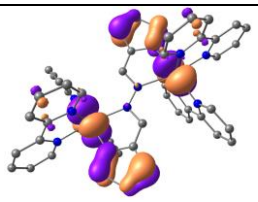
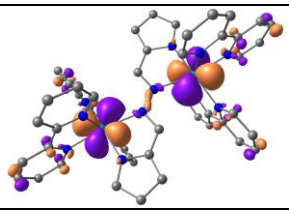
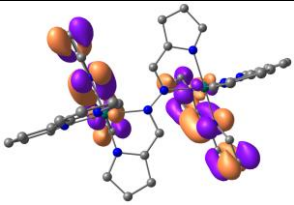
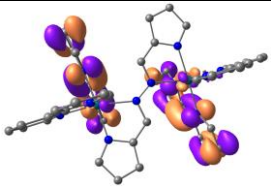
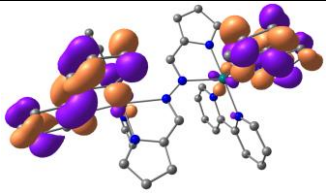
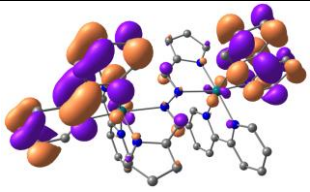
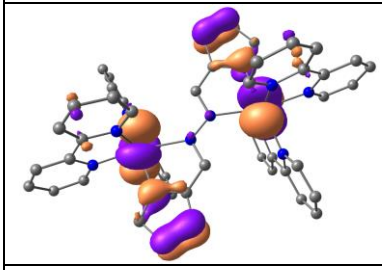
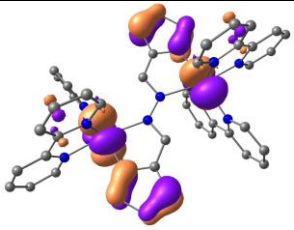
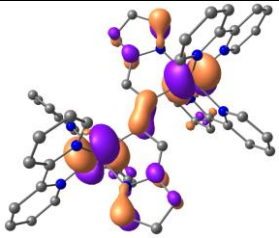
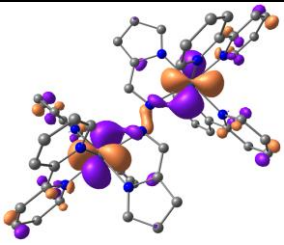
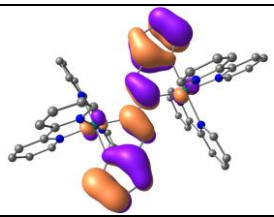
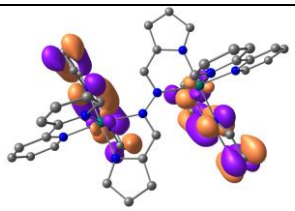
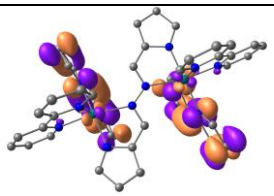
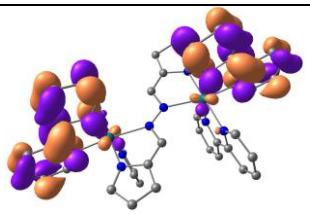
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18 DFT calculated MO composition for $\mathbf{2}^{2+}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	bpy
LUMO+5	–5.733	03	03	94
LUMO+4	–5.923	06	02	92
LUMO+3	–6.366	07	01	91
LUMO+2	–6.379	08	01	91
LUMO+1	–6.571	05	01	94
LUMO	–6.708	07	03	90
HOMO	–8.754	14	83	03
HOMO–1	–9.337	54	36	10
HOMO–2	–9.360	51	39	10
HOMO–3	–9.649	37	54	09
HOMO–4	–9.865	78	05	17
HOMO–5	–9.983	77	08	15

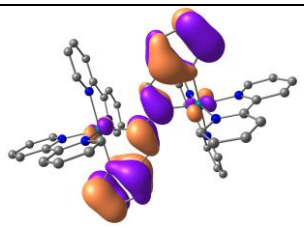
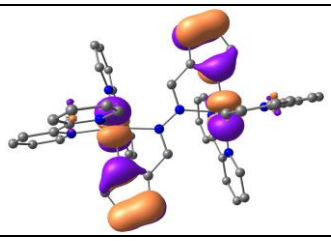
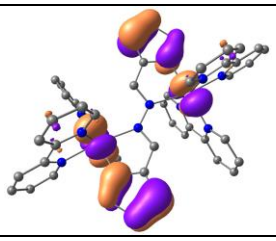
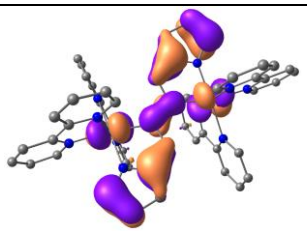
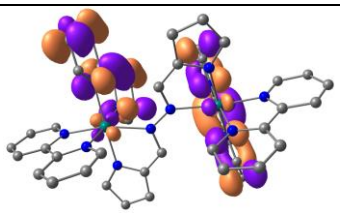
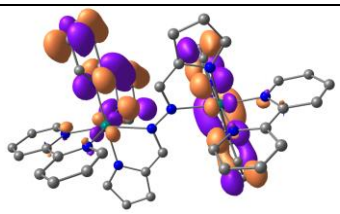
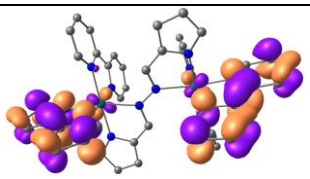
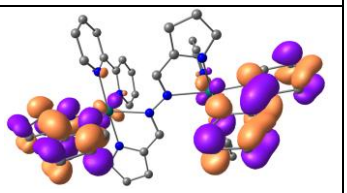
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19 DFT calculated MO composition for $\mathbf{2}^{+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	bpy
		α-MO		
LUMO+5	–3.004	07	63	30
LUMO+4	–3.154	05	02	93
LUMO+3	–3.191	05	16	79
LUMO+2	–4.003	09	02	89
LUMO+1	–4.065	08	01	91
LUMO	–4.202	05	01	94
SOMO	–4.561	04	01	95
HOMO–1	–6.277	11	87	02
HOMO–2	–6.871	62	29	09
HOMO–3	–6.886	60	30	10
HOMO–4	–7.254	64	22	14
HOMO–5	–7.280	79	09	12
		β-MO		
LUMO+5	–3.130	05	02	93
LUMO+4	–3.173	05	19	76
LUMO+3	–3.714	07	02	90
LUMO+2	–3.732	06	01	93
LUMO+1	–3.879	06	01	93
LUMO	–3.884	06	01	93
HOMO	–6.277	11	87	02
HOMO–1	–6.861	62	28	09
HOMO–2	–6.873	61	29	10
HOMO–3	–7.245	64	25	12
HOMO–4	–7.278	81	05	14
HOMO–5	–7.362	80	07	13

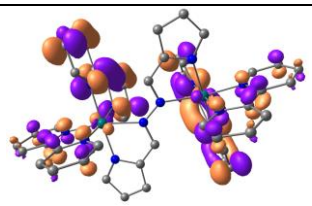
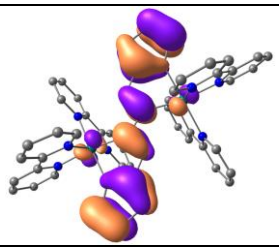
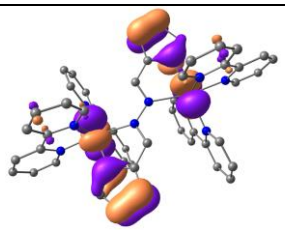
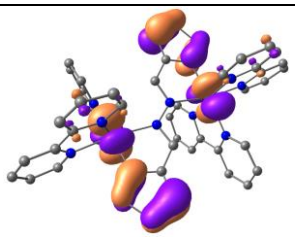
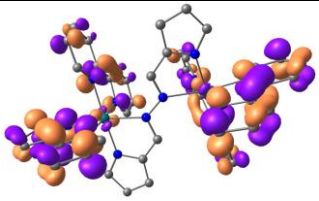
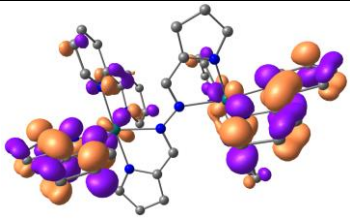
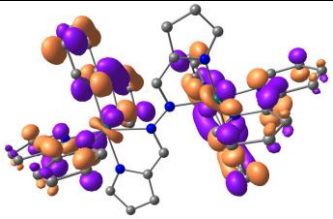
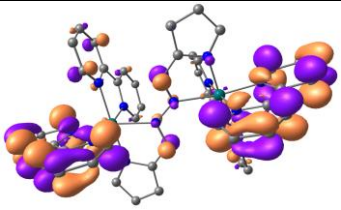
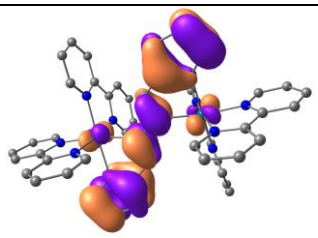
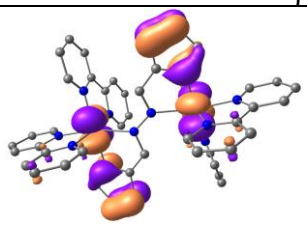
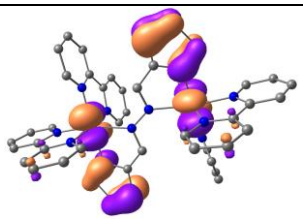
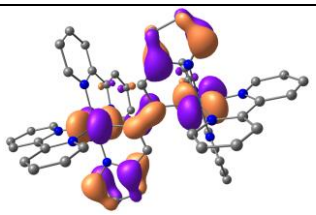
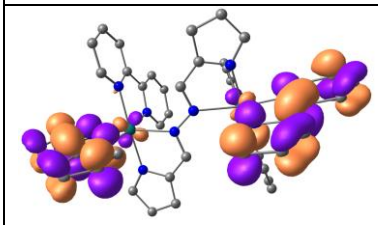
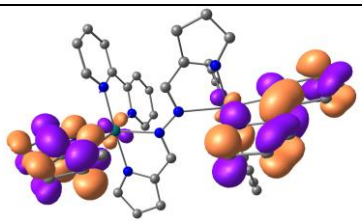
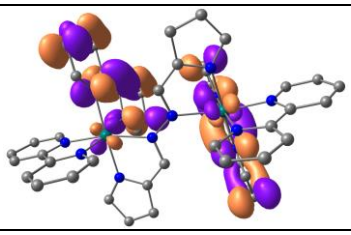
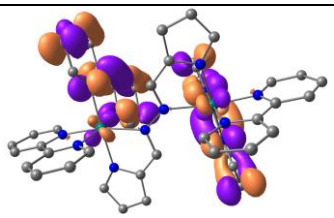
α-MO			
			
SOMO1	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 DFT calculated MO composition for $\mathbf{2}^{0}$ in $S = 1$ state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	bpy
		α-MO		
LUMO+5	–0.493	08	02	90
LUMO+4	–0.637	06	35	59
LUMO+3	–0.702	07	02	91
LUMO+2	–0.787	06	47	47
LUMO+1	–1.691	10	02	88
LUMO	–1.721	09	01	90
SOMO1	–2.343	05	01	94
SOMO2	–2.351	04	01	95
HOMO–2	–3.973	15	83	02
HOMO–3	–4.454	67	23	10
HOMO–4	–4.476	64	26	10
HOMO–5	–4.777	76	07	17
		β-MO		
LUMO+5	–0.650	07	02	91
LUMO+4	–0.768	06	57	37
LUMO+3	–1.177	07	01	92
LUMO+2	–1.189	07	01	92
LUMO+1	–1.246	06	02	92
LUMO	–1.259	05	02	93
HOMO	–3.972	15	83	02
HOMO–1	–4.431	68	22	10
HOMO–2	–4.444	66	24	10
HOMO–3	–4.771	79	09	12
HOMO–4	–4.801	75	09	16
HOMO–5	–4.877	79	08	13

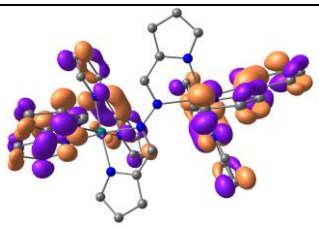
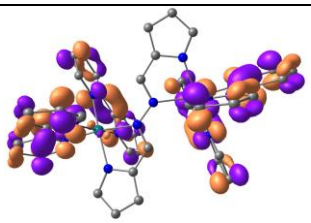
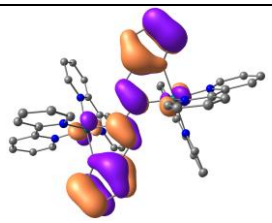
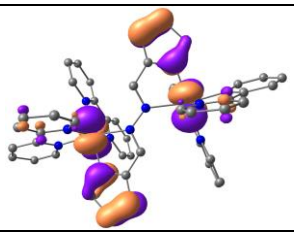
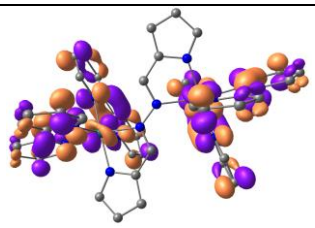
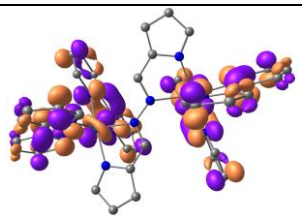
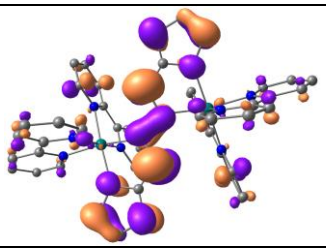
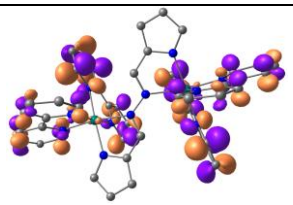
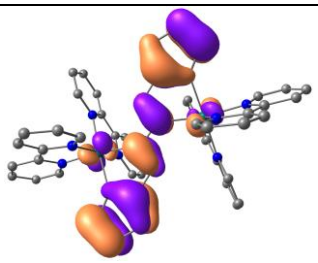
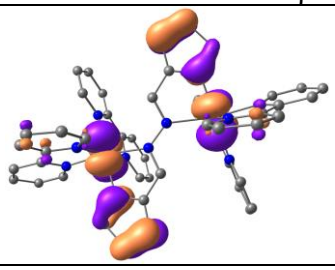
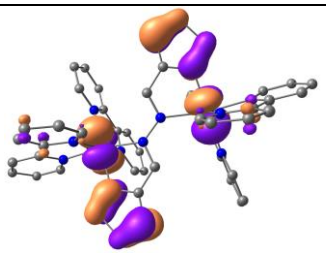
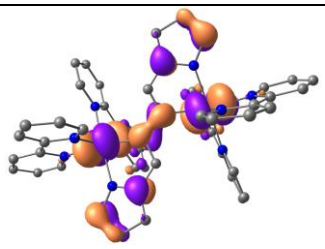
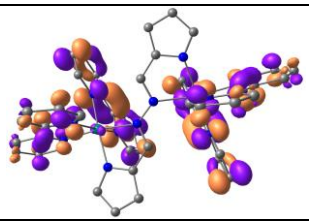
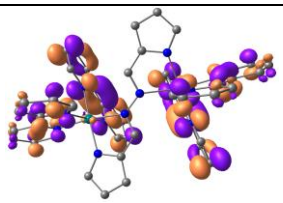
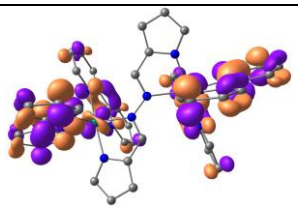
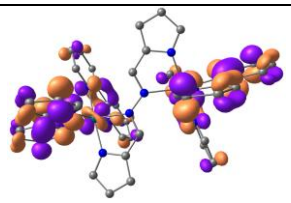
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 DFT calculated MO composition for **3a**$^{3+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
		α-MO		
LUMO+5	–8.081	06	26	68
LUMO+4	–9.082	04	92	04
LUMO+3	–9.676	12	02	86
LUMO+2	–9.691	11	02	87
LUMO+1	–9.838	09	03	88
LUMO	–9.885	10	03	87
SOMO	–12.594	38	53	09
HOMO–1	–12.705	60	21	19
HOMO–2	–12.766	45	42	13
HOMO–3	–13.009	28	06	66
HOMO–4	–13.035	08	09	83
HOMO–5	–13.169	05	00	95
		β-MO		
LUMO+5	–8.936	04	92	04
LUMO+4	–9.675	13	02	85
LUMO+3	–9.690	11	02	87
LUMO+2	–9.836	09	03	88
LUMO+1	–9.882	10	03	87
LUMO	–11.187	08	90	02
HOMO	–12.640	62	21	17
HOMO–1	–12.672	60	22	18
HOMO–2	–12.960	46	18	36
HOMO–3	–13.010	20	08	72
HOMO–4	–13.113	12	38	50
HOMO–5	–13.169	03	01	96

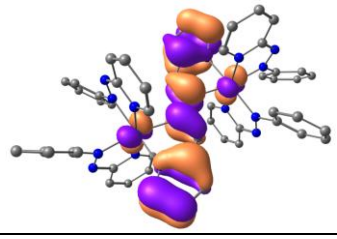
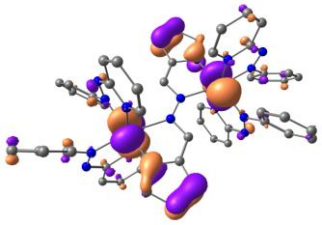
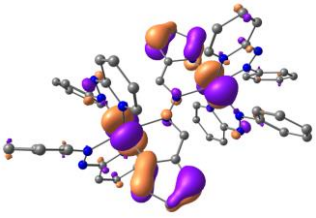
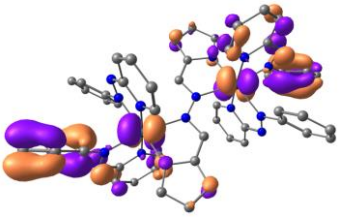
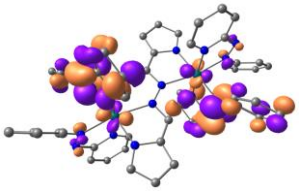
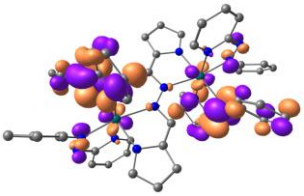
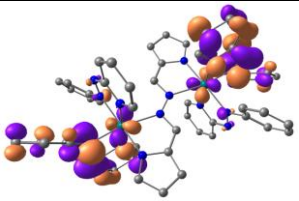
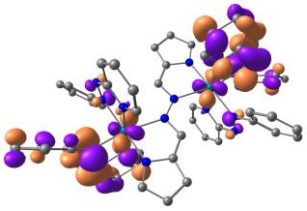
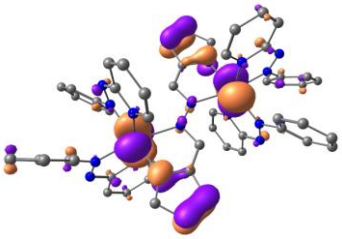
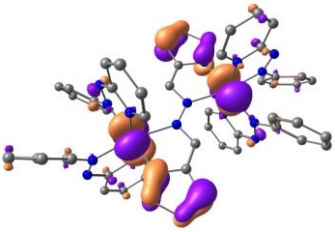
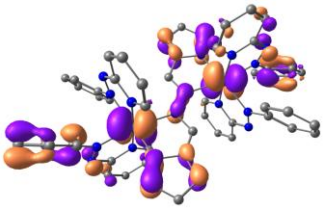
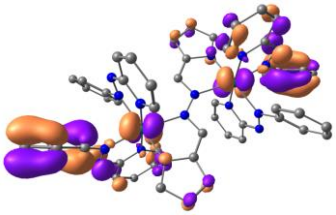
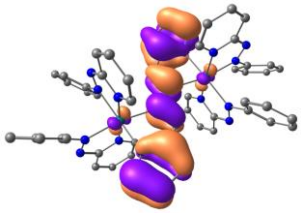
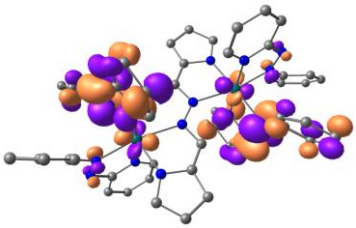
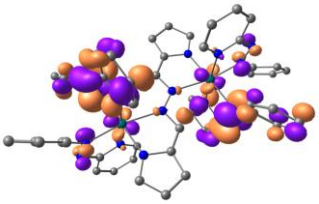
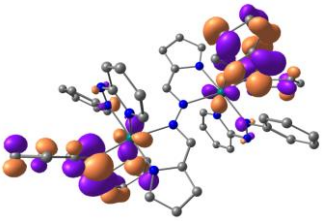
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22 DFT calculated MO composition for **3a**$^{2+}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
LUMO+5	–5.941	05	02	93
LUMO+4	–6.113	04	61	35
LUMO+3	–7.394	17	03	80
LUMO+2	–7.477	13	03	84
LUMO+1	–7.534	12	02	86
LUMO	–7.543	14	02	84
HOMO	–9.261	06	92	02
HOMO–1	–10.001	42	44	14
HOMO–2	–10.008	42	43	15
HOMO–3	–10.414	11	83	06
HOMO–4	–10.867	53	14	33
HOMO–5	–10.877	60	10	30

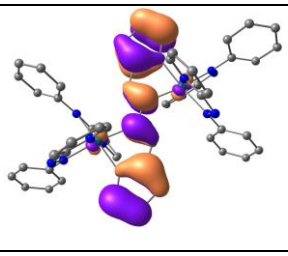
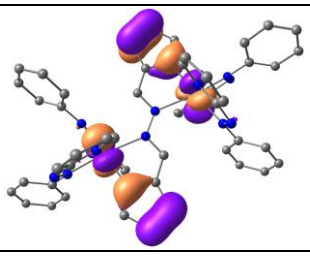
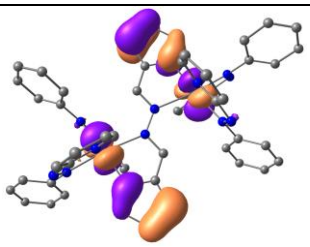
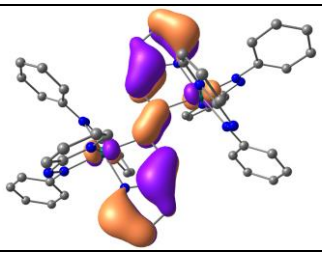
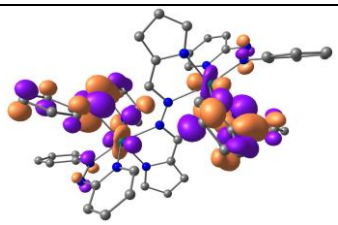
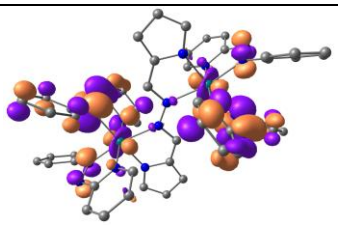
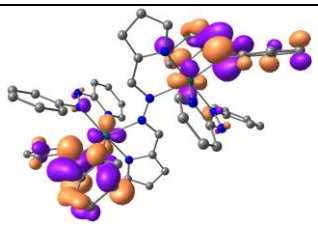
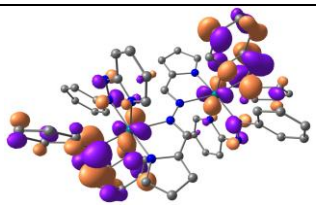
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 DFT calculated MO composition for **3a**$^{+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
		α-MO		
LUMO+5	–3.340	03	01	96
LUMO+4	–3.346	05	02	93
LUMO+3	–3.471	05	87	08
LUMO+2	–5.006	19	02	79
LUMO+1	–5.037	18	02	80
LUMO	–5.317	08	03	89
SOMO	–5.716	09	02	89
HOMO–1	–6.705	06	91	03
HOMO–2	–7.457	53	36	11
HOMO–3	–7.466	52	36	12
HOMO–4	–7.909	28	65	07
HOMO–5	–8.098	60	20	20
		β-MO		
LUMO+5	–3.326	05	02	93
LUMO+4	–3.468	05	88	07
LUMO+3	–4.597	11	03	86
LUMO+2	–4.649	11	02	87
LUMO+1	–4.924	11	02	87
LUMO	–4.931	11	02	87
HOMO	–6.705	06	91	02
HOMO–1	–7.451	53	36	11
HOMO–2	–7.455	53	35	12
HOMO–3	–7.899	32	60	08
HOMO–4	–8.086	56	23	22
HOMO–5	–8.096	65	11	24

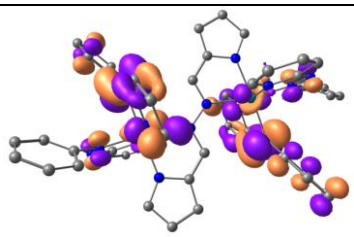
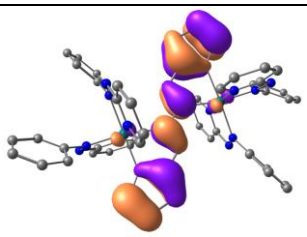
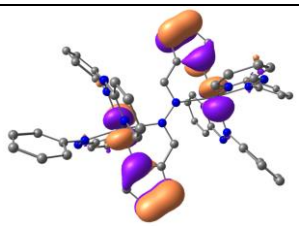
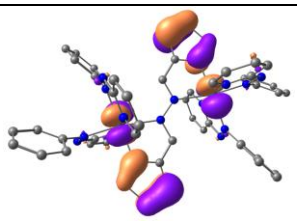
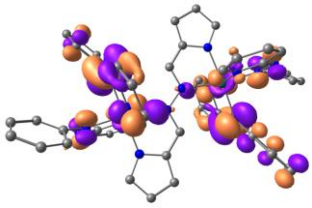
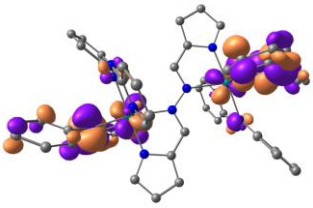
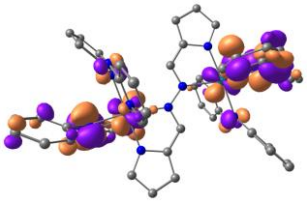
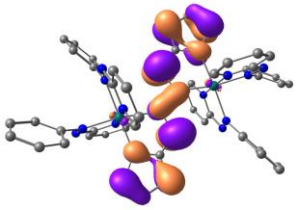
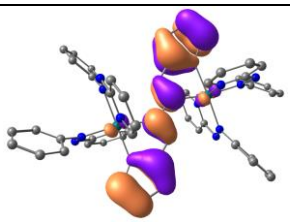
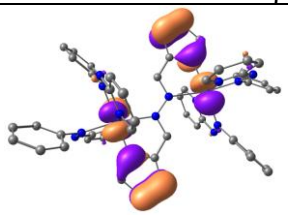
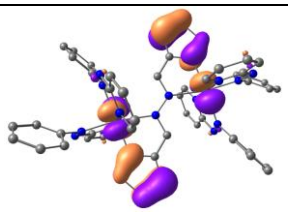
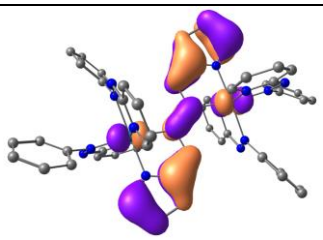
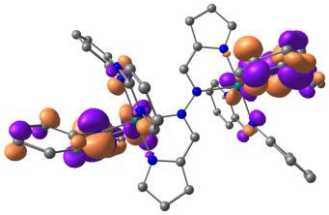
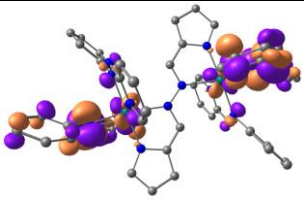
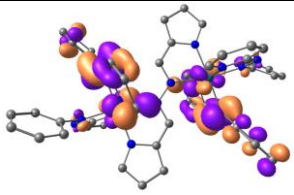
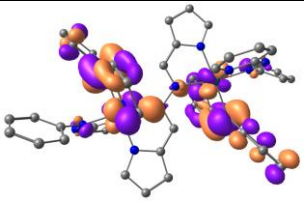
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S24 DFT calculated MO composition for **3a**^{0} in *S* = 1 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
		α-MO		
LUMO+5	–0.854	04	02	94
LUMO+4	–0.923	05	02	93
LUMO+3	–0.924	04	01	95
LUMO+2	–1.158	05	89	06
LUMO+1	–2.607	23	02	75
LUMO	–2.662	22	02	76
SOMO1	–3.540	08	03	90
SOMO2	–3.564	08	02	90
HOMO–2	–4.410	08	89	03
HOMO–3	–5.049	61	27	12
HOMO–4	–5.061	59	29	12
HOMO–5	–5.520	61	26	13
		β-MO		
LUMO+5	–0.852	06	01	93
LUMO+4	–1.151	05	89	06
LUMO+3	–2.022	11	03	86
LUMO+2	–2.072	10	03	87
LUMO+1	–2.195	10	02	87
LUMO	–2.202	10	02	87
HOMO	–4.411	08	89	03
HOMO–1	–5.039	60	28	12
HOMO–2	–5.040	59	28	13
HOMO–3	–5.481	66	20	14
HOMO–4	–5.610	67	11	22
HOMO–5	–5.689	30	53	17

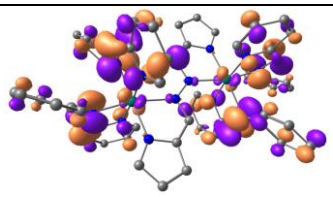
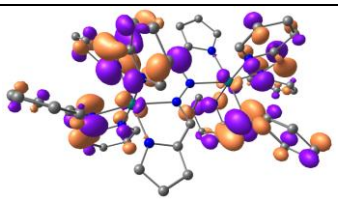
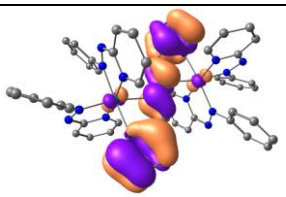
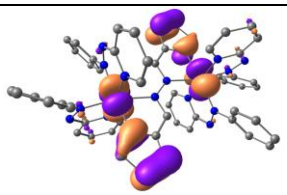
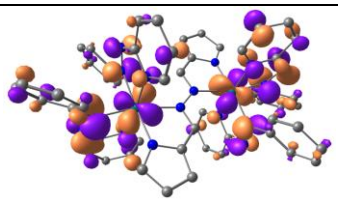
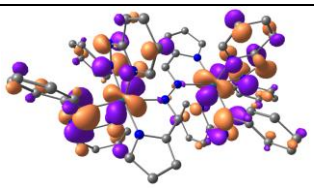
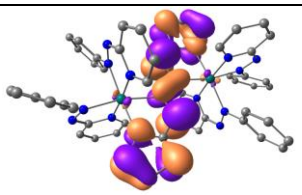
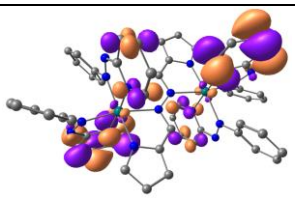
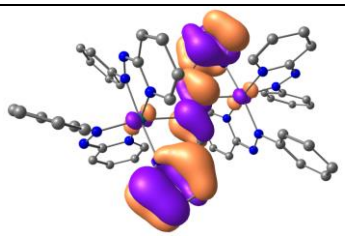
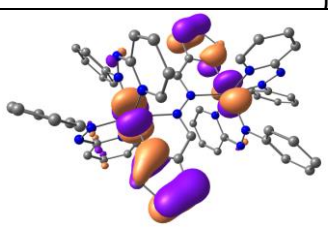
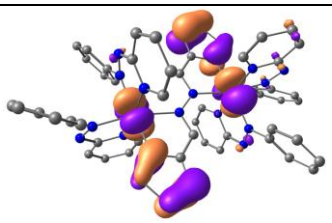
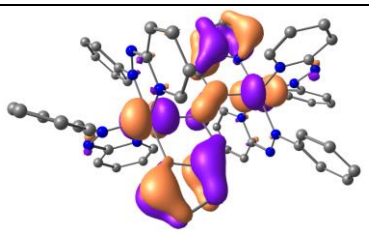
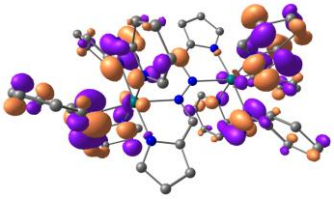
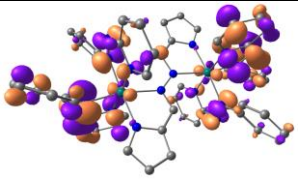
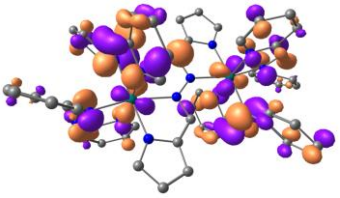
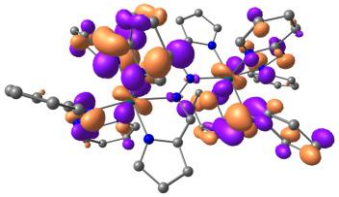
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25 DFT calculated MO composition for **3b**$^{3+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
		α-MO		
LUMO+5	–8.282	18	62	20
LUMO+4	–9.120	05	88	07
LUMO+3	–9.716	13	02	85
LUMO+2	–9.737	12	03	85
LUMO+1	–9.927	08	02	90
LUMO	–9.973	08	04	88
SOMO	–12.722	33	60	07
HOMO–1	–12.827	60	22	18
HOMO–2	–12.856	51	32	17
HOMO–3	–13.004	26	07	67
HOMO–4	–13.089	10	11	79
HOMO–5	–13.149	01	00	99
		β-MO		
LUMO+5	–8.986	04	70	06
LUMO+4	–9.714	14	02	84
LUMO+3	–9.735	12	03	85
LUMO+2	–9.923	09	02	89
LUMO+1	–9.965	09	03	88
LUMO	–11.306	09	88	03
HOMO	–12.755	59	25	15
HOMO–1	–12.799	59	23	18
HOMO–2	–12.908	47	26	27
HOMO–3	–13.038	15	07	77
HOMO–4	–13.137	14	12	73
HOMO–5	–13.150	03	02	94

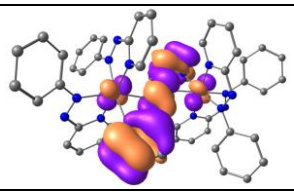
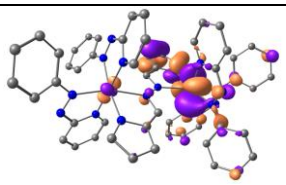
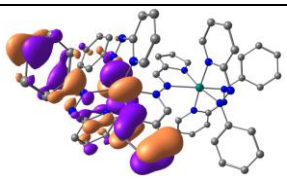
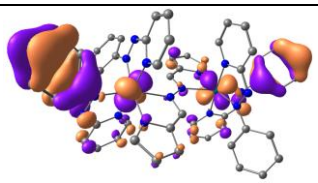
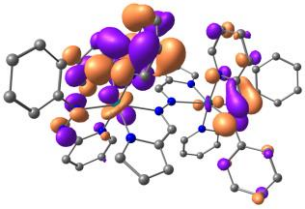
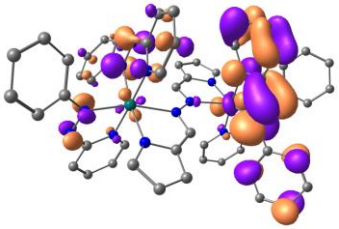
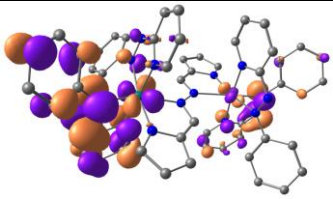
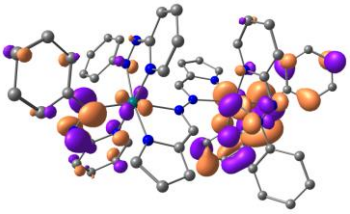
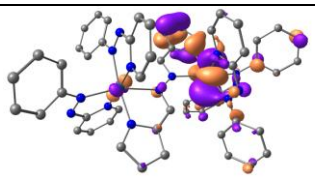
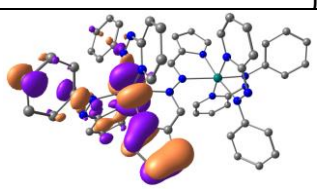
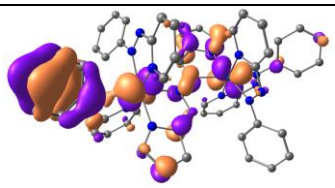
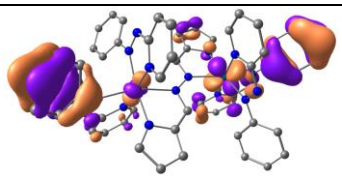
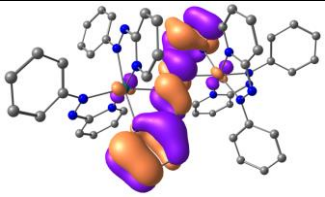
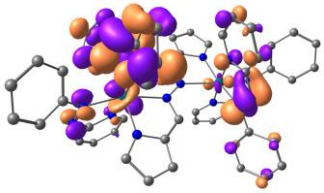
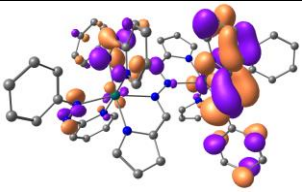
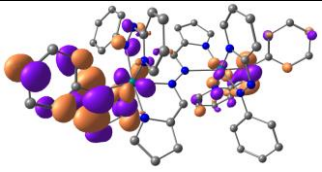
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26 DFT calculated MO composition for **3b**$^{2+}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
LUMO+5	–6.051	03	10	87
LUMO+4	–6.086	06	70	24
LUMO+3	–7.306	19	03	78
LUMO+2	–7.390	19	03	78
LUMO+1	–7.639	08	02	90
LUMO	–7.776	09	03	88
HOMO	–9.426	08	87	05
HOMO–1	–10.069	41	49	09
HOMO–2	–10.127	47	41	12
HOMO–3	–10.316	19	68	13
HOMO–4	–10.864	69	09	22
HOMO–5	–10.922	64	07	29

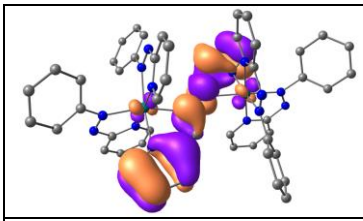
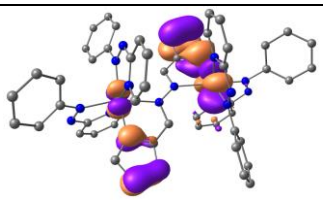
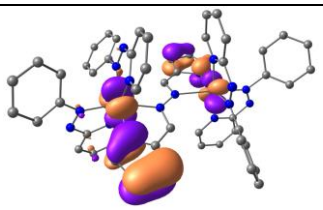
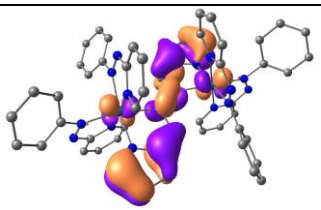
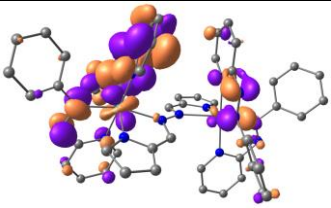
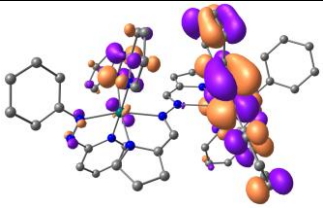
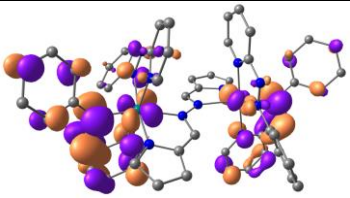
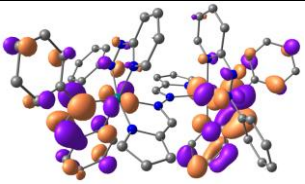
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S27 DFT calculated MO composition for **3b**$^{+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
		α-MO		
LUMO+5	–3.308	04	02	94
LUMO+4	–3.383	05	04	91
LUMO+3	–3.490	05	84	11
LUMO+2	–4.983	19	02	79
LUMO+1	–5.028	18	02	80
LUMO	–5.321	08	02	90
SOMO	–5.754	09	02	89
HOMO–1	–6.784	07	90	03
HOMO–2	–7.515	52	38	10
HOMO–3	–7.546	52	38	10
HOMO–4	–7.831	30	58	12
HOMO–5	–8.108	69	07	24
		β-MO		
LUMO+5	–3.358	05	04	91
LUMO+4	–3.477	06	83	11
LUMO+3	–4.636	12	02	86
LUMO+2	–4.683	11	02	87
LUMO+1	–4.860	11	02	87
LUMO	–4.926	12	02	86
HOMO	–6.781	07	90	03
HOMO–1	–7.500	53	37	10
HOMO–2	–7.541	53	37	10
HOMO–3	–7.810	34	54	12
HOMO–4	–8.099	65	09	26
HOMO–5	–8.141	66	09	25

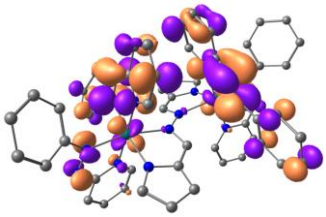
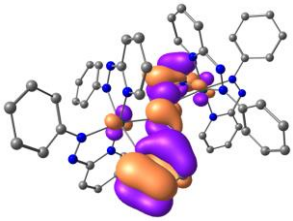
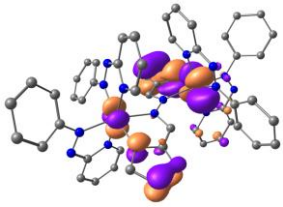
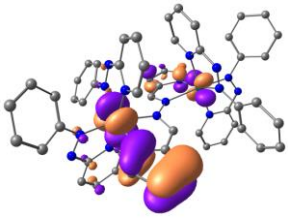
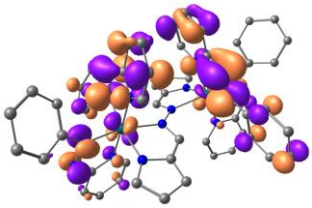
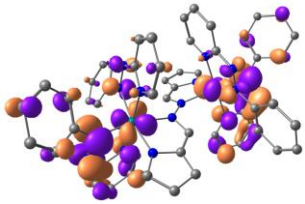
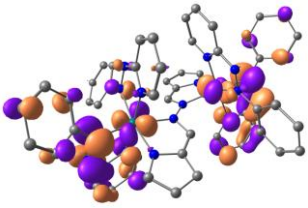
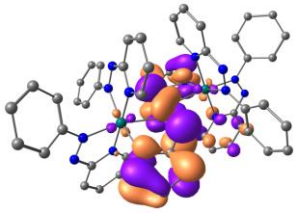
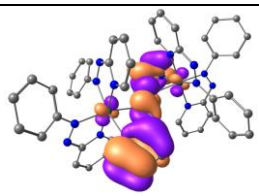
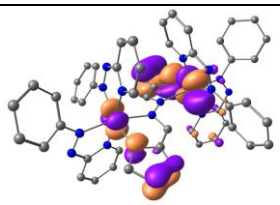
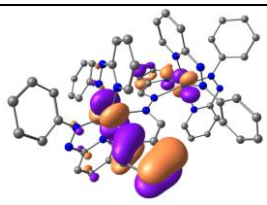
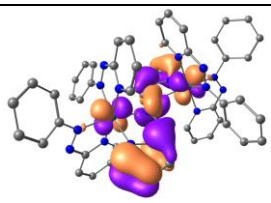
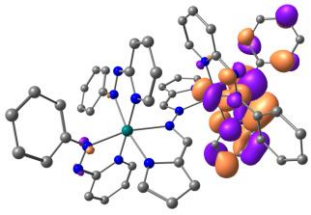
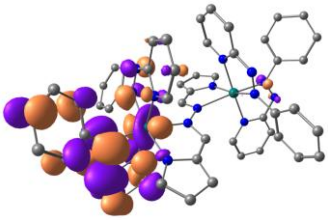
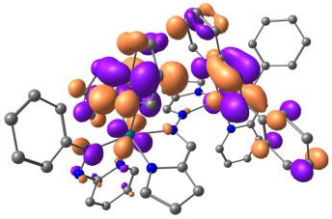
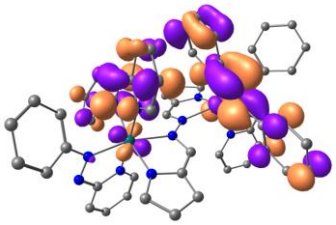
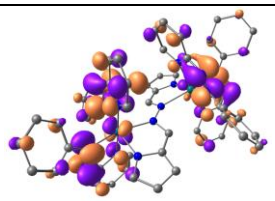
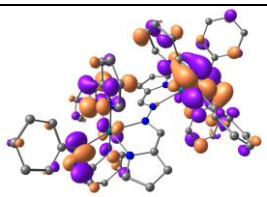
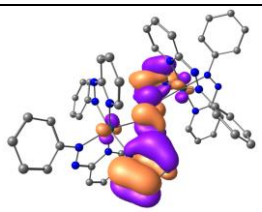
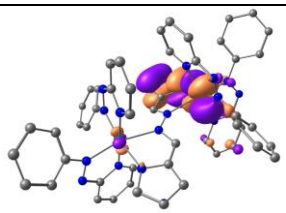
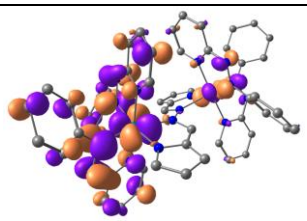
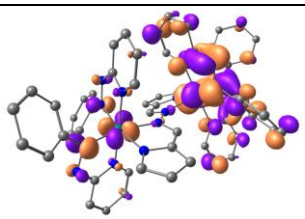
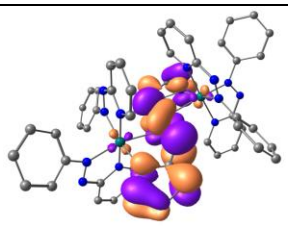
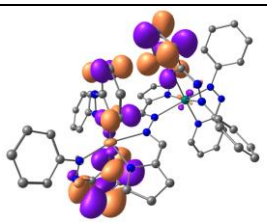
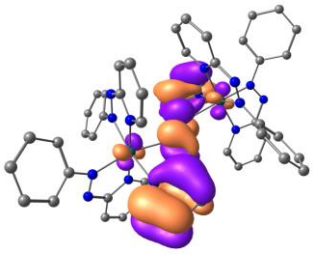
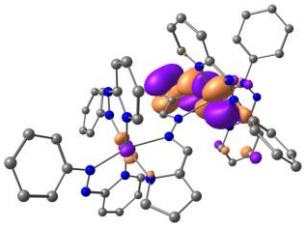
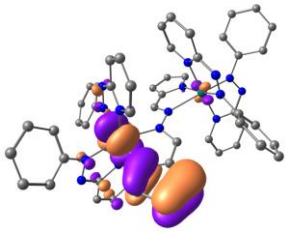
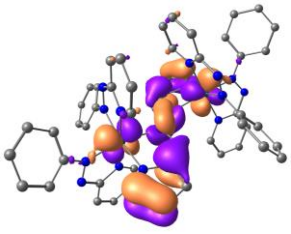
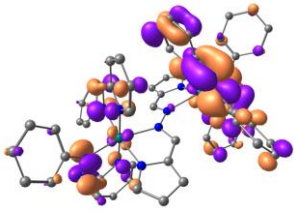
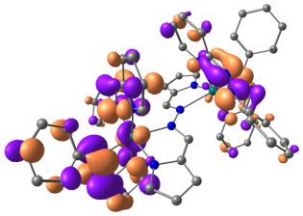
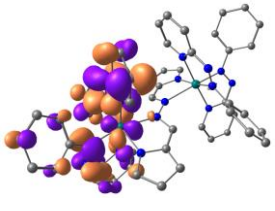
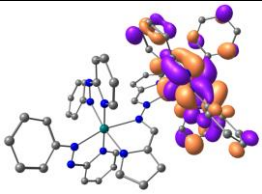
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S28 DFT calculated MO composition for **3b**^{0} in *S* = 1 state

MO	Energy (eV)	% Composition		
		Ru	L^{-}	pap
		α-MO		
LUMO+5	–0.834	04	01	95
LUMO+4	–0.888	05	01	94
LUMO+3	–0.903	05	02	93
LUMO+2	–1.142	06	86	08
LUMO+1	–2.585	24	02	74
LUMO	–2.626	22	03	75
SOMO1	–3.528	08	02	90
SOMO2	–3.573	09	02	89
HOMO–2	–4.454	10	87	03
HOMO–3	–5.079	62	28	10
HOMO–4	–5.117	58	31	11
HOMO–5	–5.416	46	37	17
		β-MO		
LUMO+5	–0.821	05	02	93
LUMO+4	–1.122	06	85	09
LUMO+3	–2.064	11	02	87
LUMO+2	–2.092	12	02	86
LUMO+1	–2.119	10	03	87
LUMO	–2.140	09	03	88
HOMO	–4.452	10	87	03
HOMO–1	–5.066	61	29	10
HOMO–2	–5.079	60	30	10
HOMO–3	–5.375	55	29	16
HOMO–4	–5.591	61	15	24
HOMO–5	–5.598	66	09	25

α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3