Bidirectional noninnocence of hinge like deprotonated bis-lawsone on selective ruthenium platform. A function of varying ancillary ligands†

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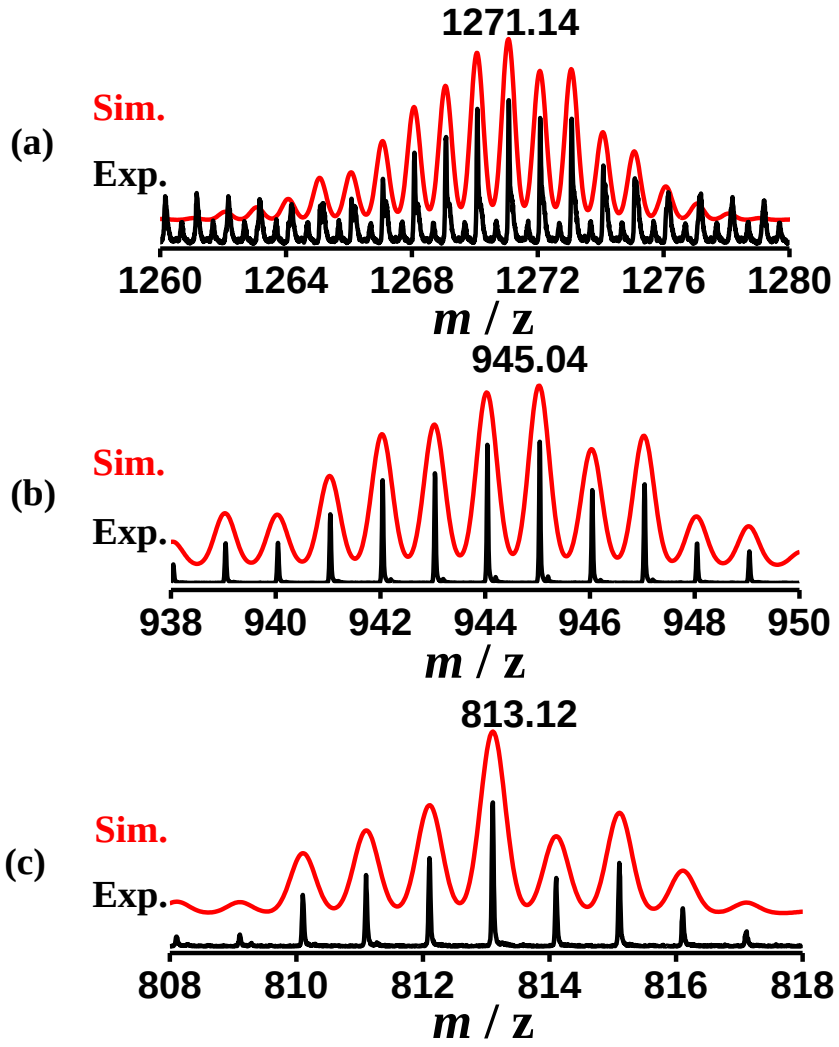


Fig. S1 Experimental and simulated ESI(+) mass spectra of (a) {[**1**]ClO_4}$^+$, (b) {**2**+H}$^+$ and (c) {**3**+H}$^+$ in CH_3CN.

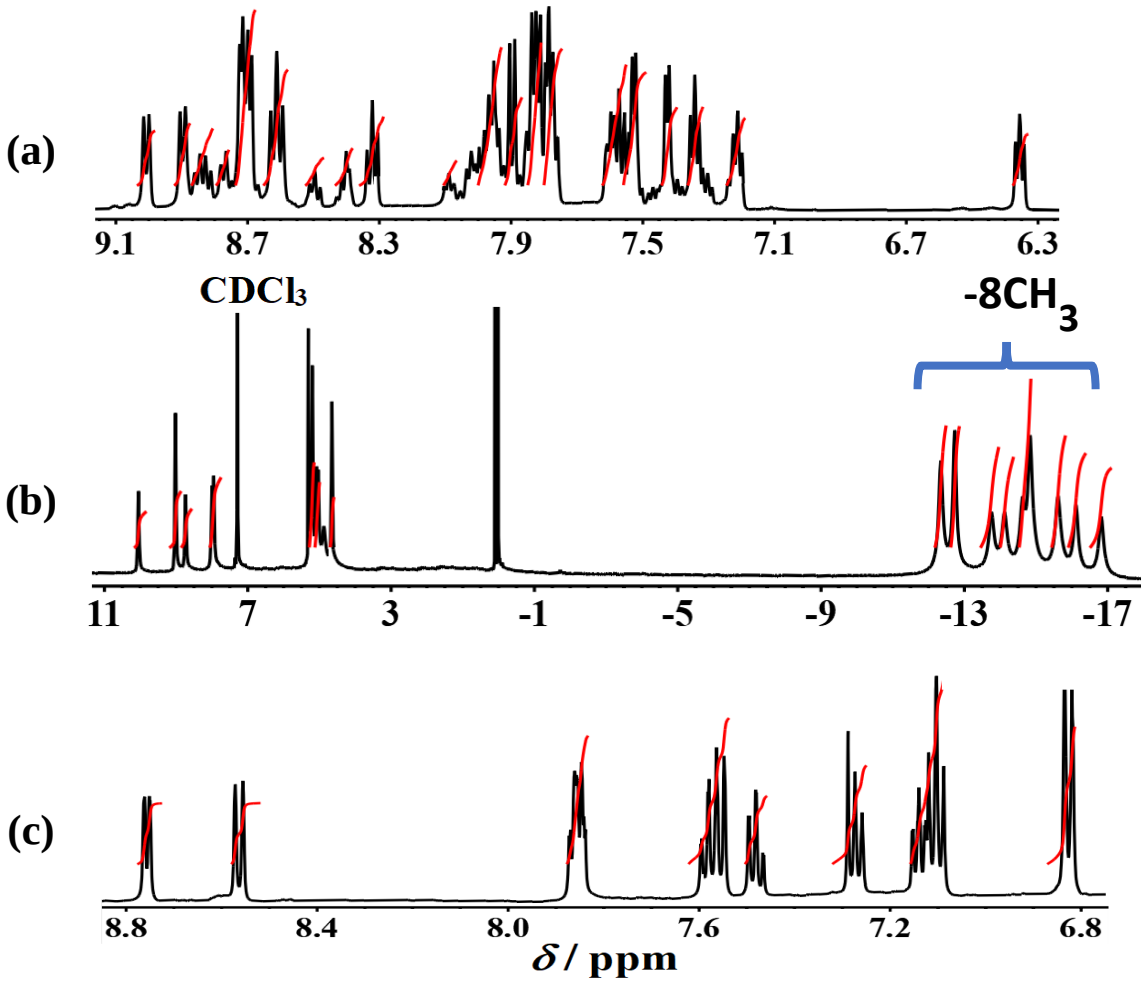


Fig. S2 ^{1}H NMR of (a) [**1**]$(ClO_4)_2$ in $(CD_3)_2SO$ and (b) **2**, (c) **3** in $CDCl_3$ with TMS (δ = 0 ppm) as an internal standard.

Determination of solution magnetic moments (Evans method) of 2

Solution magnetic moment of diruthenium (III) derived complex **2** was determined by Evans method on a 500 MHz NMR spectrometer at 298 K. Complex **2** in $CDCl_3$ was taken in a 5 mm NMR tube. The reference $CDCl_3$ solvent was taken in another coaxial NMR tube. Proton NMR of **2** together with the Evans tube was recorded, which showed two peaks corresponding to the solvent residual peak of $CDCl_3$ in the sample and reference. The shift in the position of $CDCl_3$ due to the paramagnetic Ru(III) was noted.

$$\chi_g = \frac{-3\Delta f}{4\pi \nu_0 m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad \text{-------- eq. 1}$$

The mass susceptibility (χ_g) was calculated using eq. 1, where Δf (Hz), ν_0 (Hz), m (g/cm^3), d_0/ d_s and χ_0 corresponded to shift in frequency, operating frequency of NMR spectrometer, concentration of the substance, densities of pure solvent and solution, and mass susceptibility of the solvent, respectively. The molar susceptibility (χ_m) was obtained by multiplying the mass susceptibility (χ_g) by the molar mass. These results were used to calculate the effective magnetic moment μ_{eff} in eq. 2.

$$\mu_{eff} = 2.83 \times (\chi_M T)^{1/2} \ \text{BM} \qquad \text{-------- eq. 2}$$

Calculation for **2**:

4.26 mg of **2** was dissolved in ~0.55 cm^3 of $CDCl_3$. The shift in the position due to the paramagnetic Ru(III) = 0.1 ppm.

$$\chi_M = 3.123 \times 10^{-3} \ \text{cm}^3/\text{mol}$$
$$\mu_{eff} = 2.83 \times (3.123 \times 10^{-3} \times 298)^{1/2} \ \text{BM}$$
$$= 2.73 \ \text{BM}$$

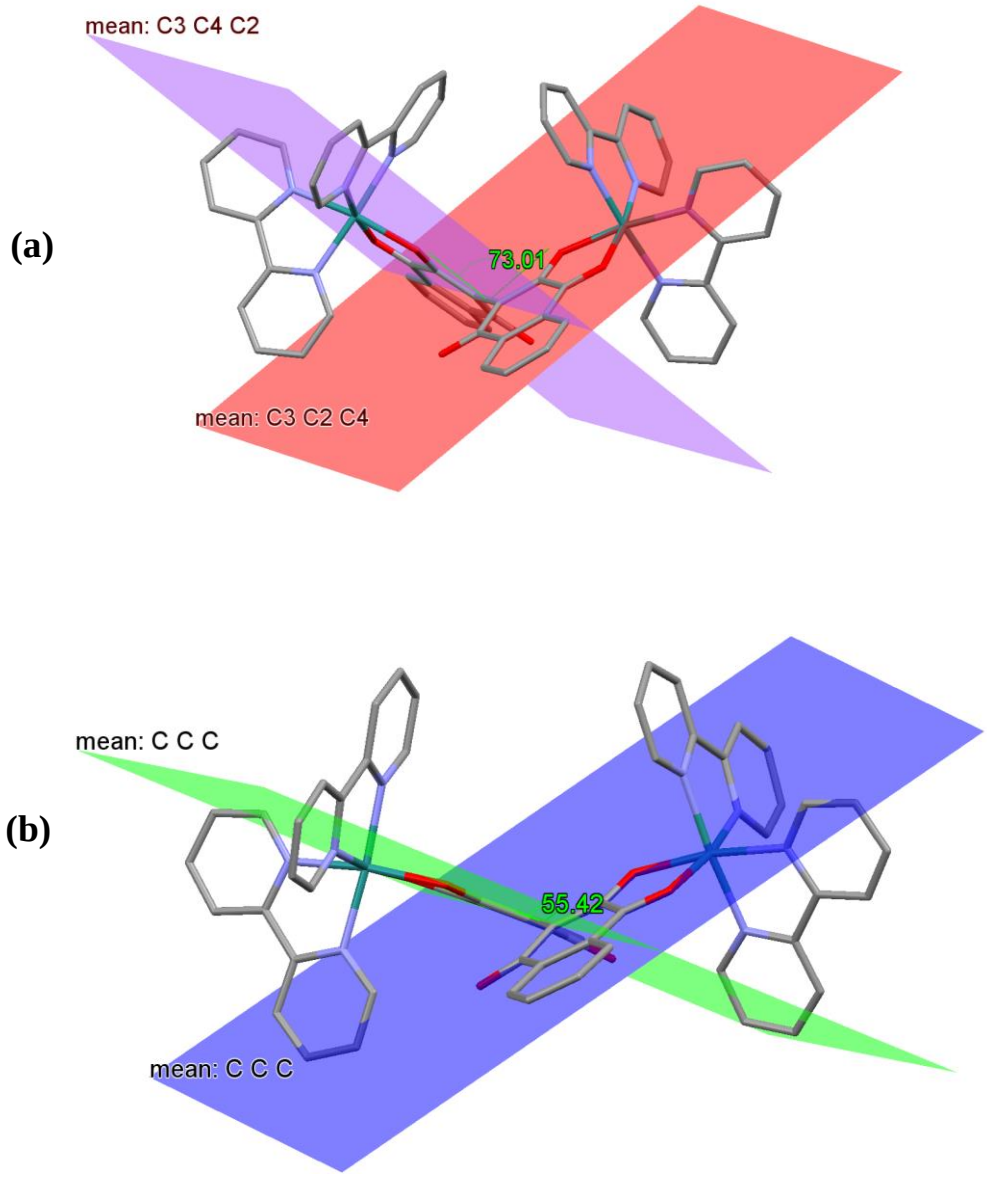


Fig. S3 Torsional angle (deg) between the planes in (a) crystal and (b) DFT for [**1**]$(ClO_4)_2$.

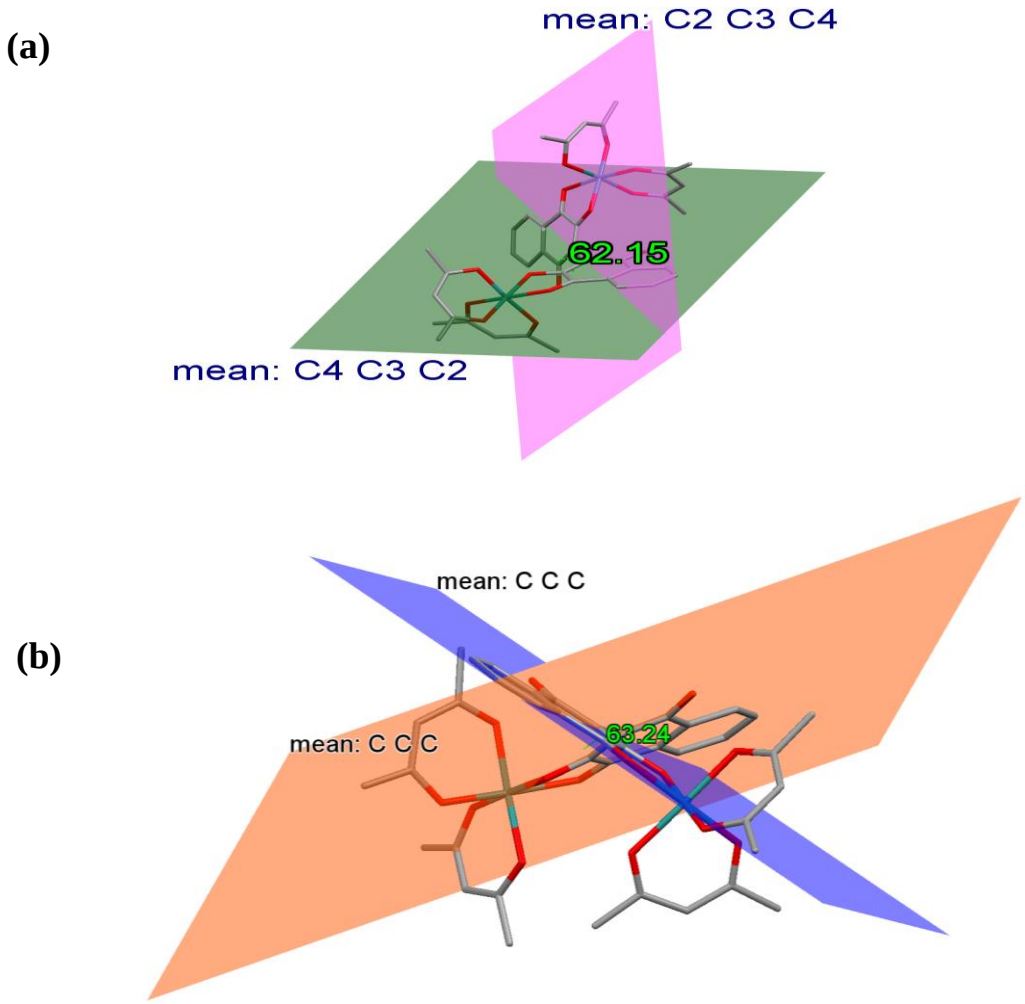
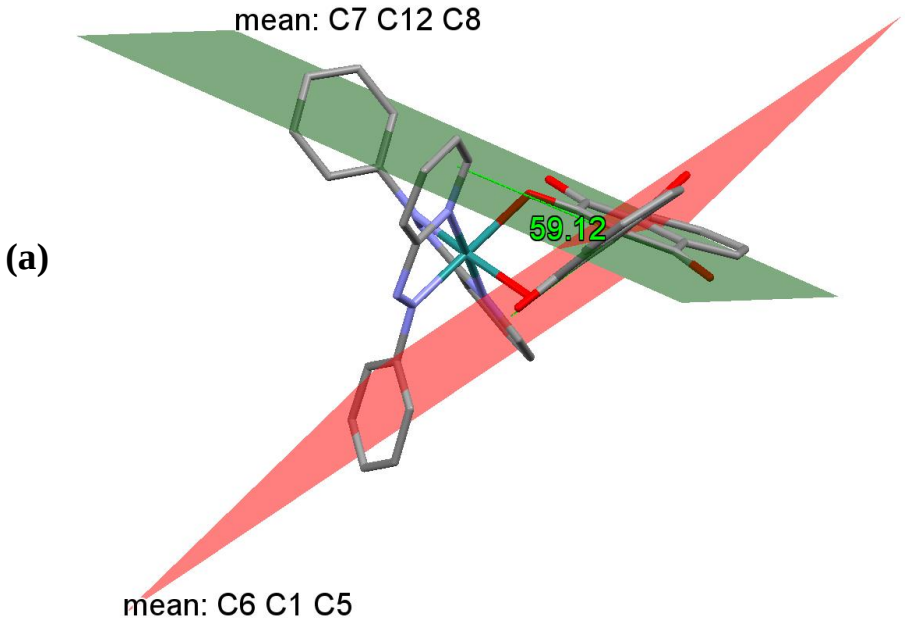
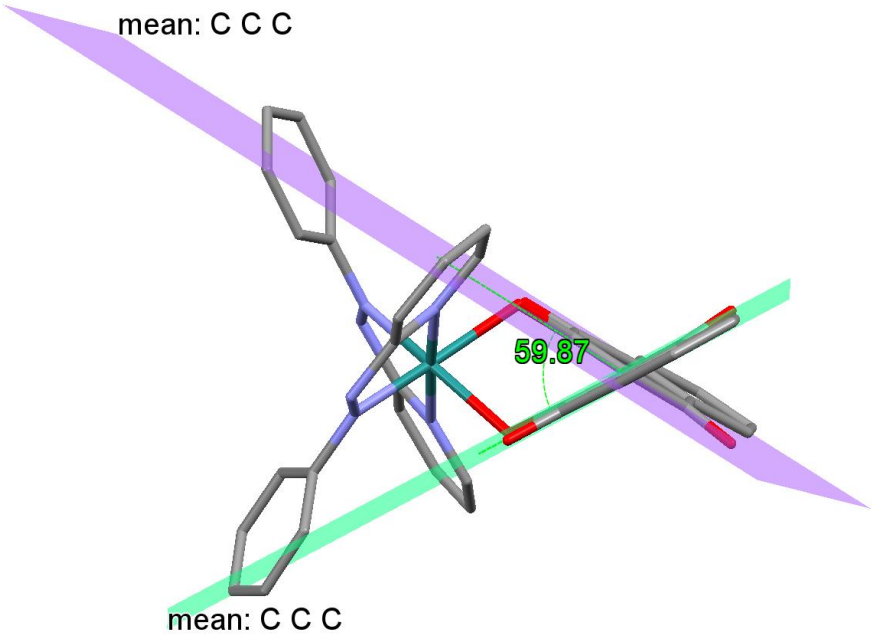


Fig. S4 Torsional angle (deg) between the planes in (a) crystal and (b) DFT for **2**.



(a)



(b)

Fig. S5 Torsional angle (deg) between the planes in (a) crystal and (b) DFT for **3**.

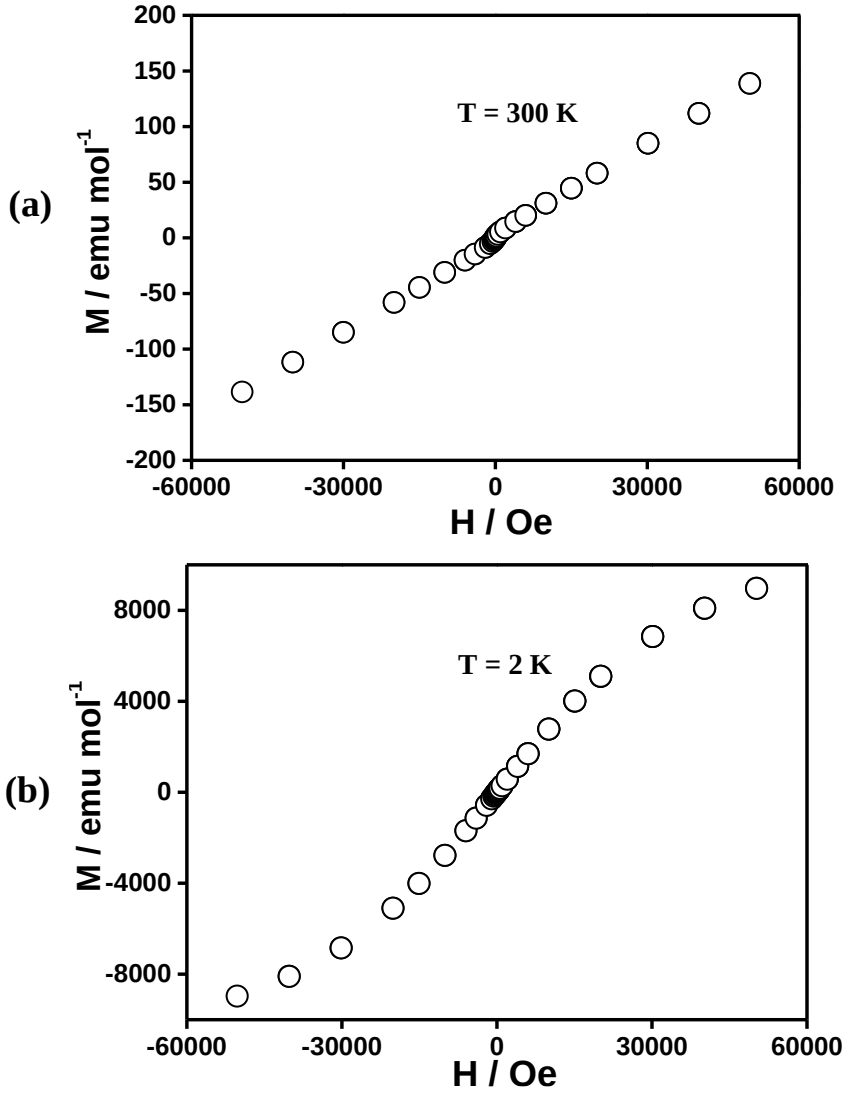


Fig. S6 Magnetisation towards magnetic field from -5 to 5 T for **3**, measured at **(a)** 300 and **(b)** 2 K.

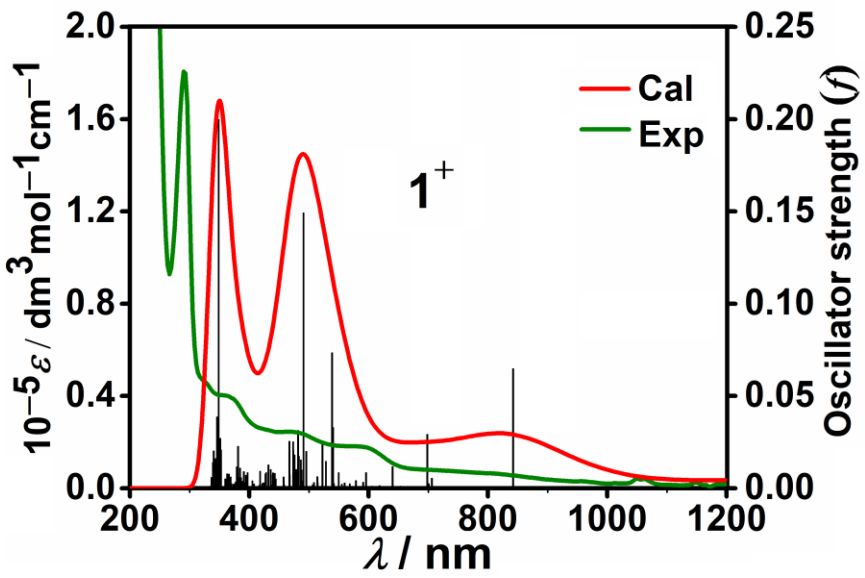


Fig. S7 Experimental (CH_3CN) and TD-DFT ((U)B3LYP/CPCM/CH_3CN) calculated electronic spectra. Oscillator strengths are shown by black vertical lines; the spectra (red) are convoluted with a Gaussian function having fullwidth at half-maximum of 3000.

Table S1 Selected crystallographic parameters

Complex	[**1**]$(ClO_4)_2$	**2**	**3**
empirical formula	$C_{60}H_{40}N_8O_6Ru_2$	$C_{40}H_{36}O_{14}Ru_2$	$C_{42}H_{26}N_6O_6Ru$
formula weight	1370.04	940.81	811.76
crystal system	orthorhombic	monoclinic	triclinic
space group	*P2n2ab*	*C2/c*	*P-1*
a (Å)	18.9906(7)	19.0894(9)	10.5921(2)
b (Å)	20.0361(9)	15.1764(8)	10.6083(3)
c (Å)	14.8190(6)	15.8508(7)	17.9619(4)
α (deg)	90	90	101.563(2)
β (deg)	90	113.229(5)	93.856(2)
γ (deg)	90	90	117.094(3)
V (Å^3)	5638.6(4)	4219.9(4)	1731.00(8)
μ (mm^{-1})	0.707	0.779	0.514
T (K)	293(2)	150.00(10)	150.00(10)
Dcalcd (g cm^{-3})	1.614	1.481	1.557
F (000)	2760	1896	824
θ range(deg)	2.0150 to 22.142	3548 to 49.994	2.2030 to 30.6430
data/restraints/parameters	4969/ 0 / 388	3717 /0/ 257	6103 /0/ 496
R1, wR2 [I>2σ(I)]	0.0843, 0.1114	0.0700, 0.1767	0.0677, 0.0719
R1, wR2(all data)	0.1836, 0.1987	0.0984, 0.1973	0.1969, 0.2025
GOF	1.070	1.050	1.071
largest diff. peak/hole [e Å^{-3}]	1.141/-0.786	0.961/ -0.472	4.079/-1.365

Table S2 Selected experimental and DFT calculated bond lengths (Å)

Bond lengths (Å)	**[1]**$(ClO_4)_2$		**2**		**3**	
	X-ray	DFT	X-ray	DFT	X-ray	DFT
Ru1-O1	2.077(5)	2.121	2.086(5)	2.114	2.079(3)	2.101
Ru1-O2	2.067(5)	2.107	1.984(5)	2.022	2.072(3)	2.104
Ru1-O7	-	-	1.990(7)	2.026	-	-
Ru1-O6	-	-	1.991(5)	2.025	-	-
Ru1-O4	-	-	2.046(6)	2.057	-	-
Ru1-O5	-	-	1.995(6)	2.040	-	-
Ru1-N1	2.007(6)	2.093	-	-	2.028(4)	2.053
Ru1-N2	2.027(7)	2.099	-	-	-	-
Ru1-N3	2.012(8)	2.087	-	-	1.980(4)	2.021
Ru1-N4	2.016(7)	2.069	-	-	2.030(4)	2.062
Ru1-N5	-	-	-	-	1.968(4)	2.019
C11-N1	1.325(11)	1.347	-	-	-	-
C20-N2	1.338(11)	1.347	-	-	-	-
C2-O2	1.284(8)	1.297	1.323(8)	1.308	-	
C4-O3	1.231(8)	1.236	1.216(8)	1.229	-	
C1-O1	1.254(8)	1.260	1.260(8)	1.254	1.312(6)	1.306
C12-O5	-		-	-	1.224(7)	1.231
C5-O4	-		-	-	1.218(7)	1.231
C8-O2	-		-	-	1.297(6)	1.306
C2-O3	-		-	-	1.216(7)	1.228
C9-O6	-		-	-	1.222(6)	1.228
C1-C2	1.487(10)	1.493	1.496(8)	1.486	-	-
C2-C3	1.358(9)	1.393	1.354(9)	1.379	-	-
C4-C3	1.433(9)	1.461	-		-	-
C1-C6	-		-		1.355(7)	1.377
C7-C6	-		-		1.484(7)	1.471
C7-C8	-		-		1.377(7)	1.378
N5-N6	-		-		1.290(6)	1.299
N3-N2	-		-		1.287(6)	1.299
Ru1···Ru1’	7.753	8.625	8.187	8.055	-	-

Table S3 Selected experimental and DFT calculated bond angles (deg)

Bond angles (deg)	[**1**]$(ClO_4)_2$		**2**		**3**	
	X-ray	DFT	X-ray	DFT	X-ray	DFT
O2-Ru1-O1	77.69(18)	76.84	79.91(18)	78.73	85.57(14)	84.75
O7-Ru1-O4	-	-	175.1(2)	178.0	-	-
O5-Ru1-O2	-	-	177.45(19)	175.7	-	-
O1-Ru1-O6	-	-	174.27(19)	174.0	-	-
O7-Ru1-O1	-	-	178.4(2)	178.0	-	-
O6-Ru1-O7	-	-	94.6(2)	89.2	-	-
O4-Ru1-O5	-	-	91.7(3)	93.3	-	-
N2-Ru1-O2	93.8(2)	94.32	-	-	-	-
N2-Ru1-O1	87.9(2)	87.44	-	-	-	-
N3-Ru1-O2	89.1(2)	89.61	-	-	-	-
N3-Ru1-O1	95.0(3)	96.05	-	-	-	-
N1-Ru1-O2	172.2(3)	169.9	-	-	90.76(16)	90.56
N1-Ru1-O1	97.6(2)	96.00	-	-	90.12(15)	87.72
N5-Ru1-O1	-	-	-	-	167.06(16)	165.1
N3-Ru1-O2	-	-	-	-	165.81(16)	165.7
N3-Ru1-N2	176.3(3)	175.2	-	-	-	-
N3-Ru1-N4	79.2(3)	78.46	-	-	-	-
N1-Ru1-N2	79.7(3)	78.15	-	-	-	-
N1-Ru1-N3	97.6(3)	98.23	-	-	77.11(17)	75.94
N1-Ru1-N4	87.7(3)	92.57	-	-	178.62(14)	177.6
N5-Ru1-N4	-	-	-	-	77.06(16)	76.01

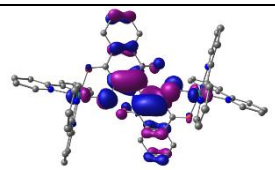
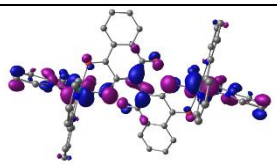
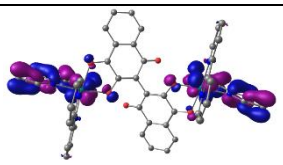
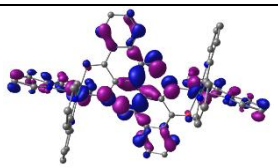
Table S4 Energies of DFT ((U)/(R)B3LYP/LanL2DZ/6-31G*) optimised structures of **1**^{n}, **2**^{n} and **3**^{n}

Complex	*E* (Hartrees)					$\Delta E_{(HE-LE)}$[a]
	S = 0	*S* = 1/2	*S* = 1	*S* = 3/2	*S* = 2	
1^{4+}	-3386.6518842	-	**-3386.666153 7**	-	-	0.0142695 Hartrees 3131.793233 cm^{-1} 37.4645751kJ/mol
1	**-3387.7725153**	-	-3387.5494653	-	-	0.22305 Hartrees 48953.816 cm^{-1} 585.61782 kJ/mol
2^{+}	-	**-2786.8057269**	-	-2786.7929033	-	0.0128236 Hartrees 2814.454865 cm^{-1} 33.66836436 kJ/mol
2	-2786.984108	-	**-2787.0197088**	-	-	0.0356008 Hartrees 7813.472408 cm^{-1} 93.46990752 kJ/mol
2^{-}	-	**-2787.1019043**	-	-2787.0922009	-	0.0097034 Hartrees 2129.650125 cm^{-1} 25.47627864 kJ/mol
2^{2-}	**-2787.0961724**	-	-2787.0829535	-	-2787.0714788	0.0246936 Hartrees 5419.6187234cm^{-1} 64.833051739 kJ/mol
3^{2-}	-2489.9174556	-	**2489.9227822**	-	-	0.0053266 Hartrees 1169.053564 cm^{-1} 13.98498937 kJ/mol
3^{3-}	-	-2489.7755633	-	**-2489.7866766**	-	0.0111133 Hartrees 2439.087406 cm^{-1} 29.17797137 kJ/mol

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

Table S5 DFT calculated MO compositions for $\mathbf{1}^{4+}$ in $S = 1$ state

MO	Energy (eV)	% Composition		
		Ru	L	bpy
		α-MO		
LUMO+5	-10.636	06	01	93
LUMO+4	-10.637	05	01	93
LUMO+3	-11.122	04	01	95
LUMO+2	-11.247	05	01	94
LUMO+1	-11.581	03	93	04
LUMO	-11.698	03	91	06
SOMO	-14.768	10	85	04
HOMO-1	-15.118	13	83	04
HOMO-2	-15.164	04	94	02
HOMO-3	-15.172	07	91	02
HOMO-4	-15.240	03	95	02
HOMO-5	-15.327	07	89	04
		β-MO		
LUMO+5	-11.107	04	01	94
LUMO+4	-11.224	06	02	92
LUMO+3	-11.473	04	91	05
LUMO+2	-11.597	05	89	07
LUMO+1	-12.978	57	30	13
LUMO	-13.124	64	22	14
HOMO	-14.581	32	58	10
HOMO-1	-14.843	36	53	11
HOMO-2	-15.134	07	91	02
HOMO-3	-15.136	10	87	03
HOMO-4	-15.179	07	89	04
HOMO-5	-15.229	35	51	14

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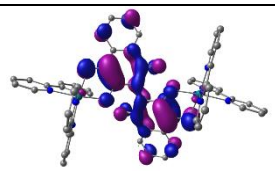
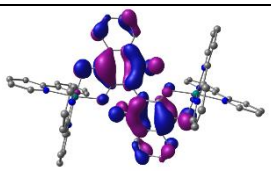
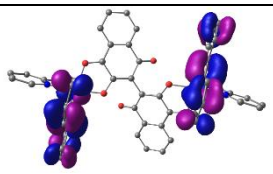
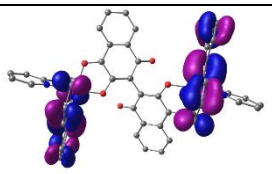
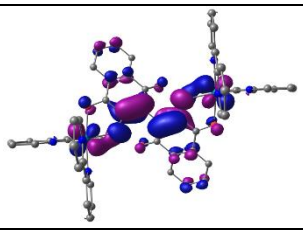
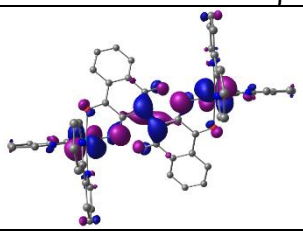
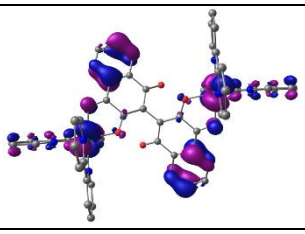
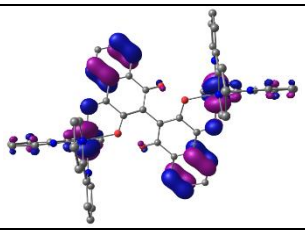
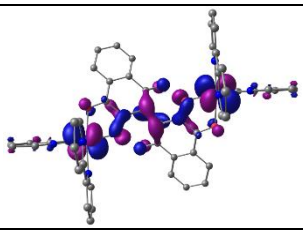
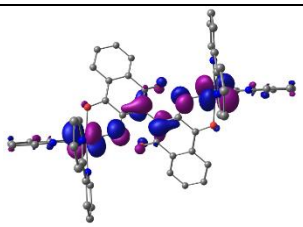
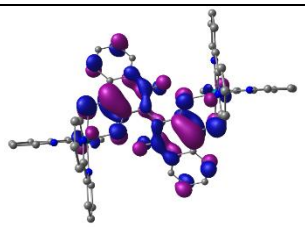
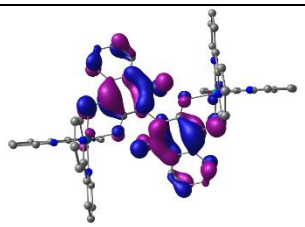
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S6 DFT calculated MO compositions for $\mathbf{1}^{3+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L	bpy
		α-MO		
LUMO+5	-8.194	06	01	93
LUMO+4	-8.197	06	01	93
LUMO+3	-8.607	04	01	94
LUMO+2	-8.715	06	01	93
LUMO+1	-9.202	04	91	05
LUMO	-9.301	05	89	06
SOMO	-12.153	47	42	10
HOMO-1	-12.165	70	13	17
HOMO-2	-12.192	59	25	15
HOMO-3	-12.393	53	35	12
HOMO-4	-12.452	72	12	17
HOMO-5	-12.457	70	14	16
		β-MO		
LUMO+5	-8.187	06	01	93
LUMO+4	-8.595	05	02	93
LUMO+3	-8.694	07	02	91
LUMO+2	-9.093	05	90	05
LUMO+1	-9.204	06	86	08
LUMO	-10.715	37	53	10
HOMO	-11.570	58	30	12
HOMO-1	-12.063	67	16	16
HOMO-2	-12.083	67	16	17
HOMO-3	-12.364	72	11	16
HOMO-4	-12.366	72	11	16
HOMO-5	-12.562	50	37	13

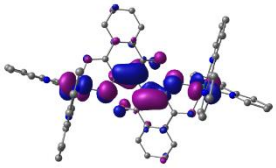
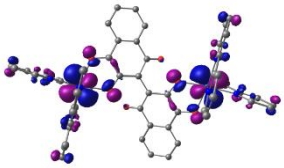
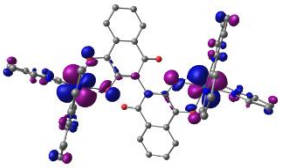
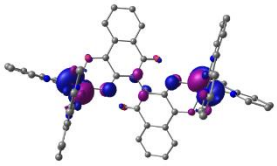
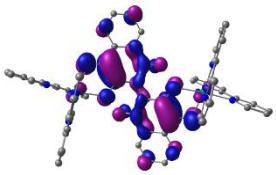
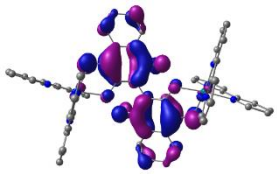
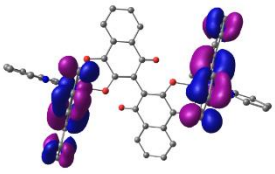
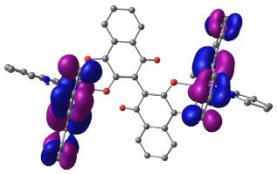
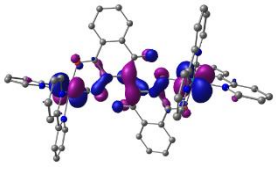
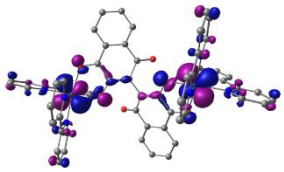
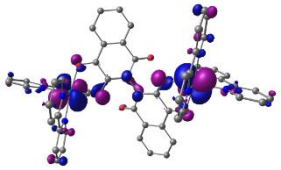
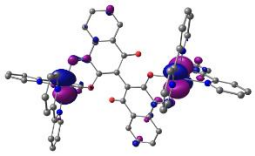
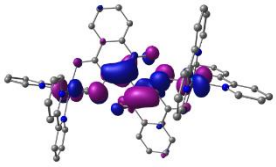
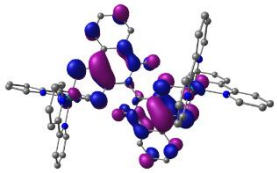
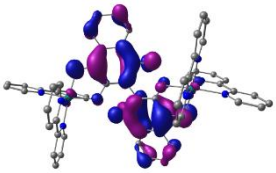
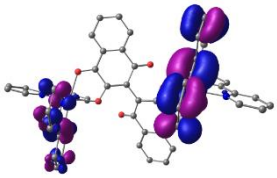
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7 DFT calculated MO compositions for $\mathbf{1}^{2+}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	L	bpy
LUMO+5	-5.927	07	02	91
LUMO+4	-5.928	07	08	86
LUMO+3	-6.234	06	08	86
LUMO+2	-6.320	08	07	85
LUMO+1	-6.400	03	82	15
LUMO	-6.500	04	81	15
HOMO	-8.819	27	64	09
HOMO-1	-9.099	40	49	10
HOMO-2	-9.349	66	17	18
HOMO-3	-9.362	67	16	17
HOMO-4	-9.702	74	09	16
HOMO-5	-9.707	74	10	16

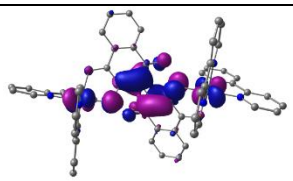
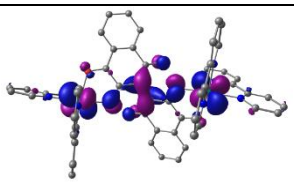
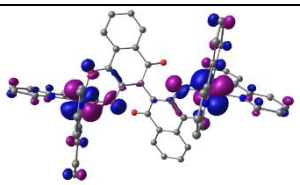
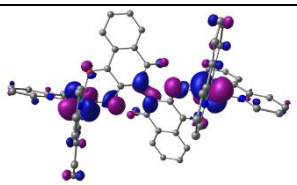
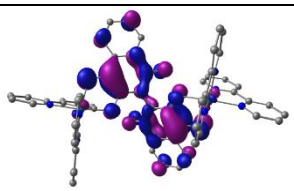
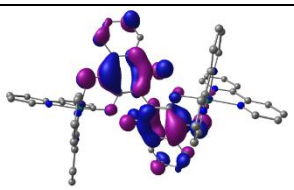
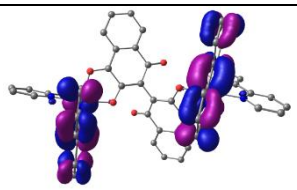
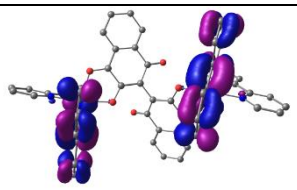
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 DFT calculated MO compositions for $\mathbf{1}^{+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L	bpy
		α-MO		
LUMO+5	-3.155	04	01	96
LUMO+4	-3.793	08	16	76
LUMO+3	-3.809	08	05	88
LUMO+2	-3.897	06	42	52
LUMO+1	-4.023	09	30	62
LUMO	-4.063	02	30	68
SOMO	-4.599	03	54	43
HOMO-1	-6.213	21	70	09
HOMO-2	-6.542	31	59	10
HOMO-3	-6.903	62	19	18
HOMO-4	-6.924	64	18	18
HOMO-5	-7.252	01	98	01
		β-MO		
LUMO+5	-3.502	05	86	09
LUMO+4	-3.583	06	80	13
LUMO+3	-3.750	07	01	91
LUMO+2	-3.789	08	04	89
LUMO+1	-3.846	03	05	92
LUMO	-3.891	04	05	91
HOMO	-6.158	19	73	08
HOMO-1	-6.480	29	62	09
HOMO-2	-6.903	62	20	18
HOMO-3	-6.927	64	19	17
HOMO-4	-7.221	01	98	01
HOMO-5	-7.280	72	12	16

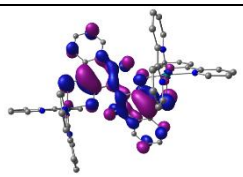
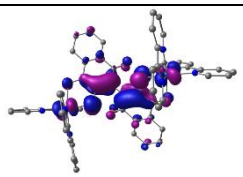
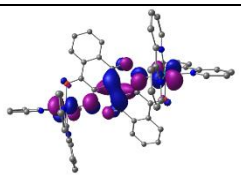
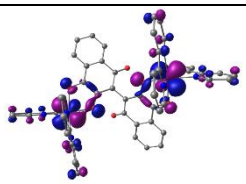
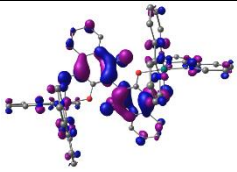
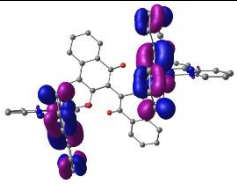
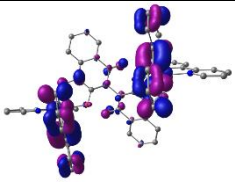
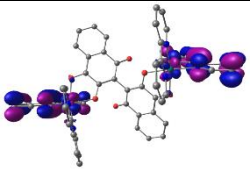
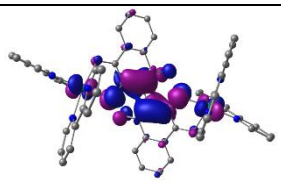
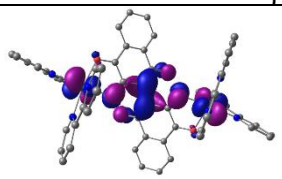
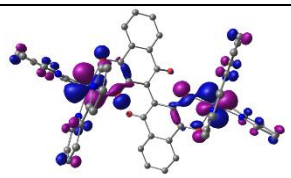
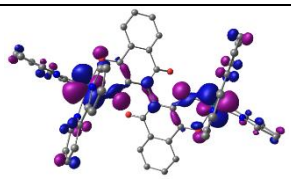
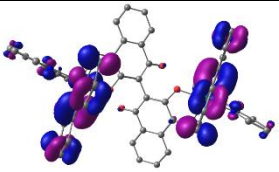
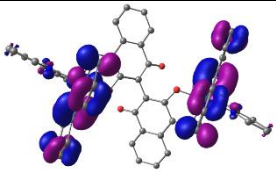
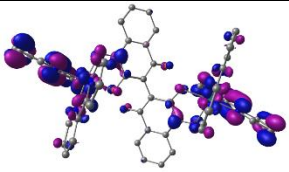
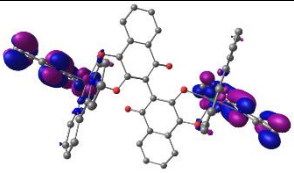
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 DFT calculated MO compositions for **1** in *S* = 0 state

MO	Energy (eV)	% Composition		
		Ru	L	bpy
LUMO+5	-0.835	04	01	95
LUMO+4	-1.393	07	72	21
LUMO+3	-1.455	07	02	91
LUMO+2	-1.472	09	29	62
LUMO+1	-1.542	08	21	71
LUMO	-1.672	02	16	81
HOMO	-2.106	02	36	62
HOMO-1	-3.824	21	70	09
HOMO-2	-4.145	31	60	10
HOMO-3	-4.529	62	20	18
HOMO-4	-4.550	64	19	18
HOMO-5	-4.919	01	98	01

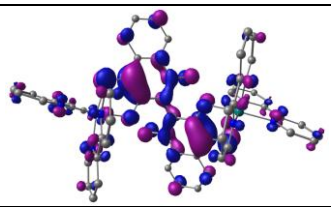
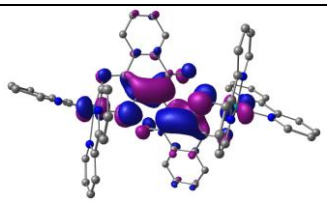
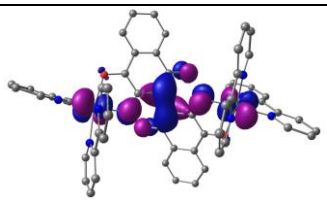
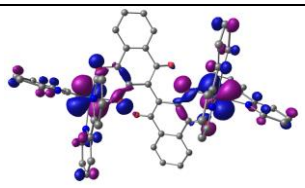
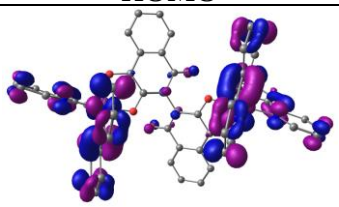
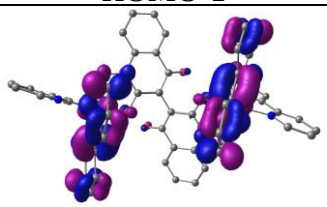
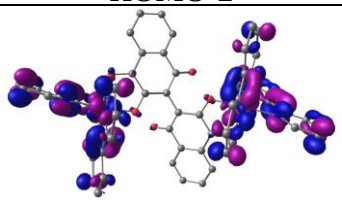
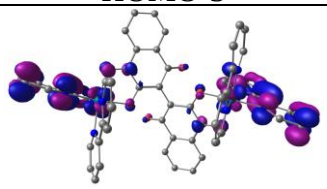
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 DFT calculated MO compositions for $\mathbf{2}^{+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L	acac
		α-MO		
LUMO+5	-3.598	10	03	87
LUMO+4	-3.663	18	04	79
LUMO+3	-3.778	53	24	23
LUMO+2	-5.487	09	88	03
LUMO+1	-5.706	42	44	14
LUMO	-5.970	30	60	10
SOMO	-8.112	38	30	33
HOMO-1	-8.378	49	15	36
HOMO-2	-8.426	39	17	44
HOMO-3	-8.604	21	24	55
HOMO-4	-8.755	27	07	66
HOMO-5	-8.817	35	14	51
		β-MO		
LUMO+5	-3.537	11	28	61
LUMO+4	-3.598	04	03	94
LUMO+3	-5.398	04	95	01
LUMO+2	-5.675	19	75	06
LUMO+1	-5.929	58	22	20
LUMO	-6.905	31	57	12
HOMO	-8.073	47	19	33
HOMO-1	-8.326	32	09	59
HOMO-2	-8.438	26	18	56
HOMO-3	-8.562	54	12	34
HOMO-4	-8.736	58	13	29
HOMO-5	-8.835	39	09	52

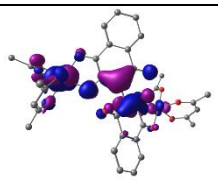
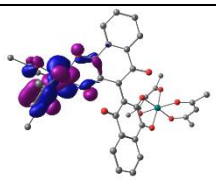
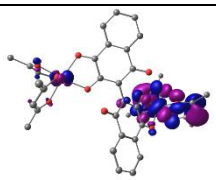
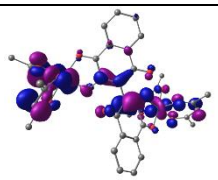
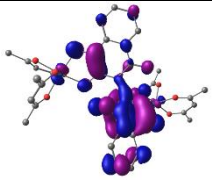
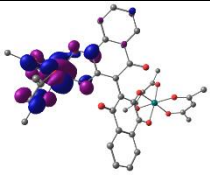
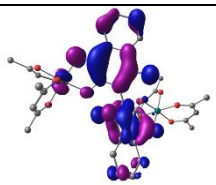
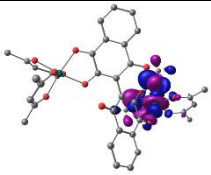
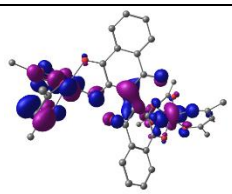
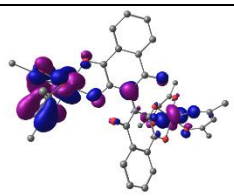
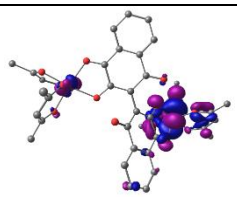
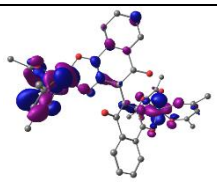
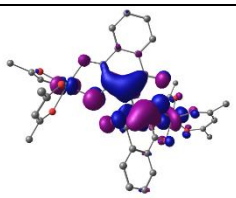
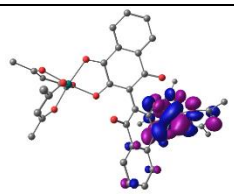
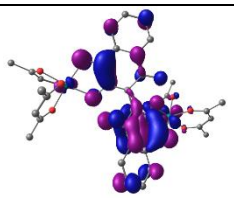
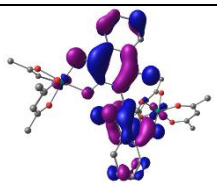
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 DFT calculated MO compositions for **2** in *S* = 1 state

MO	Energy (eV)	% Composition		
		Ru	L	acac
		α-MO		
LUMO+5	-0.465	05	85	10
LUMO+4	-0.648	05	03	92
LUMO+3	-0.666	01	99	00
LUMO+2	-1.098	04	02	95
LUMO+1	-2.374	04	95	01
LUMO	-2.599	06	93	02
SOMO	-4.906	28	38	34
HOMO-1	-5.077	27	33	41
HOMO-2	-5.307	42	09	49
HOMO-3	-5.416	46	35	19
HOMO-4	-5.671	12	04	84
HOMO-5	-5.714	64	13	23
		β-MO		
LUMO+5	-0.648	01	95	04
LUMO+4	-1.032	06	03	91
LUMO+3	-2.346	07	91	03
LUMO+2	-2.521	36	51	13
LUMO+1	-2.618	39	46	15
LUMO	-2.785	53	10	37
HOMO	-4.825	35	42	23
HOMO-1	-5.051	41	21	38
HOMO-2	-5.249	28	11	61
HOMO-3	-5.419	69	12	20
HOMO-4	-5.498	56	11	33
HOMO-5	-5.678	46	22	32

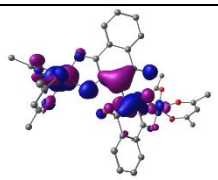
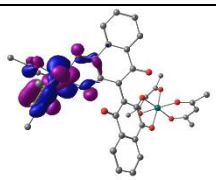
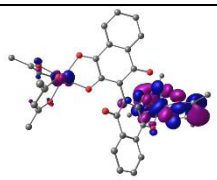
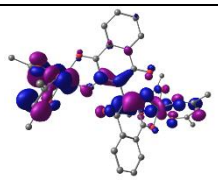
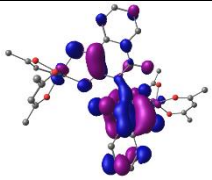
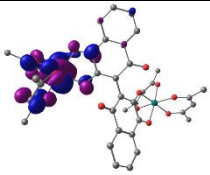
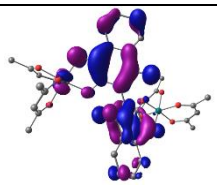
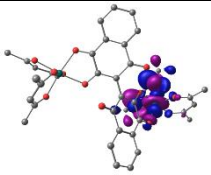
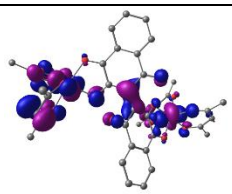
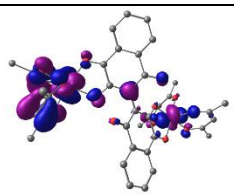
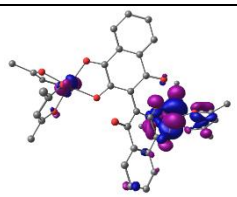
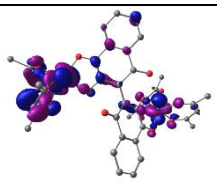
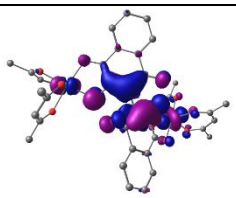
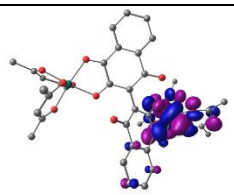
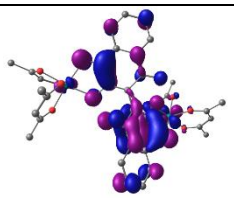
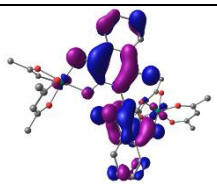
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 DFT calculated MO compositions for $\mathbf{2}^{-}$ in $S = 1/2$ state

MO	Energy (eV)	% Composition		
		Ru	L	acac
		α-MO		
LUMO+5	1.913	01	98	01
LUMO+4	1.573	04	03	93
LUMO+3	1.377	04	01	94
LUMO+2	1.262	04	01	95
LUMO+1	1.243	04	01	95
LUMO	0.021	02	97	01
SOMO	-0.865	05	93	02
HOMO-1	-2.195	16	80	05
HOMO-2	-2.939	52	18	30
HOMO-3	-2.973	55	17	28
HOMO-4	-3.035	42	40	18
HOMO-5	-3.166	65	09	25
		β-MO		
LUMO+5	1.311	06	02	92
LUMO+4	1.282	05	02	93
LUMO+3	0.699	06	90	05
LUMO+2	0.534	13	79	07
LUMO+1	-0.070	57	29	14
LUMO	-0.359	63	23	15
HOMO	-2.107	27	63	10
HOMO-1	-2.656	60	24	17
HOMO-2	-2.806	70	14	16
HOMO-3	-2.866	67	13	20
HOMO-4	-2.942	64	14	22
HOMO-5	-3.352	12	77	11

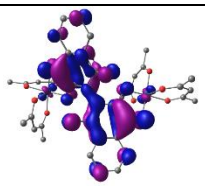
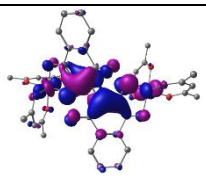
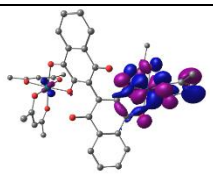
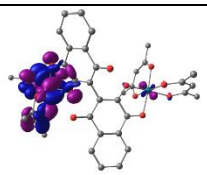
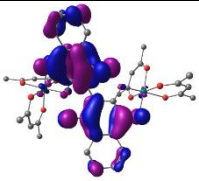
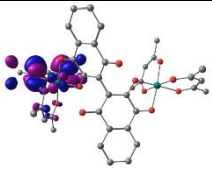
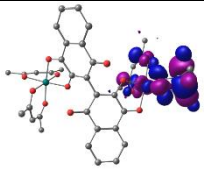
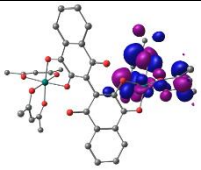
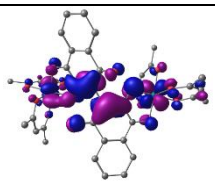
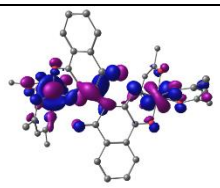
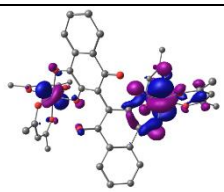
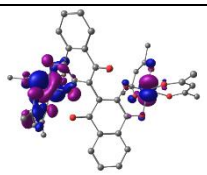
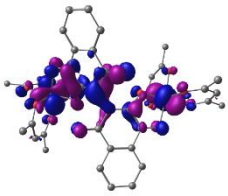
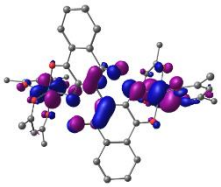
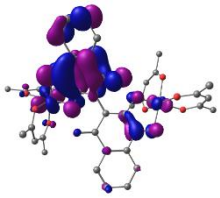
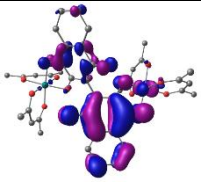
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 DFT calculated MO compositions for $\mathbf{2}^{2-}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	L	acac
LUMO+5	4.271	05	28	67
LUMO+4	4.109	05	03	92
LUMO+3	4.084	04	11	85
LUMO+2	4.081	01	87	13
LUMO+1	2.761	09	88	03
LUMO	2.573	15	80	06
HOMO	1.386	47	41	12
HOMO-1	1.025	64	19	18
HOMO-2	0.709	67	16	18
HOMO-3	0.648	71	13	16
HOMO-4	0.557	74	09	18
HOMO-5	0.476	70	13	17

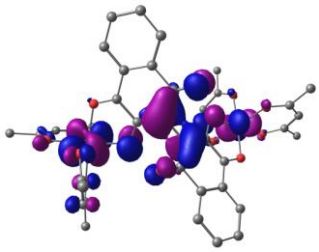
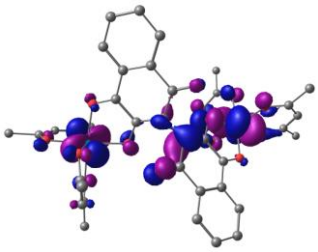
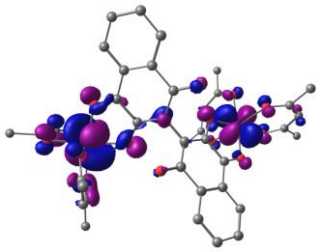
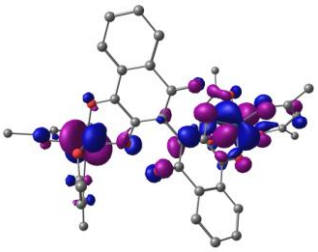
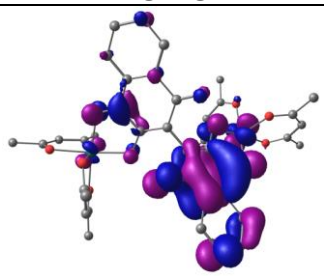
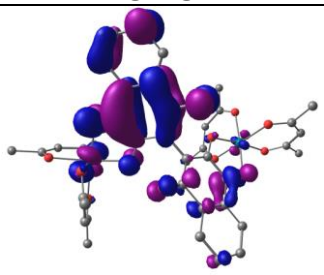
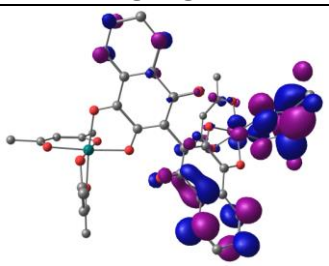
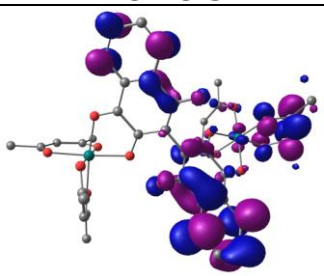
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 DFT calculated MO compositions for 2^{3-} in S = 1/2 state

MO	Energy (eV)	% Composition		
		Ru	L	acac
		α-MO		
LUMO+5	6.831	05	44	51
LUMO+4	6.774	04	49	47
LUMO+3	6.680	09	02	90
LUMO+2	6.412	06	02	93
LUMO+1	6.386	05	01	94
LUMO	5.322	04	94	02
SOMO	4.539	12	83	05
HOMO-1	4.010	46	42	12
HOMO-2	3.691	66	17	16
HOMO-3	3.424	66	18	16
HOMO-4	3.359	69	15	16
HOMO-5	3.234	72	09	19
		β-MO		
LUMO+5	6.791	05	29	66
LUMO+4	6.685	09	02	89
LUMO+3	6.455	07	04	89
LUMO+2	6.423	06	04	90
LUMO+1	5.853	05	85	10
LUMO	5.710	08	82	11
HOMO	4.156	42	48	11
HOMO-1	3.781	64	21	16
HOMO-2	3.460	66	18	17
HOMO-3	3.401	69	15	16
HOMO-4	3.288	73	08	19
HOMO-5	3.237	73	09	18

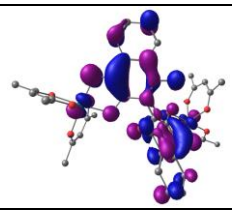
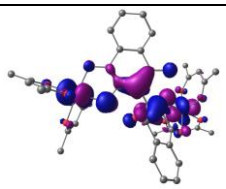
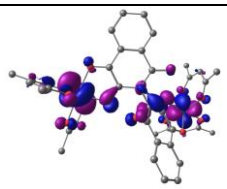
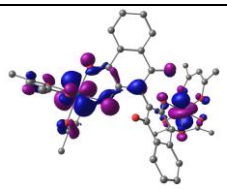
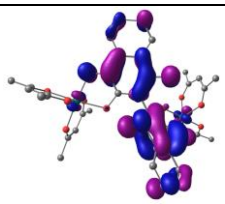
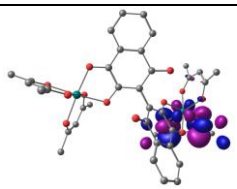
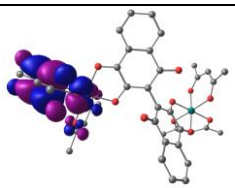
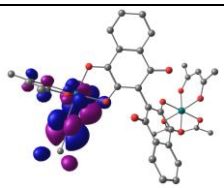
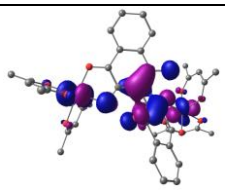
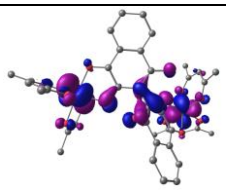
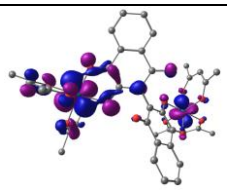
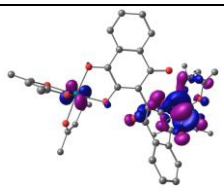
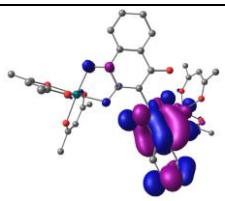
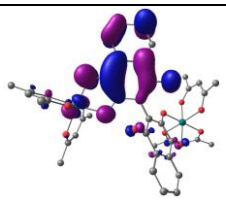
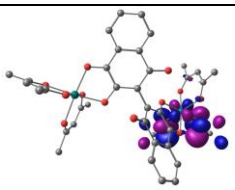
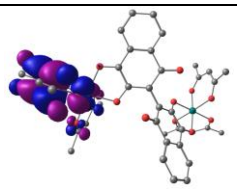
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 DFT calculated MO compositions for $\mathbf{3}^{+}$ in $S = 1/2$ state

MO	Energy (eV)	% Composition		
		Ru	L	pap
		α-MO		
LUMO+5	-3.886	05	03	92
LUMO+4	-3.911	04	04	92
LUMO+3	-5.322	01	96	03
LUMO+2	-5.593	06	88	07
LUMO+1	-5.635	20	05	75
LUMO	-5.918	08	03	90
SOMO	-8.826	48	22	30
HOMO-1	-8.875	56	18	25
HOMO-2	-9.029	41	49	10
HOMO-3	-9.179	33	50	17
HOMO-4	-9.357	08	26	67
HOMO-5	-9.374	00	91	09
		β-MO		
LUMO+5	-3.906	04	03	93
LUMO+4	-5.158	01	96	03
LUMO+3	-5.432	06	88	06
LUMO+2	-5.617	21	04	75
LUMO+1	-5.915	08	03	90
LUMO	-7.496	11	83	07
HOMO	-8.746	53	21	25
HOMO-1	-8.822	57	20	24
HOMO-2	-8.923	63	18	20
HOMO-3	-9.264	04	81	15
HOMO-4	-9.339	06	20	74
HOMO-5	-9.345	01	86	14

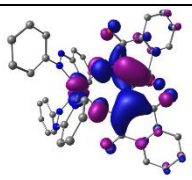
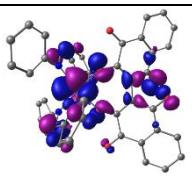
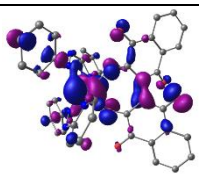
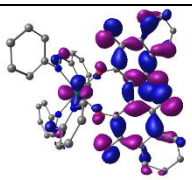
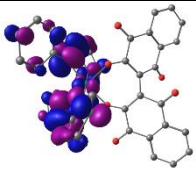
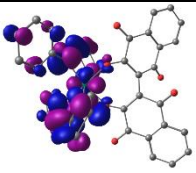
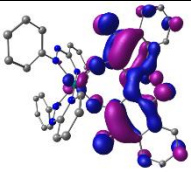
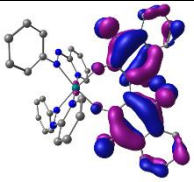
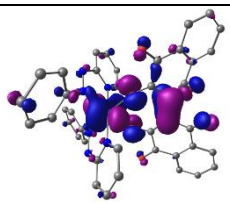
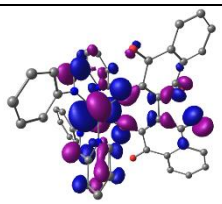
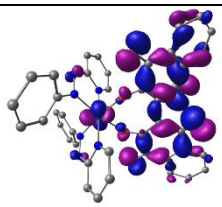
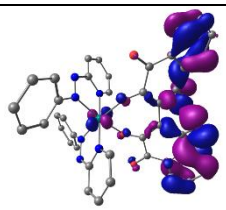
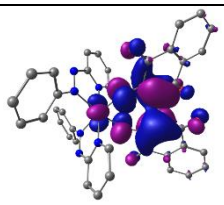
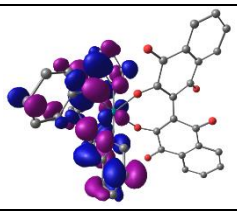
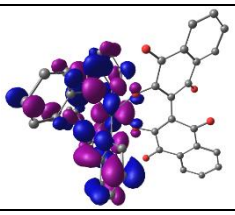
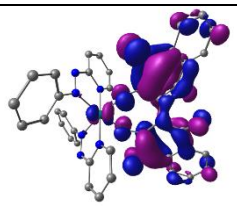
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 DFT calculated MO compositions for **3** in *S* = 0 state

MO	Energy (eV)	% Composition		
		Ru	L	pap
LUMO+5	-1.901	04	01	94
LUMO+4	-1.964	04	01	95
LUMO+3	-2.476	01	95	04
LUMO+2	-2.702	07	87	07
LUMO+1	-3.104	28	07	65
LUMO	-3.601	12	03	85
HOMO	-4.596	12	80	08
HOMO-1	-4.824	30	57	13
HOMO-2	-4.937	17	67	15
HOMO-3	-5.001	22	66	12
HOMO-4	-5.143	12	83	05
HOMO-5	-5.247	50	37	12

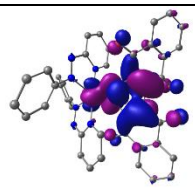
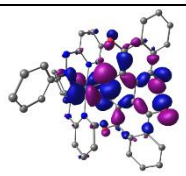
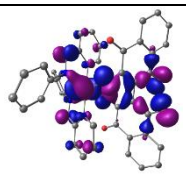
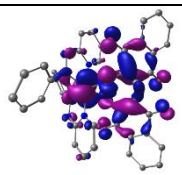
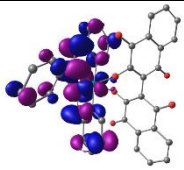
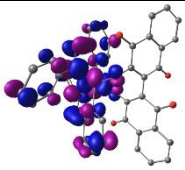
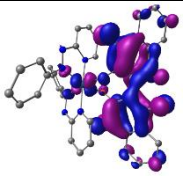
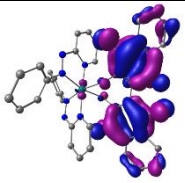
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy (eV)	% Composition		
		Ru	L	pap
		α-MO		
LUMO+5	1.849	04	06	90
LUMO+4	1.804	03	42	54
LUMO+3	1.718	01	87	12
LUMO+2	0.336	11	70	19
LUMO+1	0.301	28	29	43
LUMO	0.193	03	93	04
SOMO	-1.094	10	03	88
HOMO-1	-2.454	41	19	40
HOMO-2	-2.536	19	70	11
HOMO-3	-2.720	53	30	17
HOMO-4	-2.828	58	27	15
HOMO-5	-3.345	03	84	13
		β-MO		
LUMO+5	1.838	02	85	14
LUMO+4	1.726	01	95	04
LUMO+3	0.582	15	03	82
LUMO+2	0.487	08	03	89
LUMO+1	0.327	01	97	02
LUMO	0.195	03	93	04
HOMO	-2.526	24	66	10
HOMO-1	-2.629	59	25	17
HOMO-2	-2.651	41	38	22
HOMO-3	-2.867	64	20	16
HOMO-4	-3.334	03	81	16
HOMO-5	-3.644	05	86	08

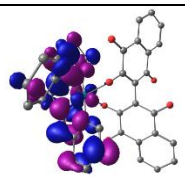
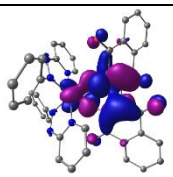
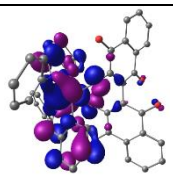
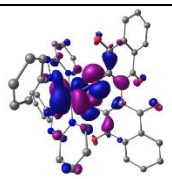
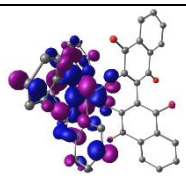
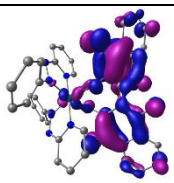
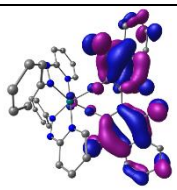
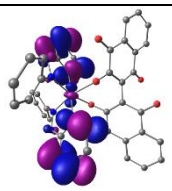
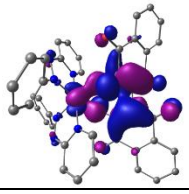
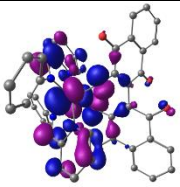
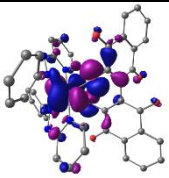
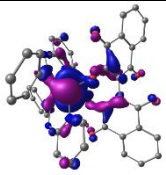
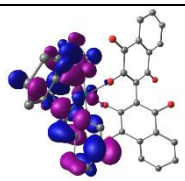
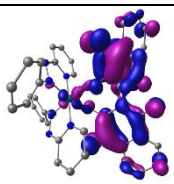
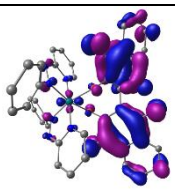
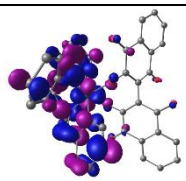
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18 DFT calculated MO compositions for $\mathbf{3}^{2-}$ in $S = 1$ state

MO	Energy (eV)	% Composition		
		Ru	L	pap
		α-MO		
LUMO+5	4.706	05	03	92
LUMO+4	4.665	06	02	92
LUMO+3	4.353	01	97	02
LUMO+2	4.217	00	98	01
LUMO+1	2.906	01	94	04
LUMO	2.831	11	66	23
SOMO	2.219	21	32	48
HOMO-1	1.822	12	03	85
HOMO-2	0.509	64	22	14
HOMO-3	0.319	33	39	28
HOMO-4	0.310	54	27	19
HOMO-5	0.168	27	60	13
		β-MO		
LUMO+5	4.381	00	98	01
LUMO+4	4.242	00	99	01
LUMO+3	3.726	22	04	74
LUMO+2	3.491	11	03	86
LUMO+1	3.121	01	97	02
LUMO	3.008	02	95	03
HOMO	0.860	53	18	30
HOMO-1	0.688	61	19	20
HOMO-2	0.568	61	26	13
HOMO-3	0.254	17	72	11
HOMO-4	-0.408	02	81	17
HOMO-5	-0.728	08	86	07

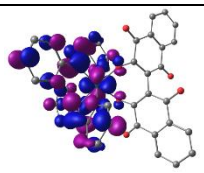
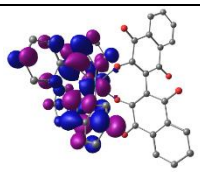
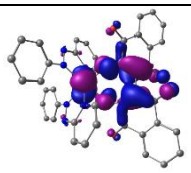
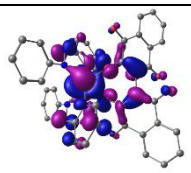
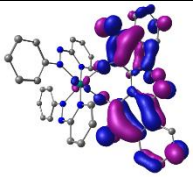
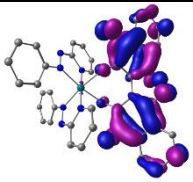
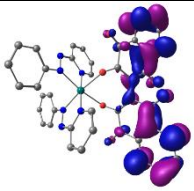
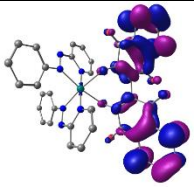
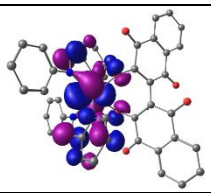
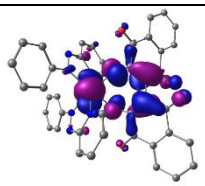
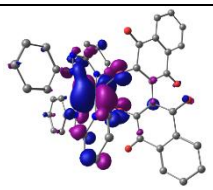
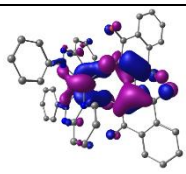
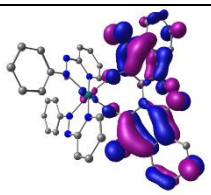
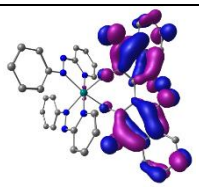
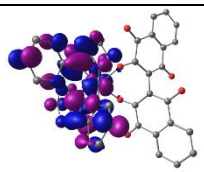
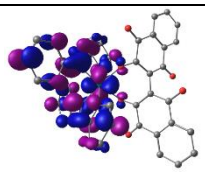
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19 DFT calculated MO compositions for $\mathbf{3}^{3-}$ in S = 3/2 state

MO	Energy (eV)	% Composition		
		Ru	L	pap
		α-MO		
LUMO+5	7.372	01	01	98
LUMO+4	7.260	05	91	04
LUMO+3	7.217	08	05	87
LUMO+2	7.104	01	91	08
LUMO+1	6.980	01	97	03
LUMO	5.590	01	98	02
SOMO	4.990	02	95	03
HOMO-1	4.691	25	06	69
HOMO-2	4.427	13	03	84
HOMO-3	3.313	34	58	09
HOMO-4	3.043	46	36	18
HOMO-5	3.034	49	32	19
		β-MO		
LUMO+5	7.175	01	94	05
LUMO+4	7.051	00	97	02
LUMO+3	6.447	25	05	70
LUMO+2	6.198	01	96	03
LUMO+1	6.147	05	70	25
LUMO	6.125	11	24	65
HOMO	3.790	46	18	36
HOMO-1	3.540	56	23	21
HOMO-2	3.458	39	50	11
HOMO-3	3.205	41	46	13
HOMO-4	2.582	03	85	12
HOMO-5	2.272	10	83	07

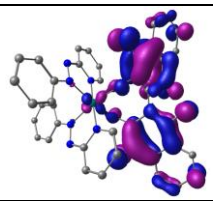
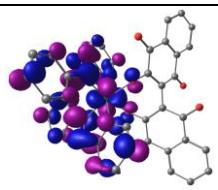
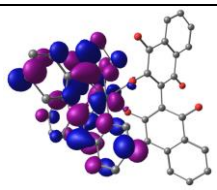
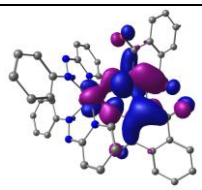
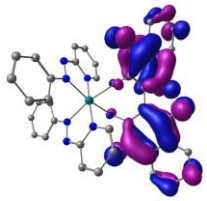
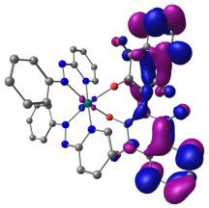
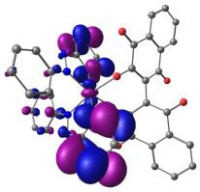
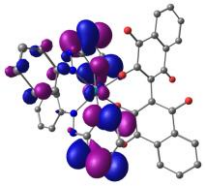
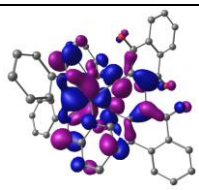
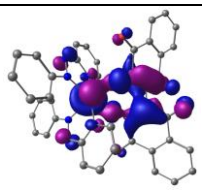
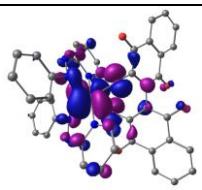
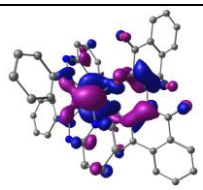
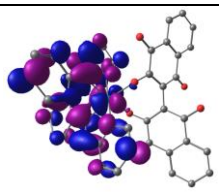
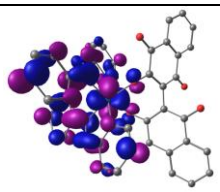
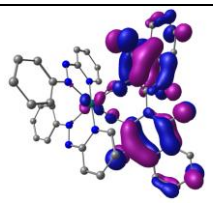
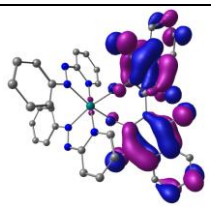
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 DFT calculated Mulliken spin density on individual atom/fragment

Complex	Ru	Carbonyl O atom	Coordinated O atom	Napthoquinone ring
$\mathbf{1}^{4+}$ (S=1)	1.532	0.064	0.261	0.122
$\mathbf{1}^{3+}$(S=1/2)	0.344	0.058	0.326	0.289
$\mathbf{1}^{+}$(S=1/2)	0.014	0.036	0.360	0.562
$\mathbf{2}^{+}$(S=1/2)	0.202	0.069	0.335	0.353
2 (S=1)	1.608	0.03	0.10	0.014
$\mathbf{2}^{-}$(S=1/2)	1.081	-0.015	0.082	-0.235
$\mathbf{2}^{3-}$(S=1/2)	0.098	-0.011	0.434	0.478
$\mathbf{3}^{+}$ (S=1/2)	0.077	0.092	0.316	0.529
$\mathbf{3}^{-}$ (S=1/2)	-0.269	0.00	-0.032	0.00
$\mathbf{3}^{2-}$ (S=1)	0.373	-0.004	0.024	-0.004
$\mathbf{3}^{3-}$ (S=3/2)	0.524	0.424	0.082	0.591