Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Diruthenium and triruthenium compounds of the potential redox active non-chelated η^1-N,η^1-N-benzothiadiazole bridge

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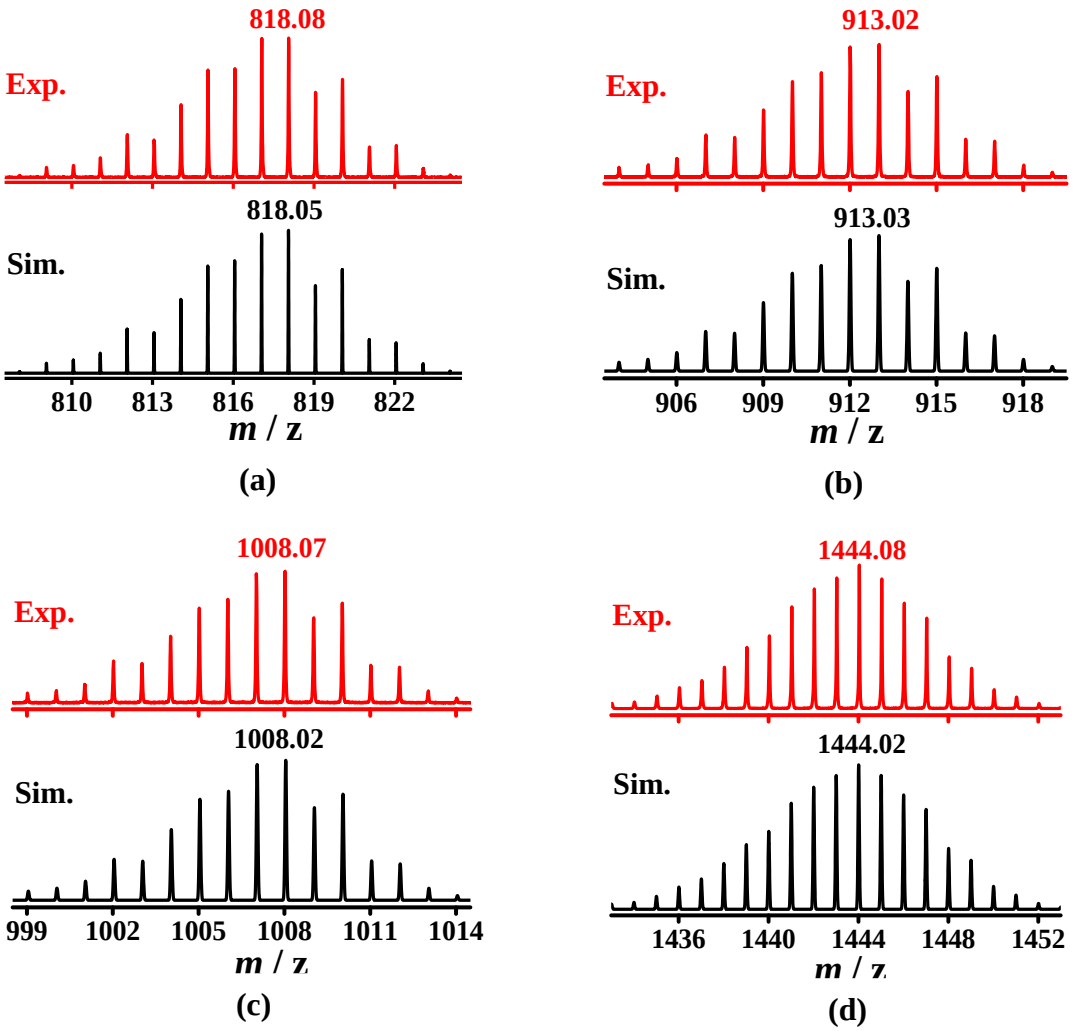


Fig. S1 Experimental and simulated ESI(+) mass spectra of (a) {**1**}$^+$, (b) {**2**}$^+$, (c) {**3**}$^+$ and (d) {**4**}$^+$ in CH_3CN.

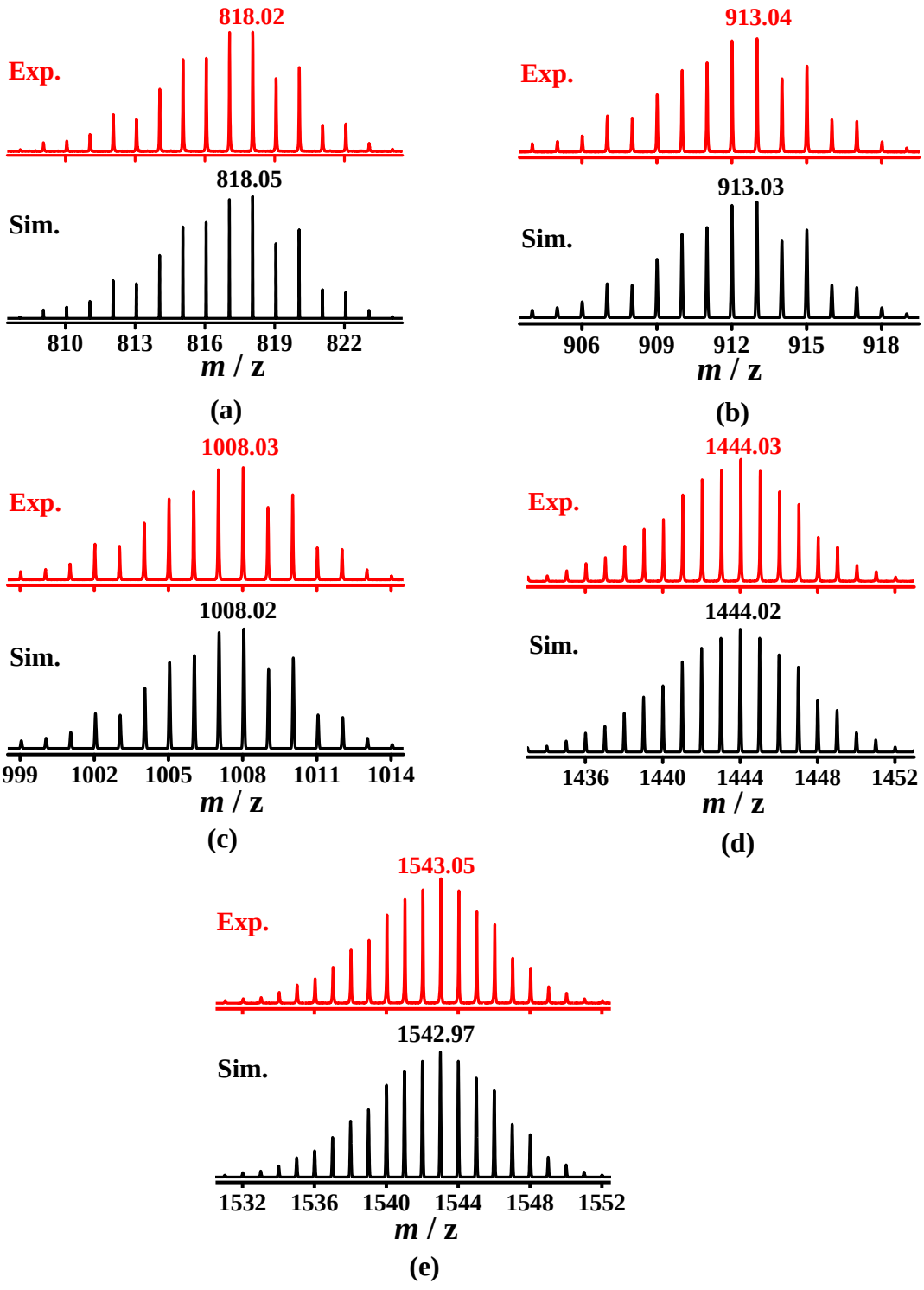


Fig. S2 Experimental and simulated ESI(+) mass spectra of (a) $\{([\mathbf{1}]ClO_4)–ClO_4\}^+$, (b) $\{([\mathbf{2}]ClO_4)–ClO_4\}^+$, (c) $\{([\mathbf{3}]ClO_4)–ClO_4\}^+$, (d) $\{([\mathbf{4}]ClO_4)–ClO_4\}^+$ and (e) $\{([\mathbf{4}](ClO_4)_2–ClO_4\}^+$ in CH_3CN.

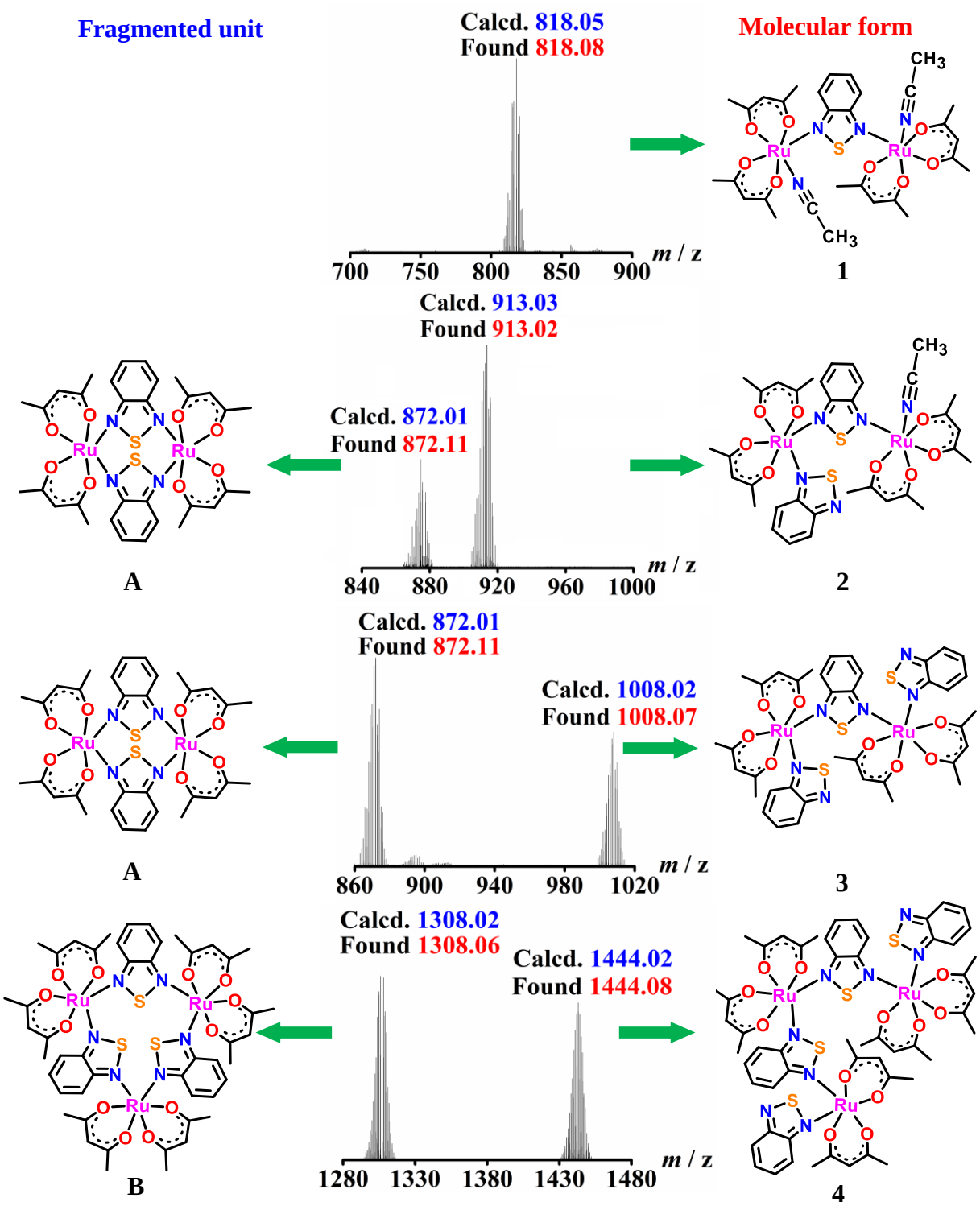


Fig. S3 ESI-mass of **1-4** in CH_3CN.

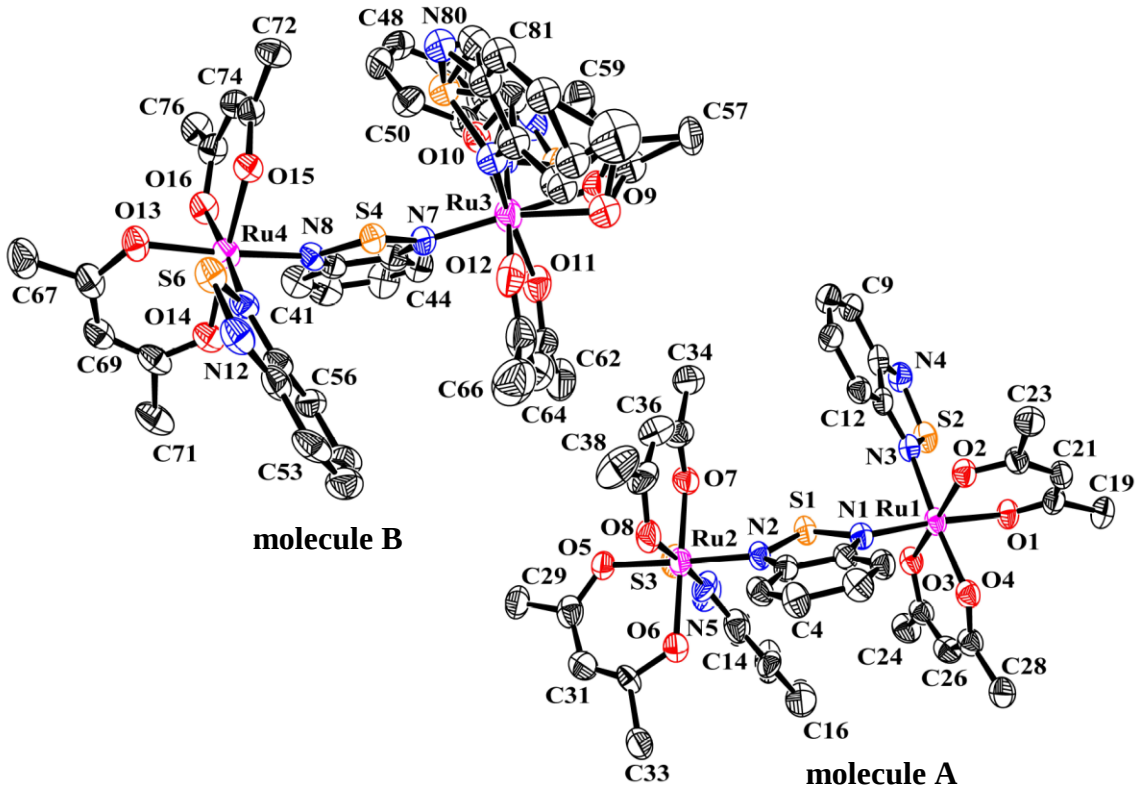


Fig. S4 Perspective view of [**3**]ClO_4. Asymmetric unit of [**3**]ClO_4 contains two molecules, (molecule A and molecule B). Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

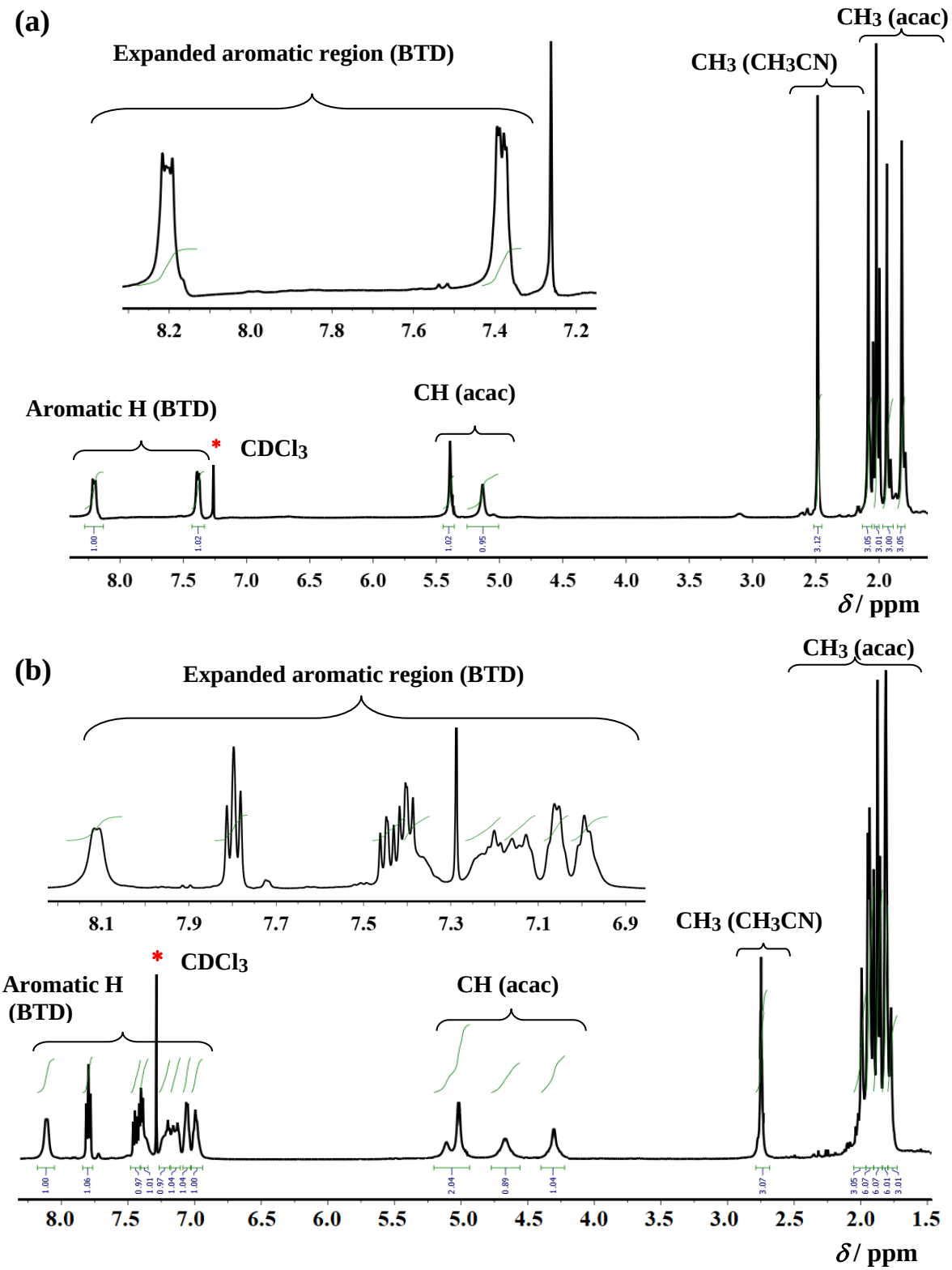


Fig. S5A ^{1}H NMR of (a) **1** and (b) **2** in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard. Inset shows the segmented spectrum.

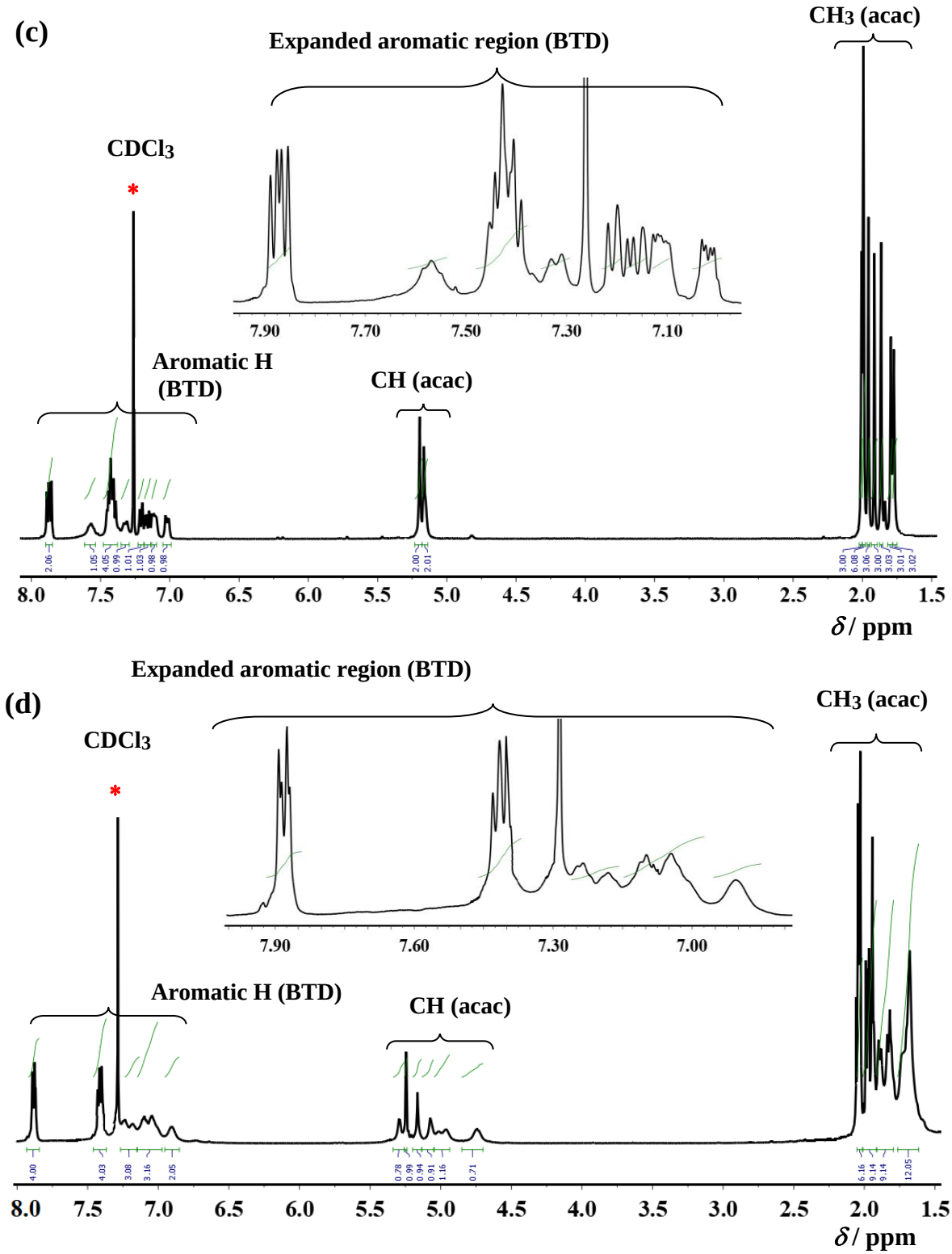


Fig. S5B ^{1}H NMR of (a) **3** and (b) **4** in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard. Inset shows the segmented spectrum.

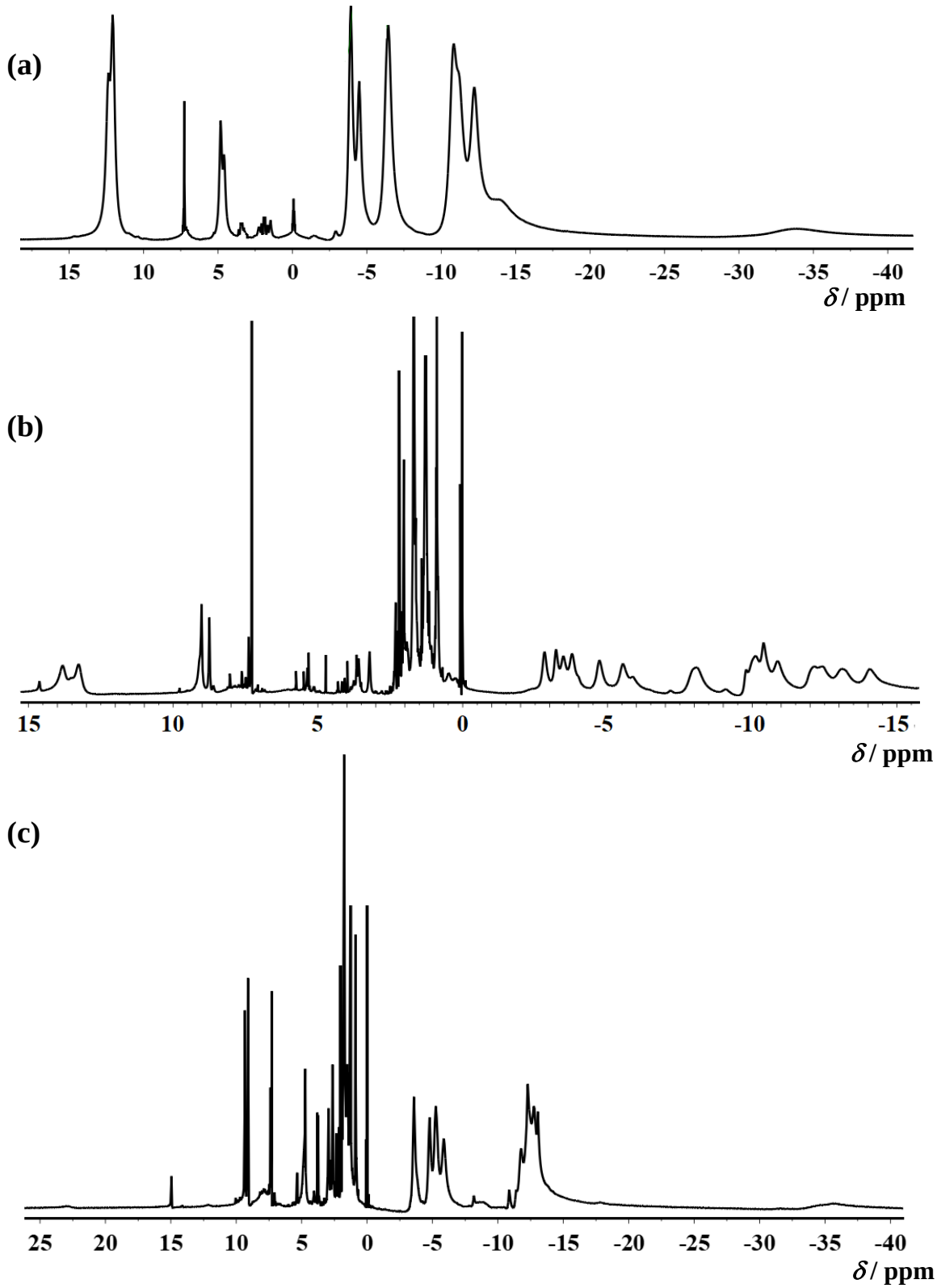


Fig. S6A ^{1}H NMR of (a) [**1**]ClO_4, (b) [**2**]ClO_4 and (c) [**3**]ClO_4 in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard.

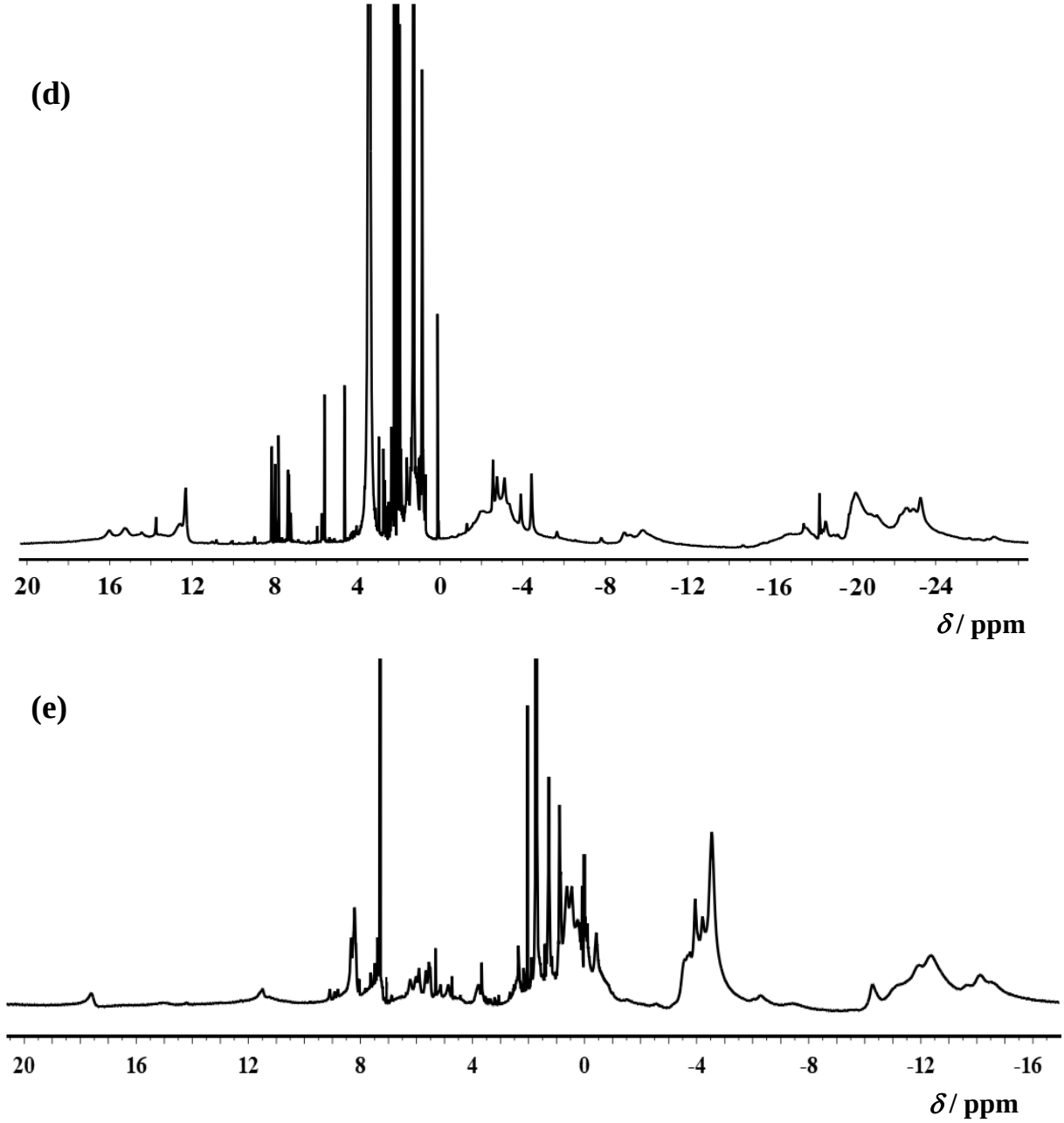


Fig. S6B ^{1}H NMR of (d) [**4**]ClO_4 and (e) [**4**]$(ClO_4)_2$ in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard.

Determination of solution magnetic moments (Evans method) of [1]ClO_4-[4]ClO_4

Solution magnetic moments of ruthenium (III) complexes [**1**]ClO_4-[**4**]ClO_4 were determined by Evans method. Each of the pure complexes in $CDCl_3$ was taken in a 5 mm NMR tube. In another coaxial NMR tube only reference $CDCl_3$ solvent was taken. Proton NMR of each sample 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 shifts in the position due to the paramagnetic Ru(III) were noted. Experiments were carried out in 400 MHz NMR spectrometer at 298 K.

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

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. This results were used to calculate the effective magnetic moment μ_{eff} in eq. 2.

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

Calculation for **[1]**ClO_4:

3.3 mg of **[1]**ClO_4 was dissolved in ~0.55 cm^3 of $CDCl_3$. The shift in the position due to the paramagnetic Ru(III) = 0.037 ppm.

$$\chi_M = 137.2 \times 10^{-5} \ \text{cm}^3/\text{mol}$$
$$\mu_{eff} = 2.83 \times (137.2 \times 10^{-5} \times 298.15)^{1/2} \ \text{BM}$$
$$= 1.81 \ \text{BM}$$

Calculation for **[2]**ClO_4:

3.5 mg of **[2]**ClO_4 was dissolved in ~0.55 cm^3 of $CDCl_3$. The shift in the position due to the paramagnetic Ru(III) = 0.035 ppm.

$$\chi_M = 132.7 \times 10^{-5} \ \ cm^3/mol$$
$$\mu_{eff} = 2.83 \times (132.7 \times 10^{-5} \times 298.15)^{1/2} \ \ BM$$
$$= 1.78 \ BM$$

Calculation for **[3]**ClO_4:

3.2 mg of **[3]**ClO_4 was dissolved in ~0.53 cm^3 of $CDCl_3$. The shift in the position due to the paramagnetic Ru(III) = 0.032 ppm.

$$\chi_M = 139.9 \times 10^{-5} \ \ cm^3/mol$$
$$\mu_{eff} = 2.83 \times (139.9 \times 10^{-5} \times 298.15)^{1/2} \ \ BM$$
$$= 1.83 \ BM$$

Calculation for **[4]**ClO_4:

3.8 mg of **[4]**ClO_4 was dissolved in ~0.50 cm^3 of $CDCl_3$. The shift in the position due to the paramagnetic Ru(III) = 0.028 ppm.

$$\chi_M = 135.5 \times 10^{-5} \ \ cm^3/mol$$
$$\mu_{eff} = 2.83 \times (135.5 \times 10^{-5} \times 298.15)^{1/2} \ \ BM$$
$$= 1.80 \ BM$$

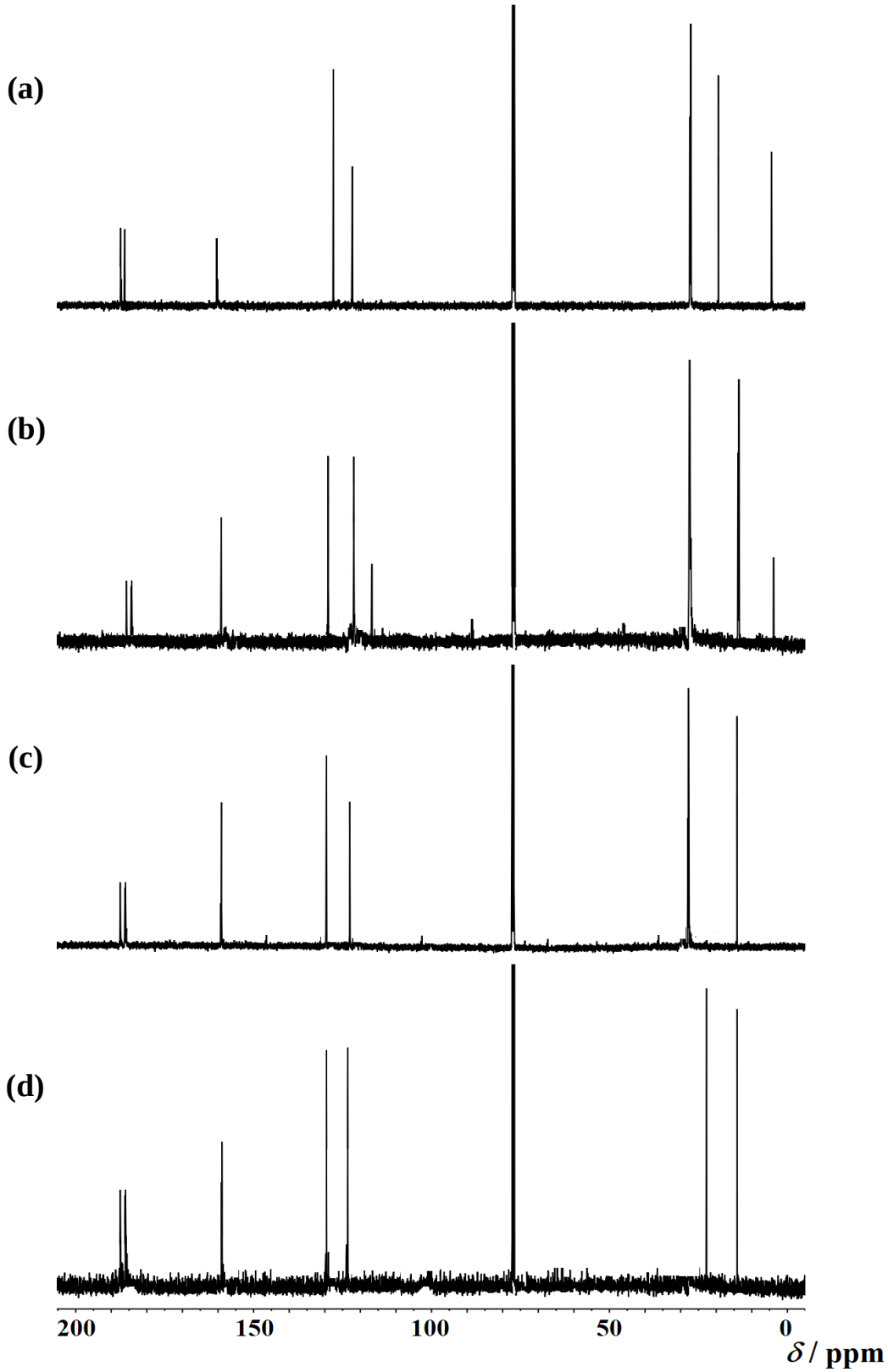


Fig. S7 $^{13}C\{1H\}$ NMR of (a) **1**, (b) **2**, (c) **3** and (d) **4** in $CDCl_3$.

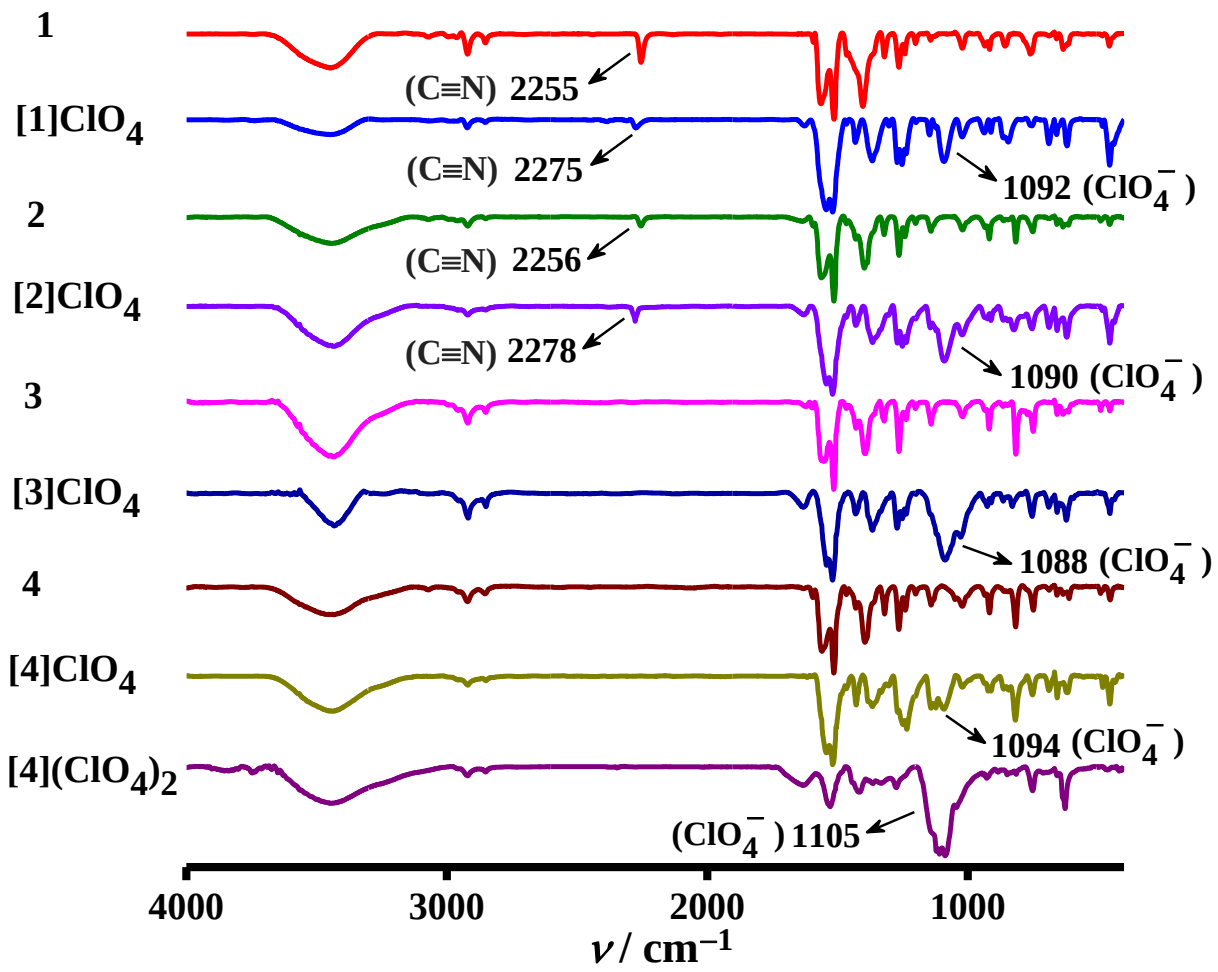


Fig. S8 FT-IR spectra as KBr pellets.

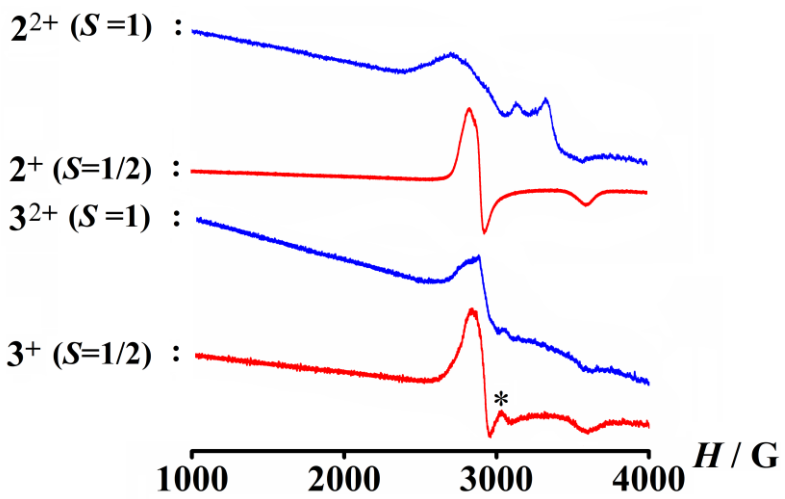


Fig. S9 EPR spectra of isolated $\mathbf{2}^{+}$, $\mathbf{3}^{+}$ and electrochemically generated $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ in CH_3CN at 100 K (*= instrumental or signal from partial dissociation).

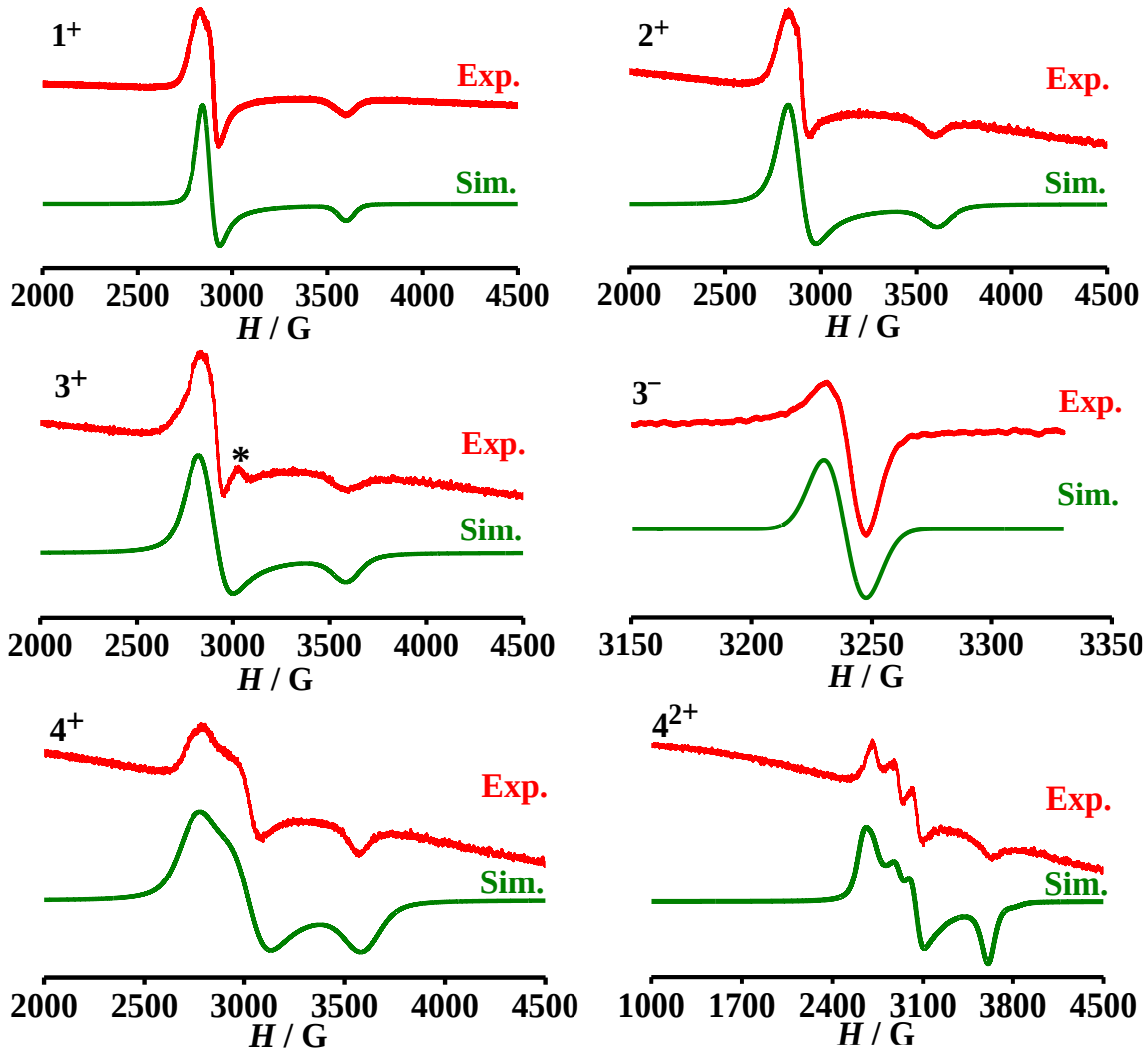


Fig. S10 Experimental and simulated EPR spectra of representative complexes (*= instrumental or signal from partial dissociation).

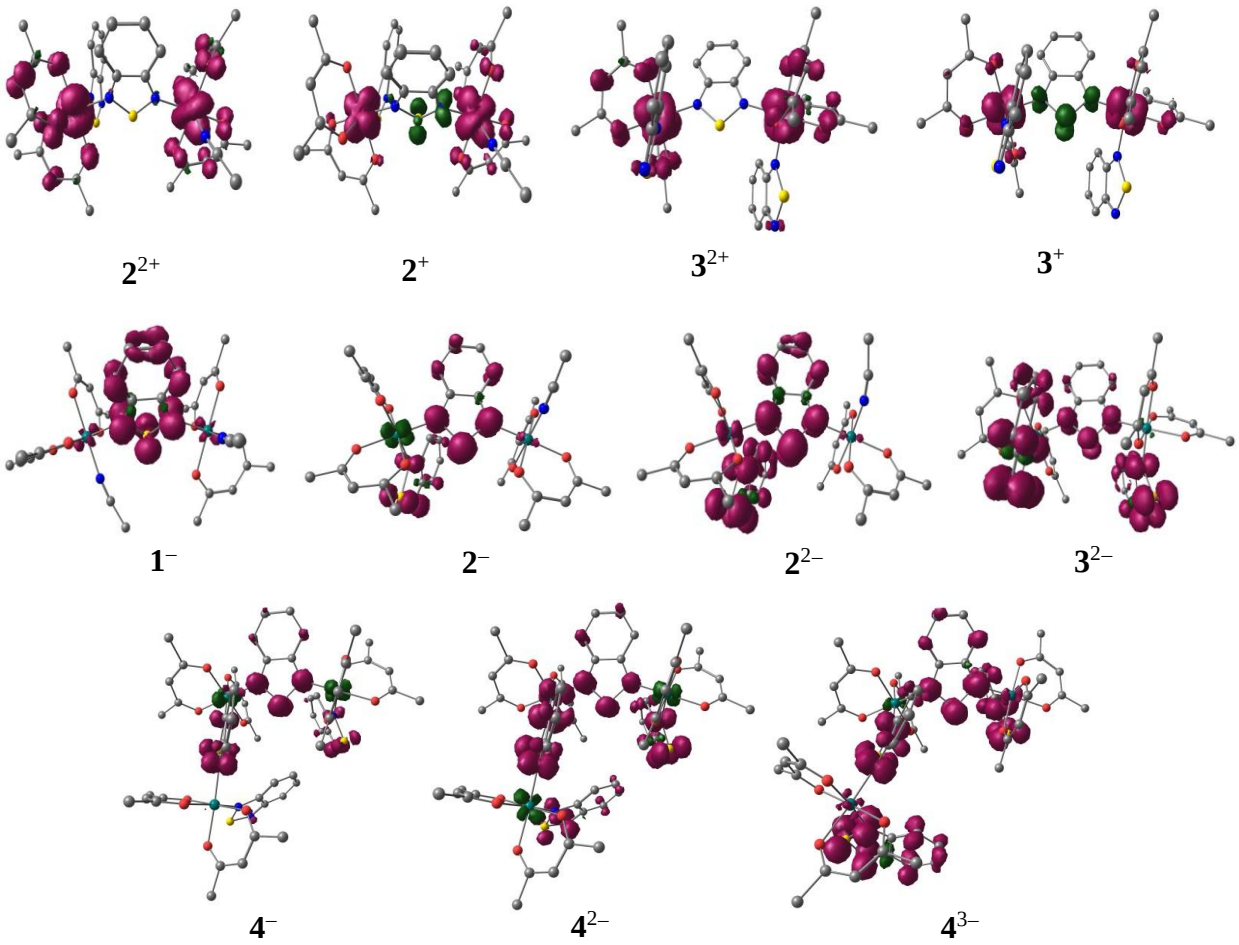


Fig. S11 DFT calculated Mulliken spin density plots for the cationic and anionic states.

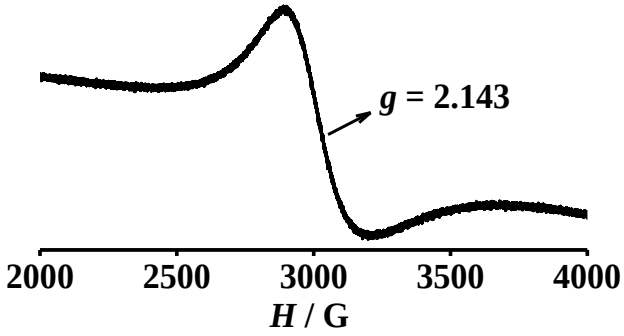


Fig. S12 Solid state EPR spectrum of [**1**]ClO_4 at 100 K.

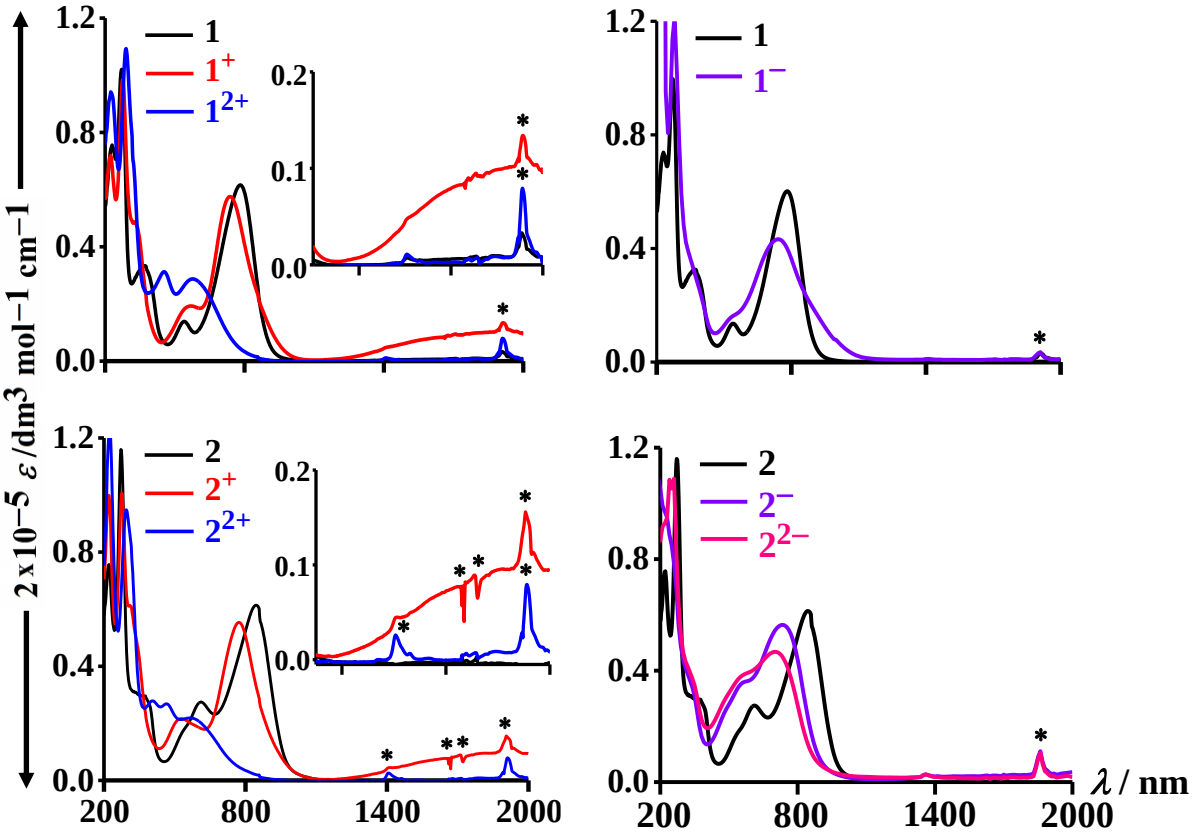


Fig. S13 UV-vis-NIR spectra of isolated **1**-**2** and electrochemically generated $\mathbf{1}^{n}$ (n= +2,+1,-1) and $\mathbf{2}^{m}$ (m= +2,+1,-1,-2) in CH_3CN (∗: Instrumental).

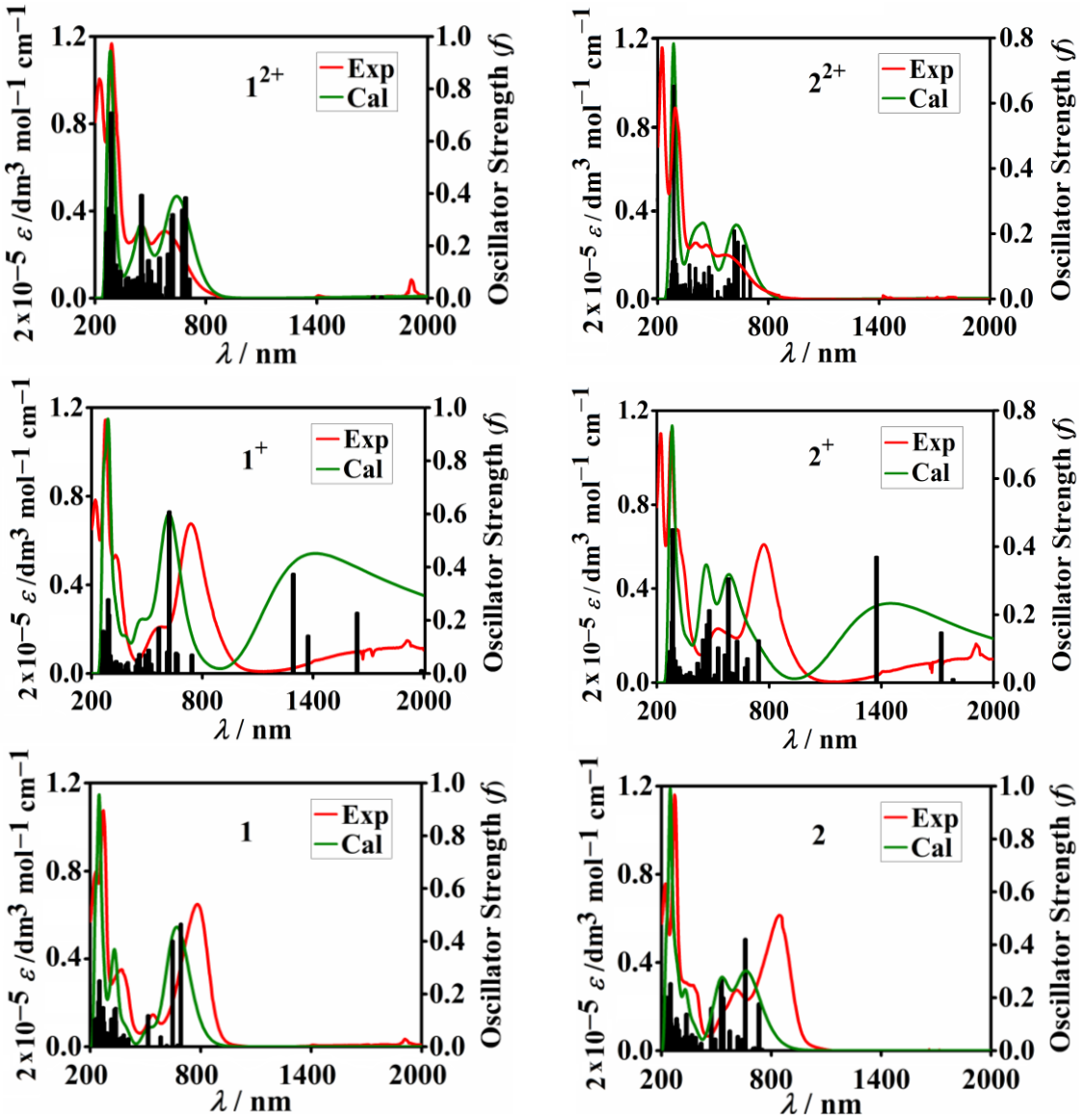


Fig. S**14A** Experimental and TD-DFT (B3LYP/CPCM/CH_3CN) calculated electronic spectra in CH_3CN. Oscillator strengths are shown by the black vertical lines; the spectra (green) are convoluted with a Gaussian function having fullwidth at half-maximum of 3000 cm^{-1}.

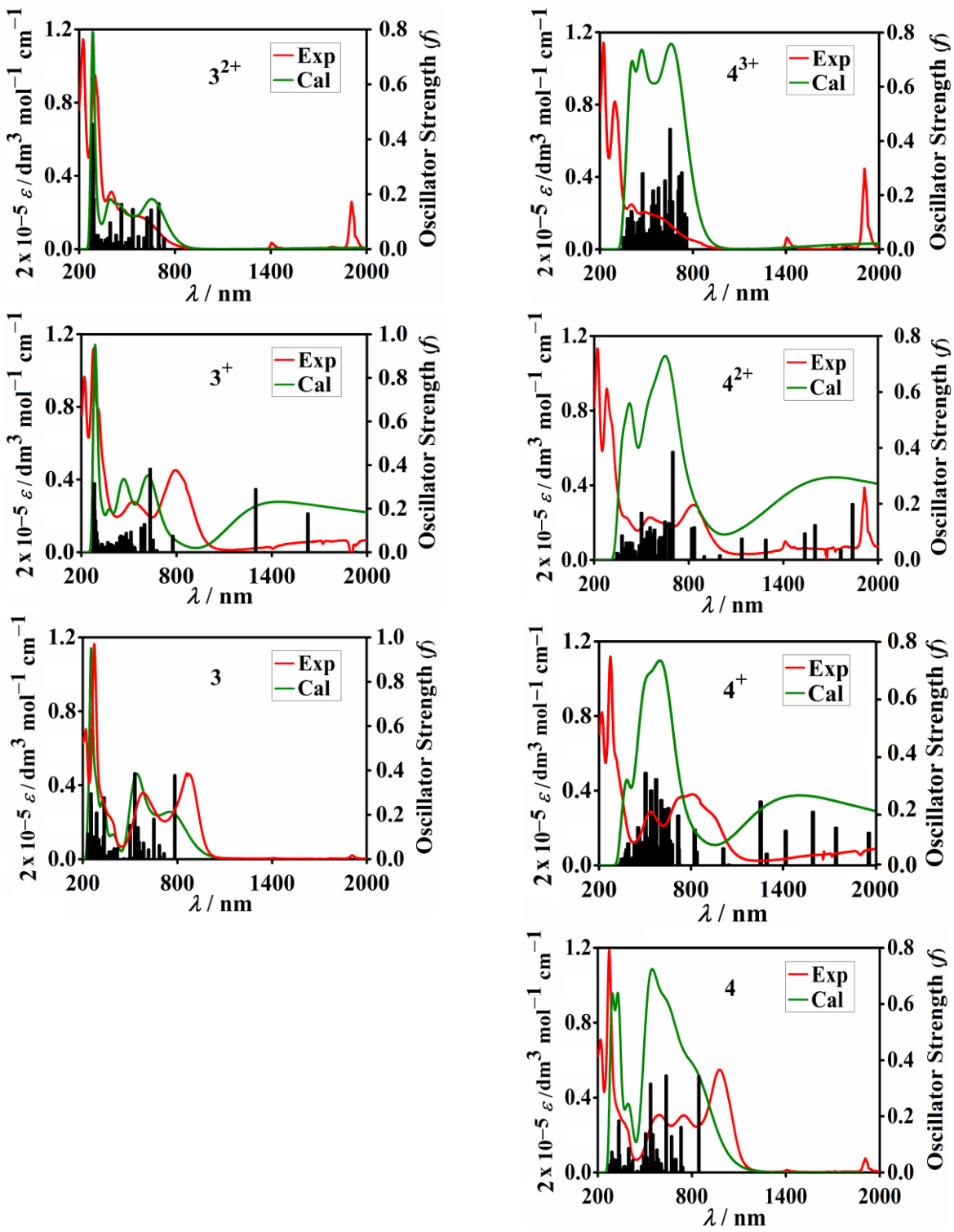


Fig. S**14B** Experimental and TD-DFT (B3LYP/CPCM/CH_3CN) calculated electronic spectra in CH_3CN. Oscillator strengths are shown by the black vertical lines; the spectra (green) are convoluted with a Gaussian function having fullwidth at half-maximum of 3000 cm^{-1}.

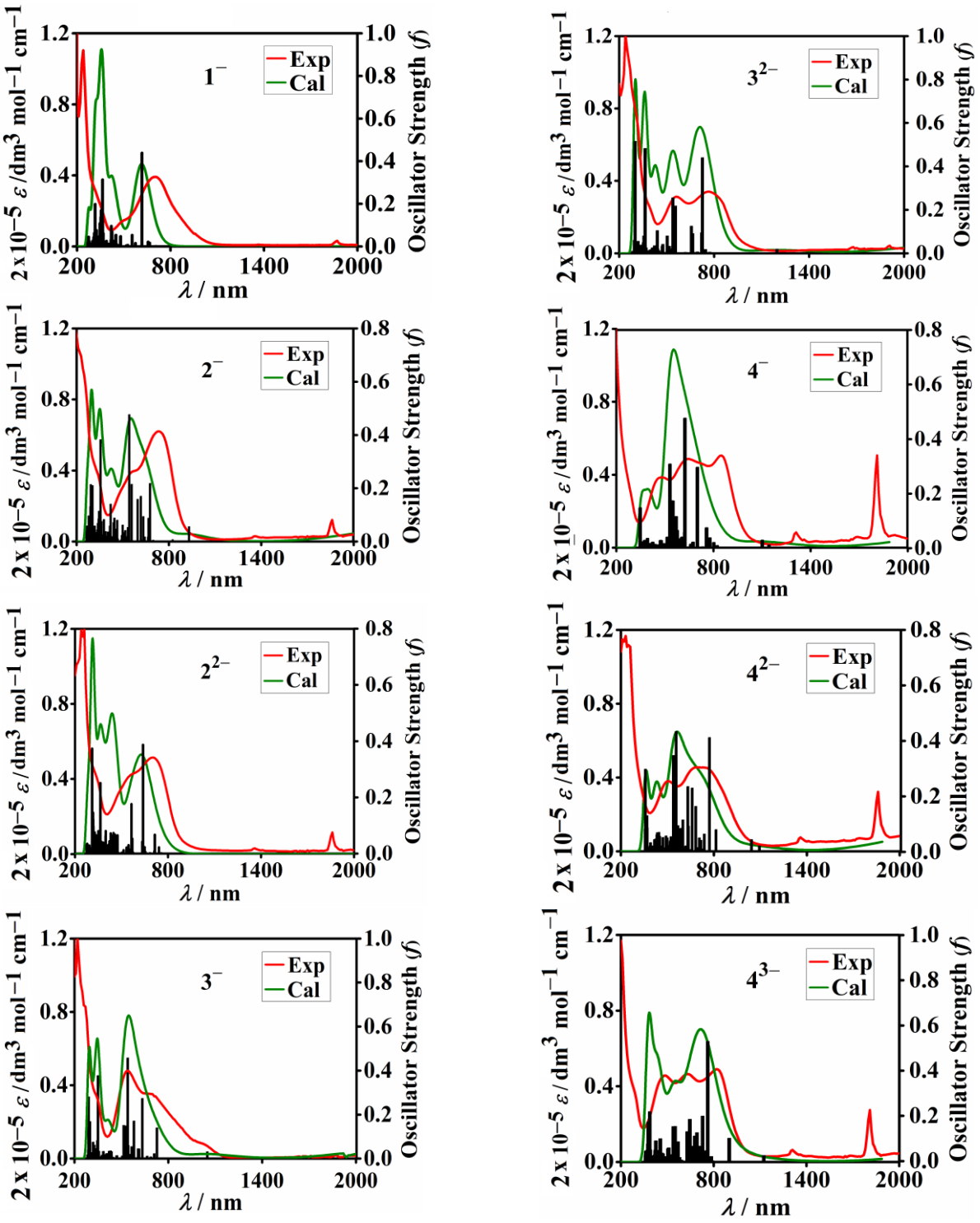


Fig. S**14C** Experimental and TD-DFT (B3LYP/CPCM/CH_3CN) calculated electronic spectra in CH_3CN. Oscillator strengths are shown by the black vertical lines; the spectra (green) are convoluted with a Gaussian function having fullwidth at half-maximum of 3000 cm^{-1}.

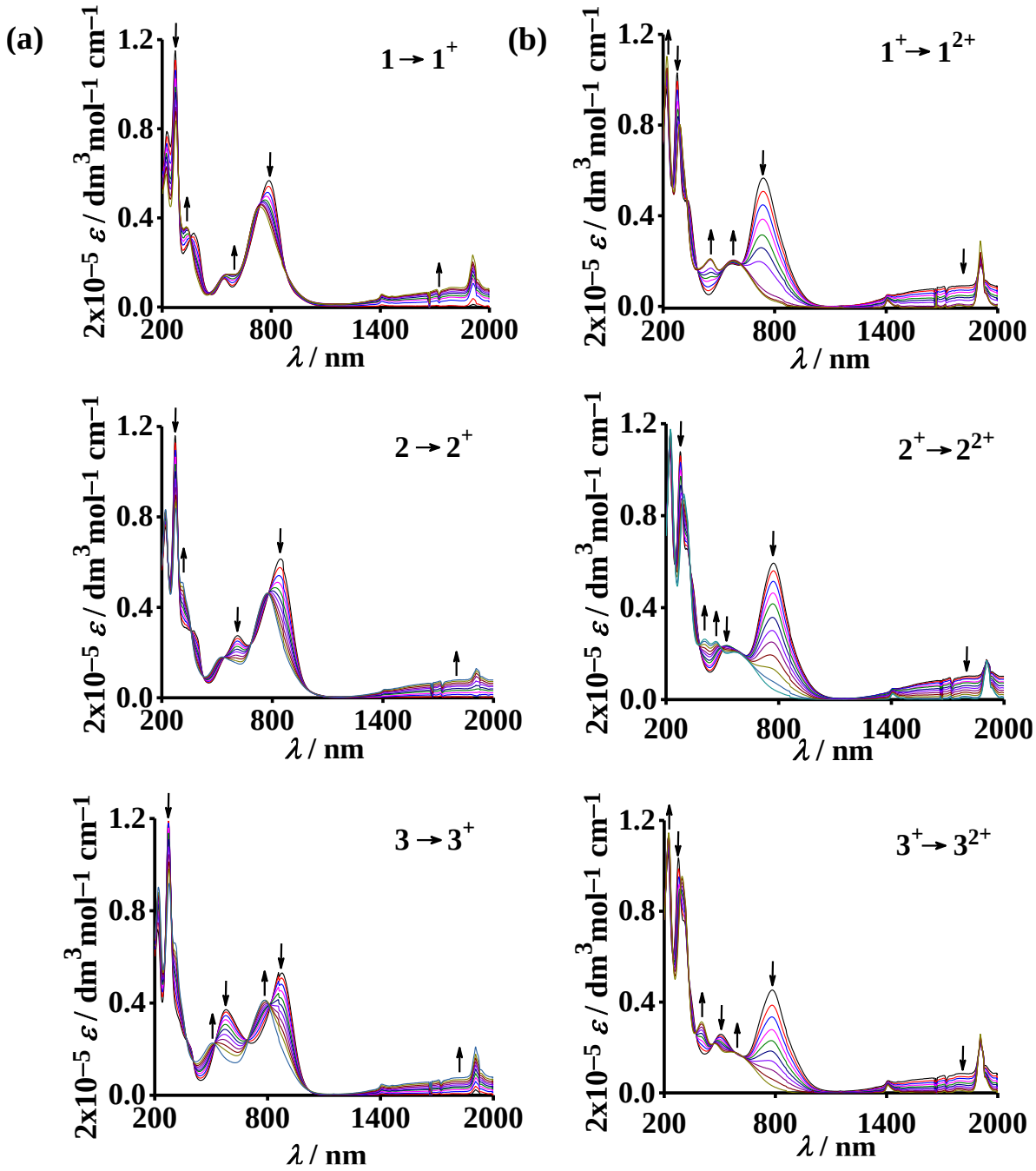


Fig. S15A UV-vis-NIR spectral changes of (a) **1-3**→ **1**$^{+}$-**3**$^{+}$ and (b) **1**$^{+}$-**3**$^{+}$ → **1**$^{2+}$-**3**$^{2+}$ by 1:1 and 1:2 $(NH_4)_2[Ce(NO_3)_6]$, respectively, in CH_3CN.

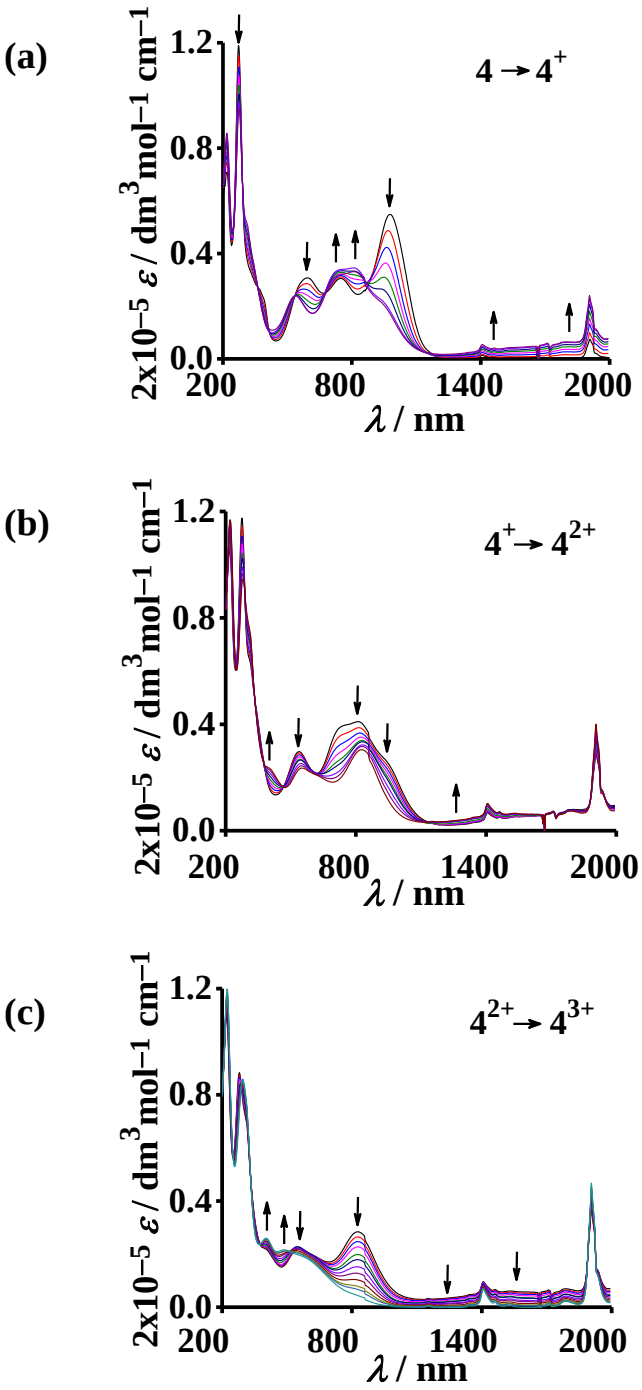


Fig. S15B UV-vis-NIR spectral changes of (a) **4**→ **4**$^{+}$, (b) **4**$^{+}$ → **4**$^{2+}$ and (c) **4**$^{2+}$ → **4**$^{3+}$ by 1:1, 1:2 and 1:3 $(NH_4)_2[Ce(NO_3)_6]$, respectively, in CH_3CN.

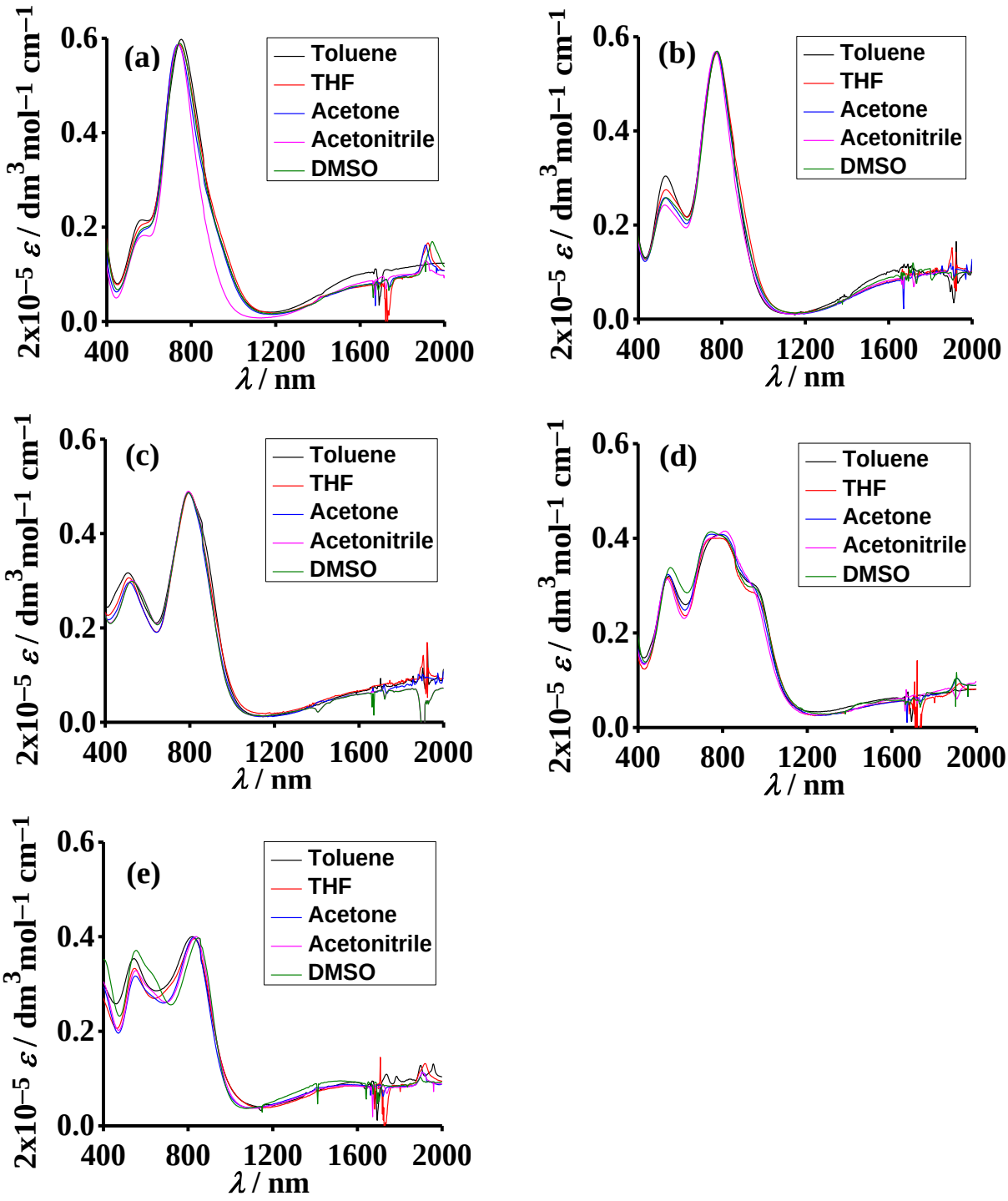


Fig. S16 UV-vis-NIR spectra of isolated (a) [**1**](ClO_4), (b) [**2**](ClO_4), (c) [**3**](ClO_4), (d) [**4**](ClO_4) and (e) [**4**]$(ClO_4)_2$ in different solvents.

Table S1 Selected crystallographic parameters

Complex	[**1**]$ClO_4.2H_2O$	[**3**]$ClO_4.1.5CH_2Cl_2$
empirical formula	$C_{30}H_{42}ClN_4O_{14}Ru_2S$	$C_{39.05}H_{42.55}Cl_{14.01}N_6O_{11.89}Ru_2S_3$
formula weight	952.335	1226.44
crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.479(4)	14.9761(4)
b (Å)	12.682(4)	19.0200(5)
c (Å)	12.995(3)	19.8607(3)
α (deg)	94.487(10)	115.273(2)
β (deg)	104.937(9)	97.684(2)
γ (deg)	90.671(11)	90.042(2)
V (Å^3)	1979.9(10)	5059.2(2)
Z	2	4
μ (mm^{-1})	0.949	0.994
T (K)	150(2)	100(2)
D_{calcd}(g cm^{-3})	1.597	1.610
F(000)	962.206	2472
θ range(deg)	2.19 to 25.1425	1.655 to 25.000
data/restraints/parameters	7018/ 57/ 507	17822/ 428/ 1292
R1, wR2 [I>2σ(I)]	0.0308, 0.0796	0.0858, 0.2247
R1, wR2(all data)	0.0363, 0.0874	0.1115, 0.2442
GOF	1.1047	1.051
largest diff. peak/hole [e Å^{-3}]	0.7094/.–0.3958	1.977/ –1.489

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

Bond	[**1**]$ClO_4.2H_2O$		[**3**]$ClO_4.1.5CH_2Cl_2$			
	X-ray	DFT	X-ray (molecule A)	Bond	X-ray (molecule B)	DFT
Ru1-N1	1.974(3)	2.046	1.988(7)	Ru3-N7	1.970(7)	2.038
Ru2-N2	2.002(3)	2.033	1.996(7)	Ru4-N8	1.987(7)	2.038
Ru1-N3	2.038(3)	2.071	2.047(7)	Ru3-N9	2.036(10)	2.107
Ru2-N4	2.039(3)	2.069	-	Ru4-N10	-	-
Ru2-N5	-	-	2.022(9)	Ru4-N11	2.051(7)	2.108
Ru1-O1	2.027(2)	2.040	1.998(5)	Ru3-O9	1.989(9)	2.041
Ru1-O2	2.034(2)	2.065	2.017(6)	Ru3-O10	2.055(9)	2.068
Ru1-O3	2.018(2)	2.050	1.996(6)	Ru3-O11	2.023(7)	2.051
Ru1-O4	2.007(2)	2.035	2.002(6)	Ru3-O12	1.953(10)	2.047
Ru2-O5	2.015(2)	2.046	2.019(6)	Ru4-O13	1.997(6)	2.041
Ru2-O6	2.014(2)	2.068	2.049(7)	Ru4-O14	2.012(6)	2.068
Ru2-O7	2.007(2)	2.057	2.003(7)	Ru4-O15	2.010(6)	2.052
Ru2-O8	2.007(2)	2.034	2.015(7)	Ru4-O16	2.009(5)	2.049
S1-N1	1.662(3)	1.679	1.657(7)	S4-N7	1.668(7)	1.681
S1-N2	1.665(3)	1.677	1.662(7)	S4-N8	1.650(6)	1.681
S2-N3	-	-	1.644(7)	S5-N9	1.686(10)	1.677
S2-N4	-	-	1.618(9)	S5-N10	1.600(13)	1.626
S3-N5	-	-	1.615(9)	S6-N11	1.639(7)	1.677
S3-N6	-	-	1.625(11)	S6-N12	1.590(8)	1.626
Ru1---Ru2	6.227	6.361	6.256	Ru3---Ru4	6.184	6.378

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

Bond angles	[**1**]$ClO_4.2H_2O$		[**3**]$ClO_4.1.5CH_2Cl_2$			
	Xray	DFT	X-ray (molecule A)	Bond angles	X-ray (molecule B)	DFT
N1-Ru1-N3	90.62(11)	91.95	92.3(3)	N7-Ru3-N9	91.8(3)	92.20
N1-Ru1-O1	174.49(10)	178.11	175.2(3)	N7-Ru3-O9	178.8(4)	177.71
N1-Ru1-O2	91.14(9)	91.23	92.6(2)	N7-Ru3-O10	88.2(3)	91.54
N1-Ru1-O3	88.70(9)	89.99	90.2(3)	N7-Ru3-O11	91.7(3)	90.18
N1-Ru1-O4	88.93(9)	90.85	91.2(3)	N7-Ru3-O12	88.0(3)	91.02
N3-Ru1-O1	93.53(11)	89.23	90.6(3)	N9-Ru3-O9	86.9(4)	88.36
N3-Ru1-O2	89.34(10)	91.33	90.0(3)	N9-Ru3-O10	89.8(4)	93.09
N3-Ru1-O3	89.31(10)	88.33	86.3(3)	N9-Ru3-O11	85.9(3)	86.41
N3-Ru1-O4	176.72(10)	176.98	176.0(2)	N9-Ru3-O12	178.2(4)	176.75
O1-Ru1-O2	92.52(9)	90.23	91.2(2)	O9-Ru3-O10	91.8(3)	90.65
O1-Ru1-O3	87.74(9)	88.56	86.2(2)	O9-Ru3-O11	88.2(3)	87.64
O1-Ru1-O4	87.13(9)	88.01	86.0(2)	O9-Ru3-O12	93.2(4)	88.41
O2-Ru1-O3	178.64(9)	178.74	175.5(2)	O10-Ru3-O11	175.7(3)	178.23
O2-Ru1-O4	87.42(9)	87.45	87.9(3)	O10-Ru3-O12	92.0(3)	87.26
O3-Ru1-O4	93.92(9)	92.84	95.5(3)	O11-Ru3-O12	92.3(3)	93.14
N2-Ru2-N4	90.59(11)	92.88	-	-	-	-
N2-Ru2-N5	-	-	92.2(3)	N8-Ru4-N11	95.6(3)	92.23
N2-Ru2-O5	177.21(10)	178.51	177.8(3)	N8-Ru4-O13	176.1(3)	177.64
N2-Ru2-O6	88.36(10)	88.28	90.3(3)	N8-Ru4-O14	90.1(3)	91.62
N2-Ru2-O7	91.96(10)	92.80	89.3(3)	N8-Ru4-O15	88.6(3)	90.11
N2-Ru2-O8	89.47(10)	89.54	91.9(3)	N8-Ru4-O16	88.4(3)	90.80
N4-Ru2-O5	92.10(11)	88.54	-	-	-	-
N5-Ru2-O5	-	-	86.8(3)	N11-Ru4-O13	87.5(3)	88.49
N4-Ru2-O6	91.10(10)	91.97	-	-	-	-
N5-Ru2-O6	-	-	93.2(3)	N11-Ru4-O14	91.0(3)	93.04
N4-Ru2-O7	88.54(11)	88.82	-	-	-	-
N5-Ru2-O7	-	-	86.4(3)	N11-Ru4-O15	86.8(2)	86.31
N4-Ru2-O8	177.10(10)	176.95	-	-	-	-
N5-Ru2-O8	-	-	175.9(3)	N11-Ru4-O16	176.0(3)	176.92
O5-Ru2-O6	92.31(10)	91.22	91.7(3)	O13-Ru4-O14	92.3(3)	90.59
O5-Ru2-O7	87.39(10)	87.68	88.6(3)	O13-Ru4-O15	89.2(2)	87.69
O5-Ru2-O8	87.87(10)	89.03	89.1(3)	O13-Ru4-O16	88.5(2)	88.46
O6-Ru2-O7	179.52(10)	178.63	179.4(3)	O14-Ru4-O15	177.4(2)	178.17
O6-Ru2-O8	86.00(9)	86.24	86.6(3)	O14-Ru4-O16	88.3(2)	87.42
O7-Ru2-O8	94.36(10)	92.92	93.9(3)	O15-Ru4-O16	93.9(2)	93.14

Table S4 DFT calculated selected MO compositions ((U/R)B3LYP/LanL2DZ/6-31G**)

Complex	Energy (eV)	MO	% Contribution of Ru/acac/BTD
$\mathbf{1}^{2+}$ (S=1) $\Delta E_{((S=0)-(S=1))}$= 5911 cm^{-1}	-9.122	β-LUMO	42/27/29
$\mathbf{1}^{+}$ (S=1/2)	-7.610	SOMO	45/44/9
	-5.645	β-LUMO	67/21/10
1 (S=0)	-3.418	HOMO	53/15/30
	-1.652	LUMO	8/4/87
$\mathbf{1}^{-}$ (S=1/2)	0.479	SOMO	5/23/71
$\mathbf{2}^{2+}$ (S=1) $\Delta E_{((S=0)-(S=1))}$= 4526 cm^{-1}	-9.001	β-LUMO	53/25/19
$\mathbf{2}^{+}$ (S=1/2)	-7.696	SOMO	42/53/5
	-6.292	β-LUMO	69/17/12
2 (S=0)	-4.364	HOMO	66/24/9
	-2.243	LUMO	4/1/95
$\mathbf{2}^{-}$ (S=1/2)	-0.053	SOMO	7/2/90
	1.161	β-LUMO	4/2/94
$\mathbf{2}^{2-}$ (S=1) $\Delta E_{((S=0)-(S=1))}$= 3536 cm^{-1}	3.099	SOMO 1	6/5/89
$\mathbf{3}^{2+}$ (S=1) $\Delta E_{((S=0)-(S=1))}$= 5407 cm^{-1}	-9.214	β-LUMO	45/22/32
$\mathbf{3}^{+}$ (S=1/2)	-7.984	SOMO	39/47/14
	-6.243	β-LUMO	64/18/18
3 (S=0)	-4.588	HOMO	65/21/14
	-2.569	LUMO	3/4/93
$\mathbf{3}^{-}$ (S=1/2)	-0.391	SOMO	6/2/93
	0.623	β-LUMO	5/2/94
$\mathbf{3}^{2-}$ (S=1) $\Delta E_{((S=0)-(S=1))}$= 2800 cm^{-1}	2.387	SOMO 1	9/3/88
$\mathbf{4}^{3+}$ (S=3/2) $\Delta E_{((S=1/2)-(S=3/2))}$= 5134 cm^{-1}	-10.975	β-LUMO	44/24/31
$\mathbf{4}^{2+}$ (S=1)	-9.758	SOMO 1	36/51/12
$\Delta E_{((S=0)-(S=1))}$= 5449 cm^{-1}	-8.386	β-LUMO	53/19/28
$\mathbf{4}^{+}$ (S=1/2)	-7.262	SOMO	49/35/16
	-5.967	β-LUMO	66/17/16
4 (S=0)	-4.452	HOMO	65/20/15
	-2.444	LUMO	7/2/91
$\mathbf{4}^{-}$ (S=1/2)	-0.666	SOMO	7/2/91
	0.096	β-LUMO	6/2/92
$\mathbf{4}^{2-}$ (S=1)	1.748	SOMO 1	10/3/87
$\Delta E_{((S=0)-(S=1))}$= 2522 cm^{-1}	2.283	β-LUMO	6/3/91
$\mathbf{4}^{3-}$ (S=3/2) $\Delta E_{((S=1/2)-(S=3/2))}$= 1029 cm^{-1}	4.231	SOMO	11/3/86

Table S5A EPR simulation data of complexes $\mathbf{1}^{+}$, $\mathbf{2}^{+}$, $\mathbf{3}^{+}$, $\mathbf{3}^{-}$and $\mathbf{4}^{+}$

Parameter	$\mathbf{1}^{+}$	$\mathbf{2}^{+}$	$\mathbf{3}^{+}$	$\mathbf{4}^{+}$	$\mathbf{3}^{-}$
S	1/2	1/2	1/2	1/2	1/2
g_x	2.2682	2.2799	2.308	2.3539	g_{iso} = 2.0068
g_y	2.2682	2.2614	2.232	2.1487	
g_z	1.8052	1.7994	1.811	1.8105	
lwpp (peak to peak)	6.2000 1.6500	7.9000 5.3370	8 6.05	12.0621 6.0610	1.7479
A_x	$A_x = A_y = A_z$ = 60.3797	74.9998	$A_x = A_y = A_z$ = 65	$A_x = A_y = A_z$ = 60.3912	
A_y		55.0004			
A_z		89.9993			

Table S5B EPR simulation data of $\mathbf{4}^{2+}$

Parameter	$\mathbf{4}^{2+}$		
	Ru	**Ru**	**Ru**
Sys. weight	39%	20%	40%
S	1		
g_x	2.4606	2.3373	2.3958
g_y	2.1332	2.0545	2.2270
g_z	1.80	1.7046	1.80
lwpp (peak to peak)	5.98594.0040	7.97201.9948	5.0113 2.9926
A	68.49	69.17	62.00

All the simulated EPR parameters are in mT unit.

Table S6 Composition and energies of selected molecular orbitals of $\mathbf{1}^{2+}$ (*S*=1)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	-5.889	35	47	9	8
LUMO+4	-5.994	7	88	3	2
LUMO+3	-6.021	21	72	2	5
LUMO+2	-6.141	15	56	28	1
LUMO+1	-6.152	33	44	22	1
LUMO	-8.116	8	2	89	0
SOMO 1	-10.805	31	60	8	1
SOMO 2	-10.950	17	80	3	1
HOMO-2	-11.096	27	69	3	1
HOMO-3	-11.129	22	73	4	1
HOMO-4	-11.434	34	45	20	1
HOMO-5	-11.631	68	26	5	2
		β-spin			
LUMO+5	-5.966	5	91	2	1
LUMO+4	-6.011	19	67	14	1
LUMO+3	-6.085	7	57	35	1
LUMO+2	-7.733	26	8	65	1
LUMO+1	-8.572	65	27	5	3
LUMO	-9.122	42	27	29	2
HOMO	-10.795	36	58	4	2
HOMO-1	-10.866	23	72	4	1
HOMO-2	-11.165	41	46	11	2
HOMO-3	-11.180	51	44	2	2
HOMO-4	-11.224	40	56	3	2
HOMO-5	-11.333	61	32	4	3

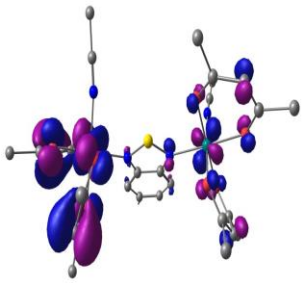
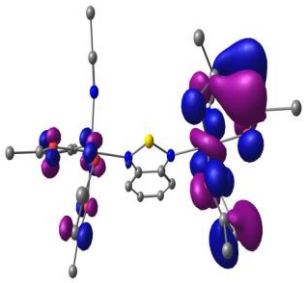
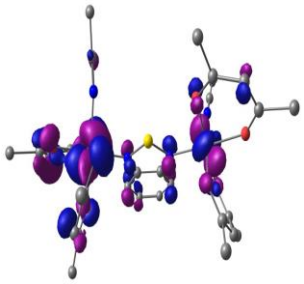
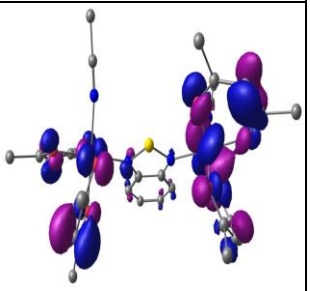
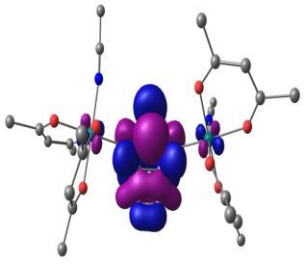
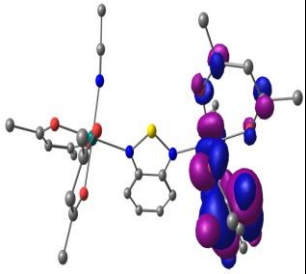
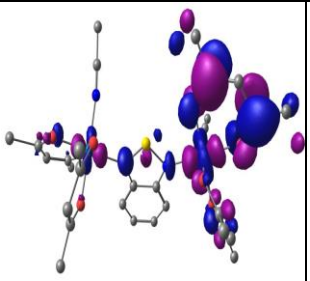
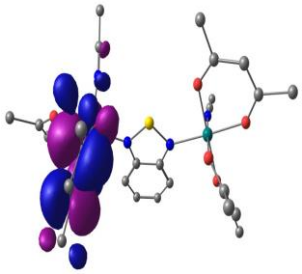
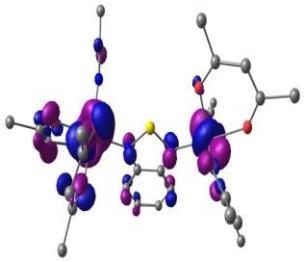
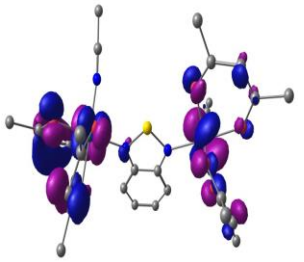
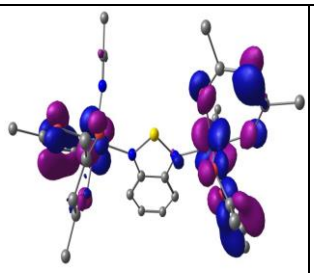
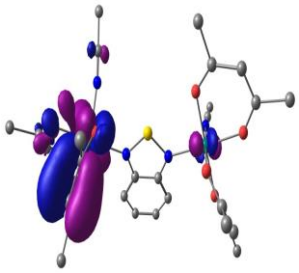
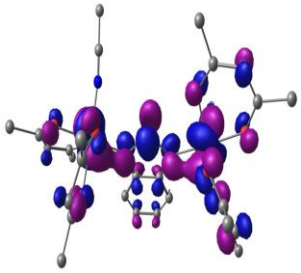
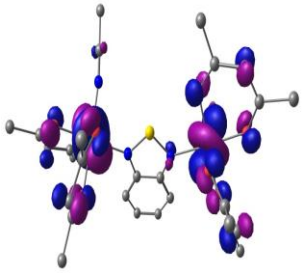
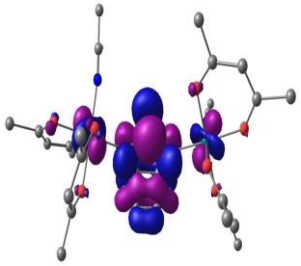
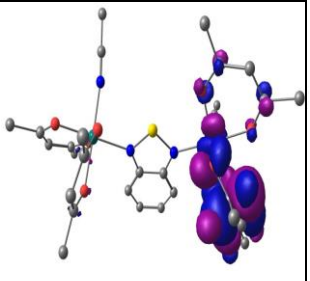
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (S=1/2)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	-2.256	35	20	29	16
LUMO+4	-2.841	5	89	5	1
LUMO+3	-3.044	4	93	2	1
LUMO+2	-3.112	3	86	10	1
LUMO+1	-3.192	5	90	5	0
LUMO	-4.730	9	3	87	0
SOMO	-7.610	45	44	9	2
HOMO-1	-7.741	48	46	4	2
HOMO-2	-7.902	50	43	5	2
HOMO-3	-8.176	46	46	7	1
HOMO-4	-8.211	73	18	6	3
HOMO-5	-8.432	70	20	6	3
		β-spin			
LUMO+5	-2.816	5	89	6	1
LUMO+4	-3.026	4	93	2	1
LUMO+3	-3.096	4	84	11	1
LUMO+2	-3.166	5	88	6	0
LUMO+1	-4.542	29	8	61	1
LUMO	-5.645	67	21	10	2
HOMO	-7.193	38	26	34	1
HOMO-1	-7.587	55	40	3	2
HOMO-2	-7.846	62	30	6	2
HOMO-3	-8.003	70	21	6	3
HOMO-4	-8.214	71	19	7	3
HOMO-5	-8.439	27	70	2	2

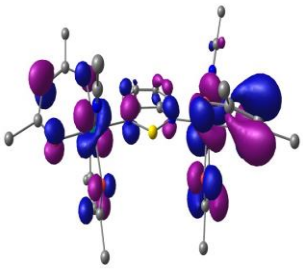
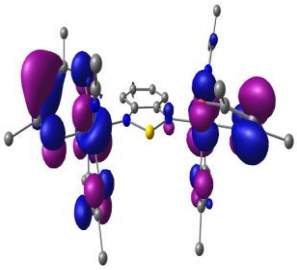
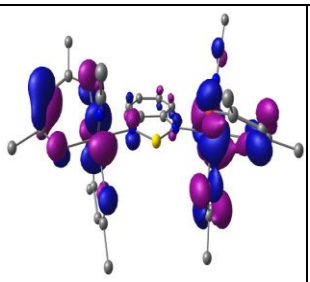
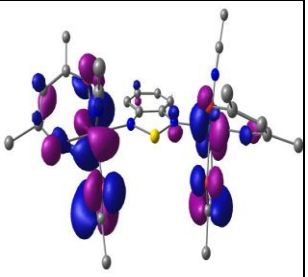
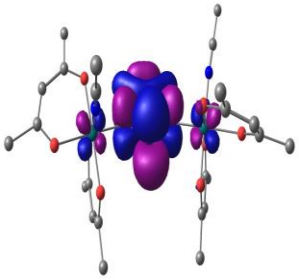
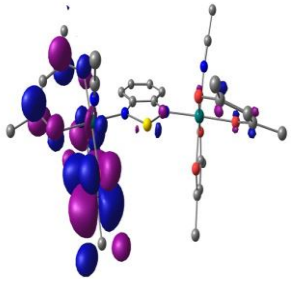
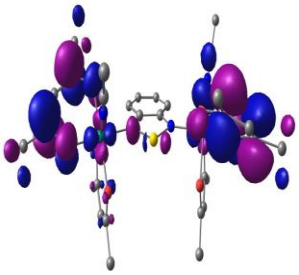
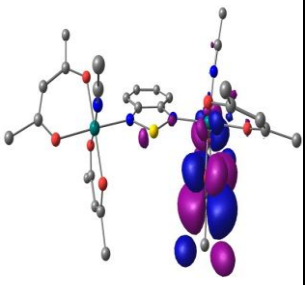
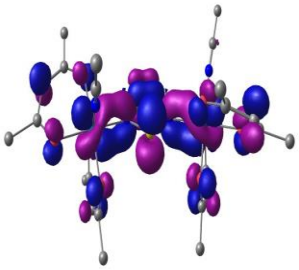
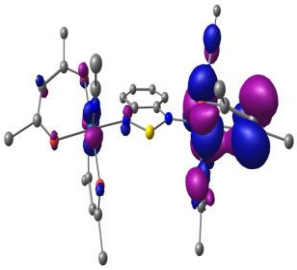
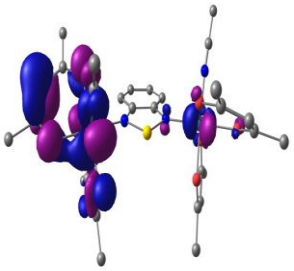
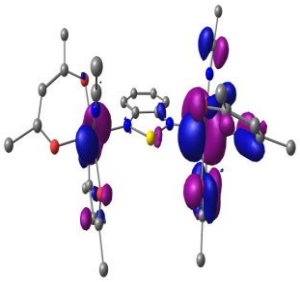
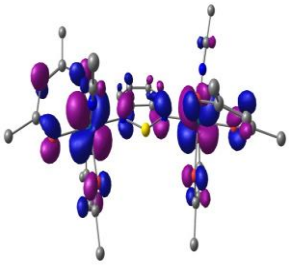
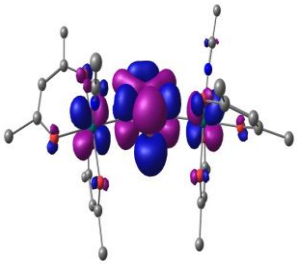
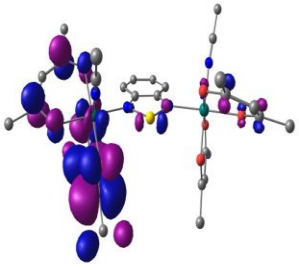
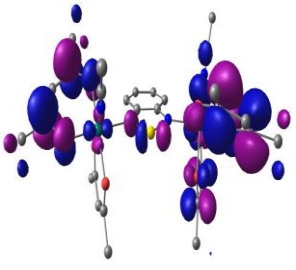
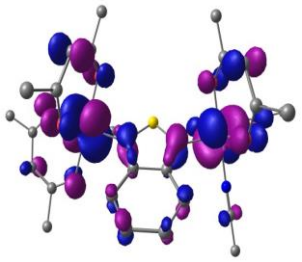
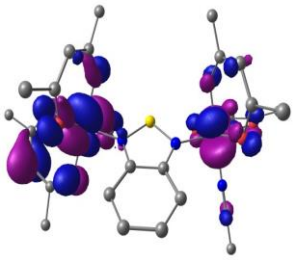
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 Composition and energies of selected molecular orbitals of **1** (*S*=0)

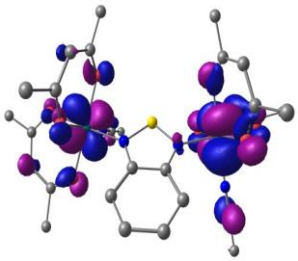
MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
LUMO+5	0.337	40	22	3	35
LUMO+4	-0.524	5	92	2	2
LUMO+3	-0.549	4	90	4	2
LUMO+2	-0.605	4	94	2	0
LUMO+1	-0.625	4	94	1	0
LUMO	-1.652	8	4	87	1
HOMO	-3.418	53	15	30	2
HOMO-1	-4.591	56	35	7	2
HOMO-2	-5.001	44	33	21	2
HOMO-3	-5.129	68	27	3	2
HOMO-4	-5.209	57	25	17	2
HOMO-5	-5.243	11	4	84	1



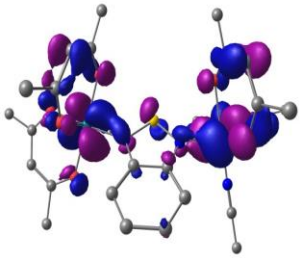
HOMO



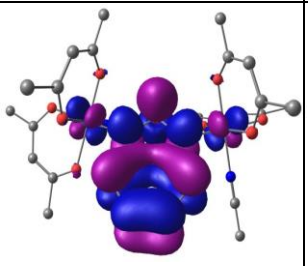
HOMO-1



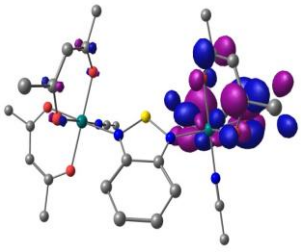
HOMO-2



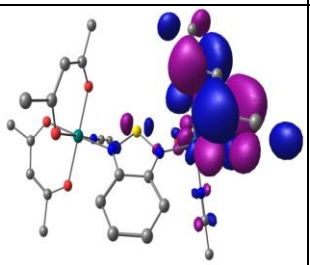
HOMO-3



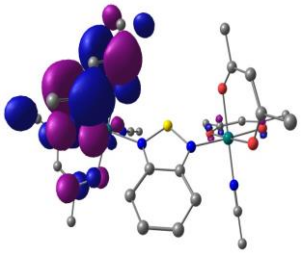
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S9 Composition and energies of selected molecular orbitals of $\mathbf{1}^{-}$ (S=1/2)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	3.151	6	77	9	8
LUMO+4	3.123	38	10	11	41
LUMO+3	2.321	0	95	2	3
LUMO+2	2.240	4	44	44	8
LUMO+1	2.210	0	98	1	1
LUMO	2.109	15	54	19	12
SOMO	0.479	5	23	71	1
HOMO-1	-1.303	30	55	14	1
HOMO-2	-1.709	10	86	3	2
HOMO-3	-1.751	35	53	10	2
HOMO-4	-1.794	67	20	9	4
HOMO-5	-1.924	12	82	6	0
		β-spin			
LUMO+5	3.128	36	15	10	39
LUMO+4	2.326	1	90	6	3
LUMO+3	2.294	5	49	44	3
LUMO+2	2.240	4	51	39	6
LUMO+1	2.191	2	78	18	2
LUMO	2.098	13	53	22	11
HOMO	-1.045	27	51	21	1
HOMO-1	-1.645	37	52	10	2
HOMO-2	-1.706	6	91	2	1
HOMO-3	-1.778	71	15	9	5
HOMO-4	-1.890	8	87	4	1
HOMO-5	-1.976	71	16	9	4

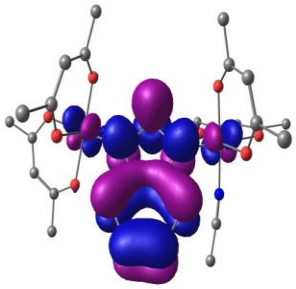
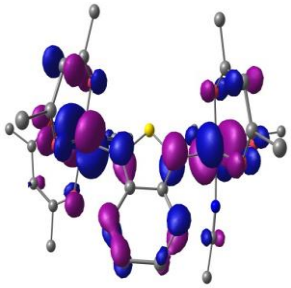
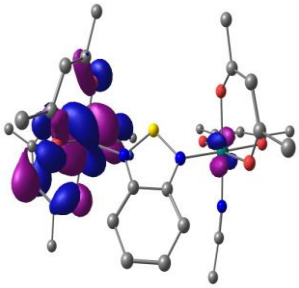
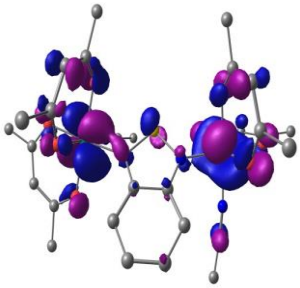
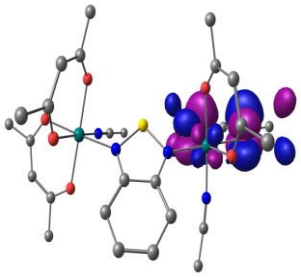
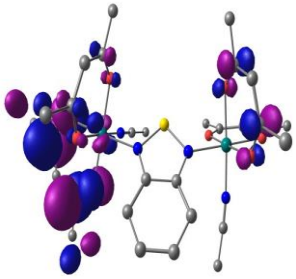
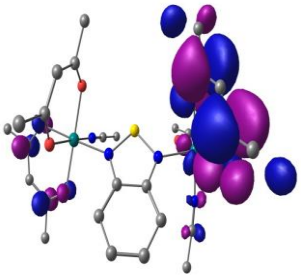
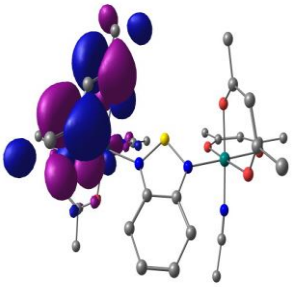
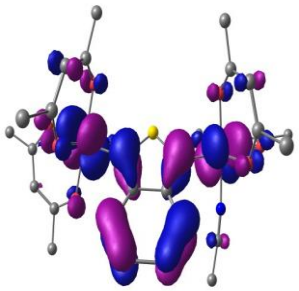
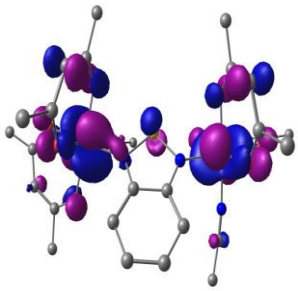
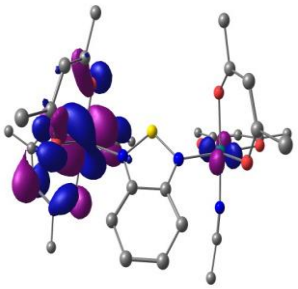
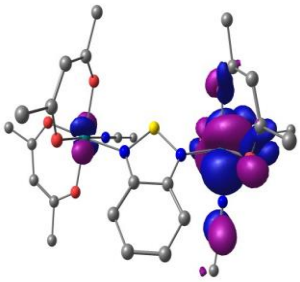
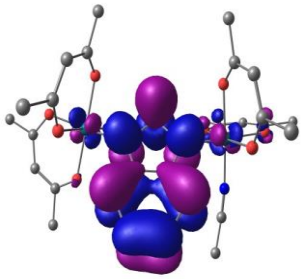
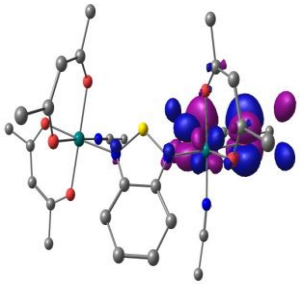
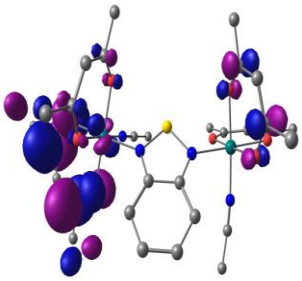
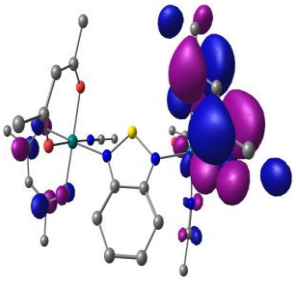
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 Composition and energies of selected molecular orbitals of $\mathbf{2}^{2+}$ (*S*=1)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	-6.053	32	51	15	2
LUMO+4	-6.087	5	86	8	0
LUMO+3	-6.285	44	28	28	0
LUMO+2	-6.379	47	39	13	0
LUMO+1	-7.444	3	1	96	0
LUMO	-8.115	6	2	92	0
SOMO 1	-10.937	22	69	8	1
SOMO 2	-11.064	25	65	8	1
HOMO-2	-11.111	21	62	17	0
HOMO-3	-11.215	21	48	32	0
HOMO-4	-11.320	23	57	21	0
HOMO-5	-11.553	34	37	27	2
		β-spin			
LUMO+5	-6.083	12	77	11	0
LUMO+4	-6.172	30	63	8	0
LUMO+3	-7.431	4	1	95	0
LUMO+2	-7.936	18	5	77	1
LUMO+1	-8.965	65	28	7	0
LUMO	-9.001	53	25	19	3
HOMO	-10.797	27	67	5	1
HOMO-1	-10.972	36	34	30	0
HOMO-2	-11.042	31	53	16	0
HOMO-3	-11.218	41	55	2	3
HOMO-4	-11.319	38	42	18	1
HOMO-5	-11.463	63	26	8	3

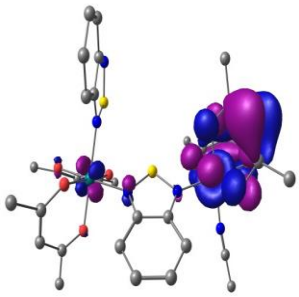
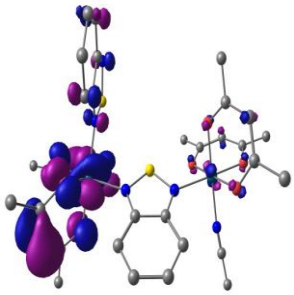
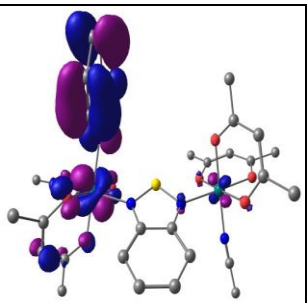
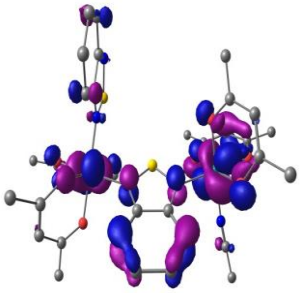
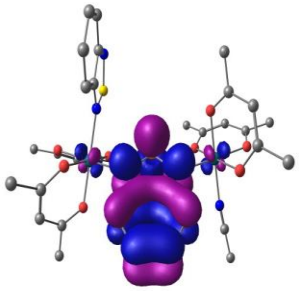
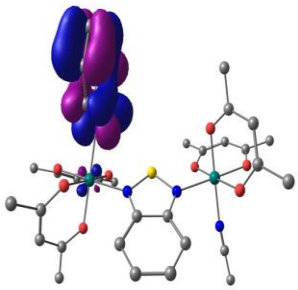
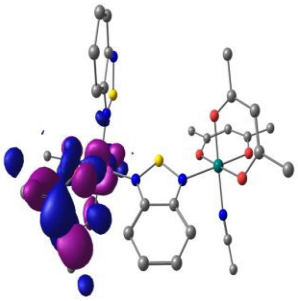
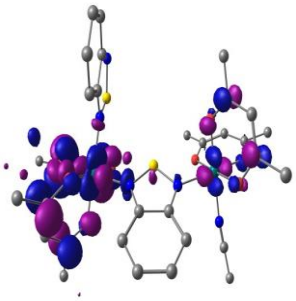
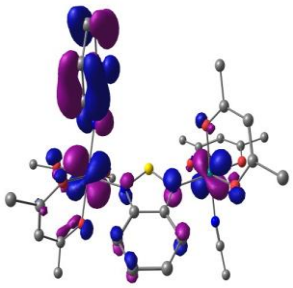
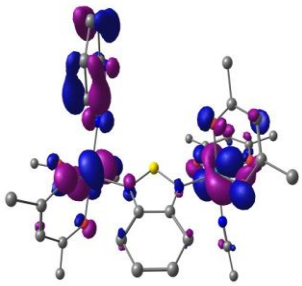
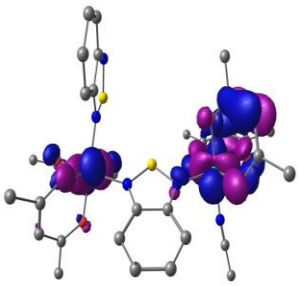
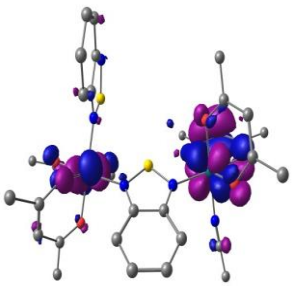
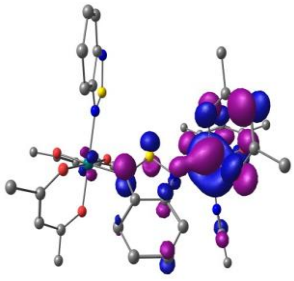
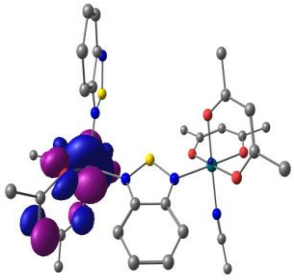
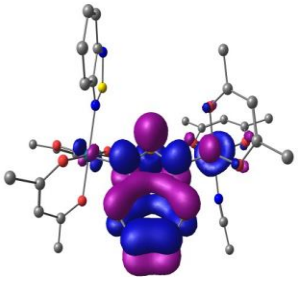
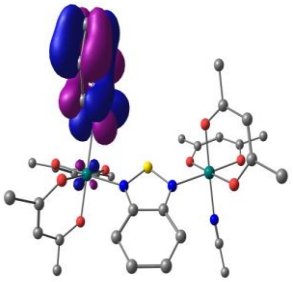
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Composition and energies of selected molecular orbitals of $\mathbf{2}^{+}$ (*S*=1/2)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	-3.148	10	83	7	0
LUMO+4	-3.191	3	93	3	0
LUMO+3	-3.326	9	82	9	0
LUMO+2	-3.373	4	88	7	1
LUMO+1	-4.808	5	1	94	0
LUMO	-5.129	6	2	92	0
SOMO	-7.696	42	53	5	0
HOMO-1	-8.049	52	33	16	0
HOMO-2	-8.111	35	57	7	1
HOMO-3	-8.268	43	43	13	1
HOMO-4	-8.413	25	65	9	1
HOMO-5	-8.627	41	44	14	1
		β-spin			
LUMO+5	-3.176	2	94	4	0
LUMO+4	-3.296	5	87	8	0
LUMO+3	-3.353	3	89	7	1
LUMO+2	-4.749	10	3	88	0
LUMO+1	-5.041	17	4	77	1
LUMO	-6.292	69	17	12	2
HOMO	-7.487	51	23	26	1
HOMO-1	-7.604	47	45	8	0
HOMO-2	-7.914	59	25	16	0
HOMO-3	-8.125	47	48	3	2
HOMO-4	-8.434	16	77	7	0
HOMO-5	-8.523	72	19	6	4

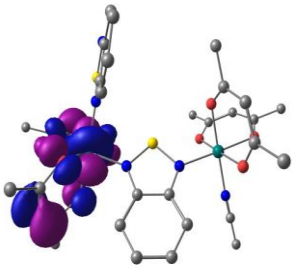
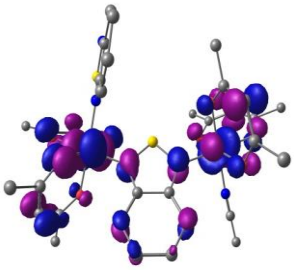
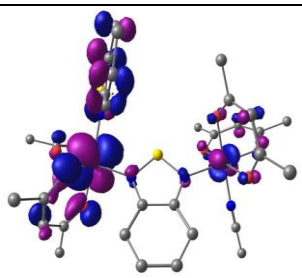
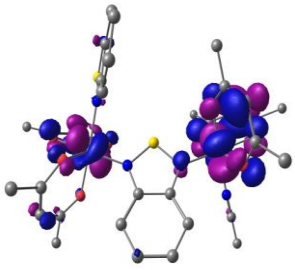
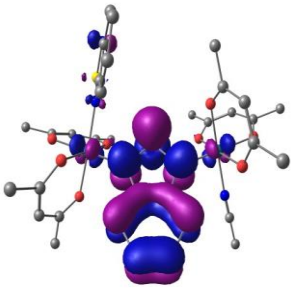
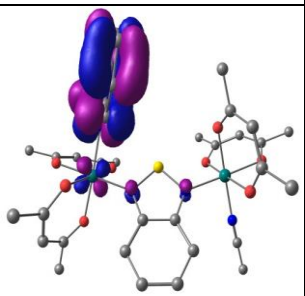
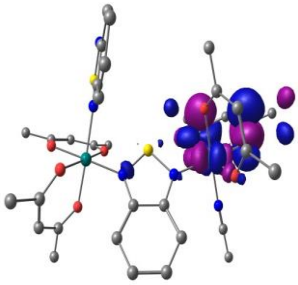
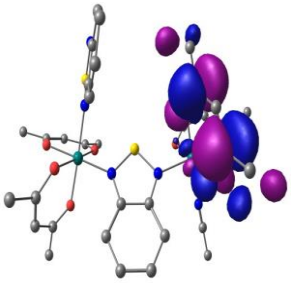
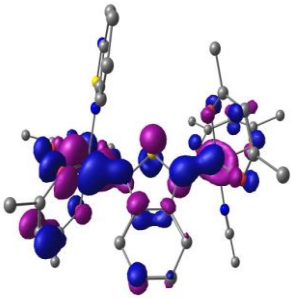
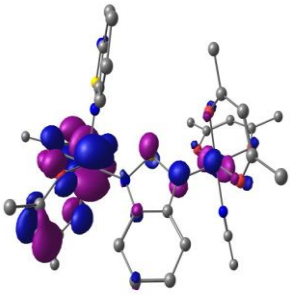
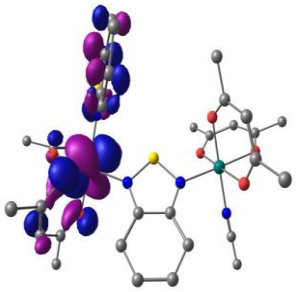
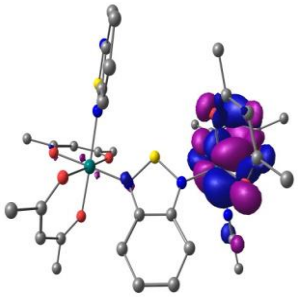
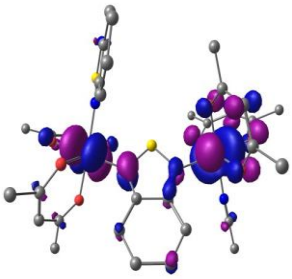
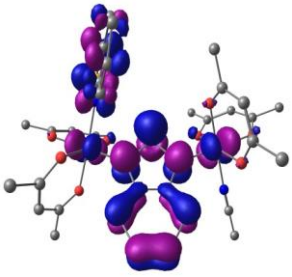
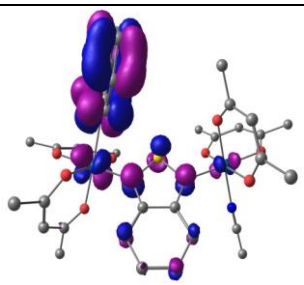
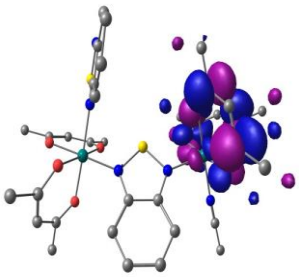
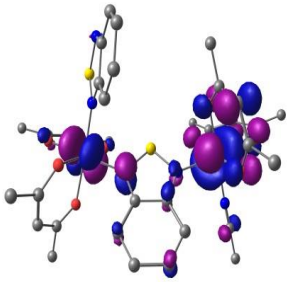
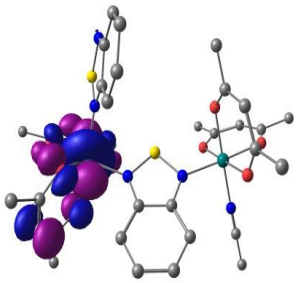
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Composition and energies of selected molecular orbitals of **2** (*S*=0)

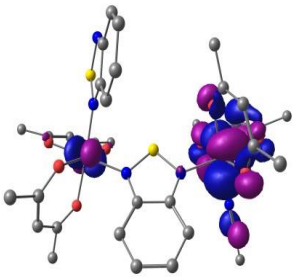
MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
LUMO+5	-0.432	2	94	2	1
LUMO+4	-0.497	4	87	8	0
LUMO+3	-0.606	3	93	4	0
LUMO+2	-1.171	52	18	30	0
LUMO+1	-2.134	13	3	83	1
LUMO	-2.243	4	1	95	0
HOMO	-4.364	66	24	9	2
HOMO-1	-4.715	63	30	4	3
HOMO-2	-4.797	70	26	3	1
HOMO-3	-4.854	71	21	8	0
HOMO-4	-5.059	74	16	5	5
HOMO-5	-5.096	73	19	8	0



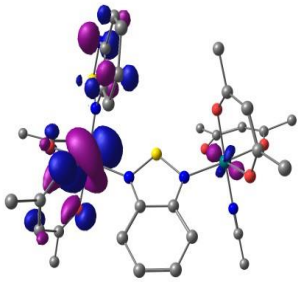
HOMO



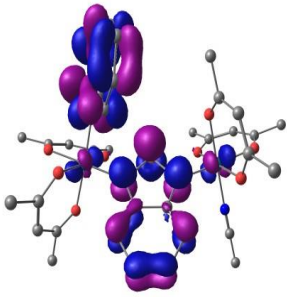
HOMO-1



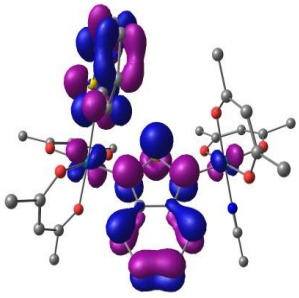
HOMO-2



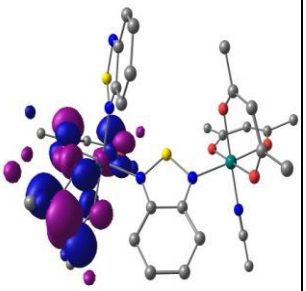
HOMO-3



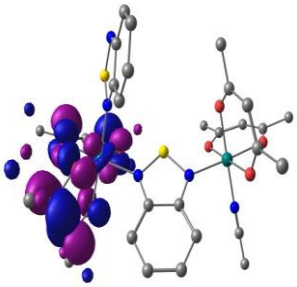
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S13 Composition and energies of selected molecular orbitals of $\mathbf{2}^{-}$ (*S*=1/2)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	2.859	24	3	3	69
LUMO+4	2.029	8	88	4	0
LUMO+3	1.998	4	89	4	3
LUMO+2	1.914	2	95	3	0
LUMO+1	1.879	3	95	1	1
LUMO	0.715	11	5	84	0
SOMO	-0.053	7	2	90	0
HOMO-1	-1.693	67	15	17	1
HOMO-2	-1.793	69	26	5	0
HOMO-3	-1.997	71	15	14	0
HOMO-4	-2.133	68	23	5	5
HOMO-5	-2.232	72	19	9	1
		β-spin			
LUMO+5	2.014	7	88	5	0
LUMO+4	1.999	4	89	4	3
LUMO+3	1.915	2	95	3	0
LUMO+2	1.886	3	93	2	1
LUMO+1	1.343	7	6	86	1
LUMO	1.161	4	2	94	0
HOMO	-1.635	65	15	18	2
HOMO-1	-1.811	69	26	5	0
HOMO-2	-1.950	71	14	15	0
HOMO-3	-2.116	67	23	6	4
HOMO-4	-2.201	74	18	6	2
HOMO-5	-2.387	75	14	6	5

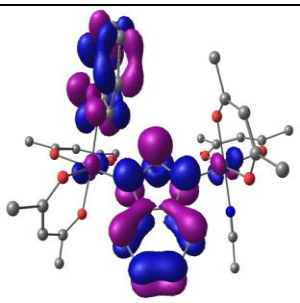
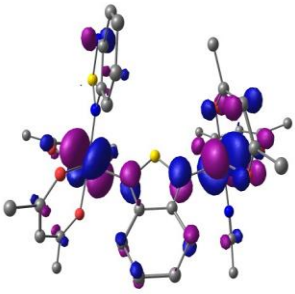
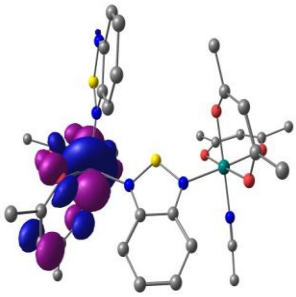
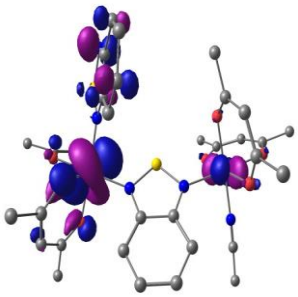
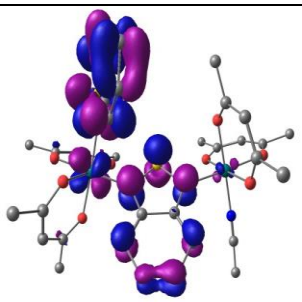
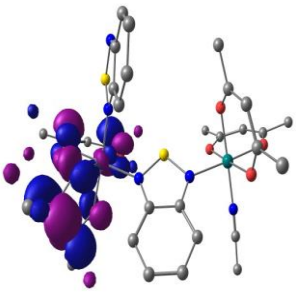
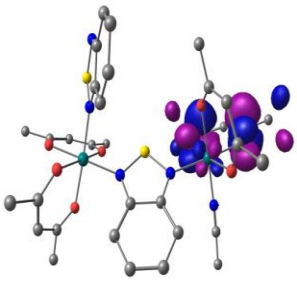
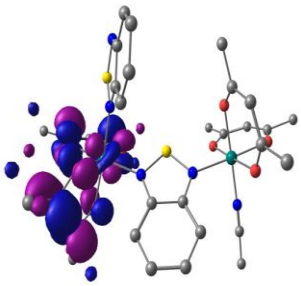
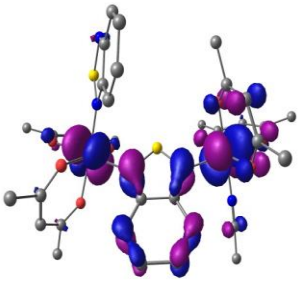
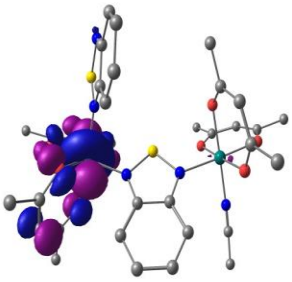
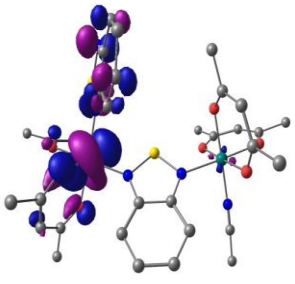
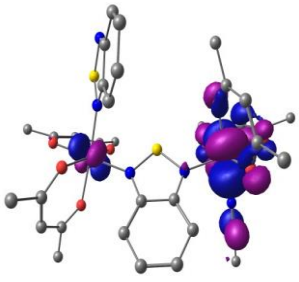
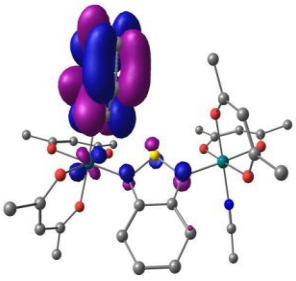
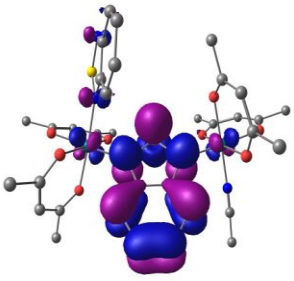
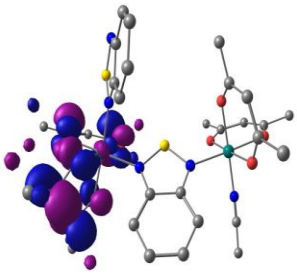
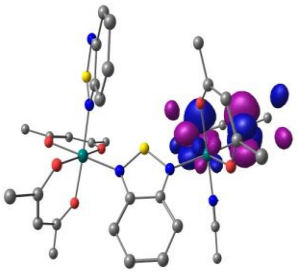
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Composition and energies of selected molecular orbitals of $\mathbf{2}^{2-}$ (*S*=1)

MO	Energy (eV)	% Composition			
		Ru	acac	BTD	CH_3CN
		α-spin			
LUMO+5	4.966	6	2	0	92
LUMO+4	4.854	34	5	3	58
LUMO+3	4.707	10	85	4	1
LUMO+2	4.557	3	94	3	0
LUMO+1	4.246	4	87	3	5
LUMO	3.968	4	93	1	1
SOMO 1	3.099	6	5	89	0
SOMO 2	2.724	9	4	86	1
HOMO-2	1.237	73	21	5	0
HOMO-3	1.085	66	12	21	1
HOMO-4	1.062	74	15	12	0
HOMO-5	0.337	64	21	12	3
		β-spin			
LUMO+5	4.861	34	5	3	59
LUMO+4	4.710	5	73	21	0
LUMO+3	4.591	4	92	4	0
LUMO+2	4.465	9	16	67	8
LUMO+1	4.247	4	88	3	4
LUMO	3.978	3	94	3	1
HOMO	1.417	59	11	30	0
HOMO-1	1.268	73	19	8	0
HOMO-2	1.205	72	16	12	0
HOMO-3	0.512	60	16	21	3
HOMO-4	0.200	34	9	56	0
HOMO-5	0.149	73	19	2	6

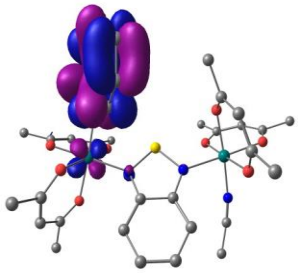
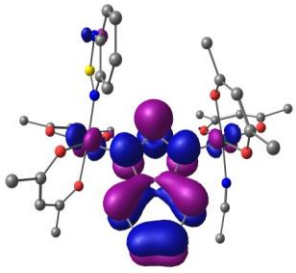
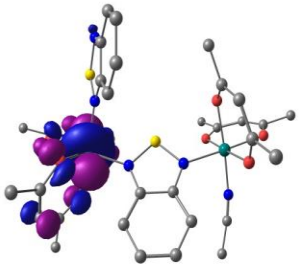
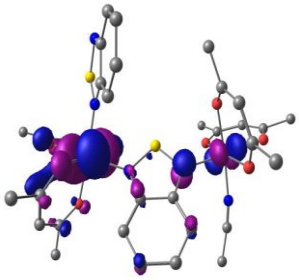
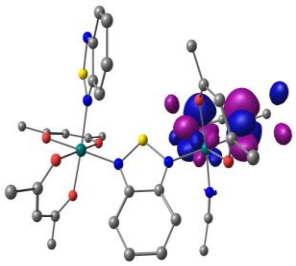
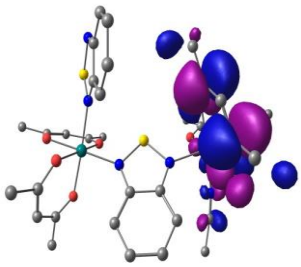
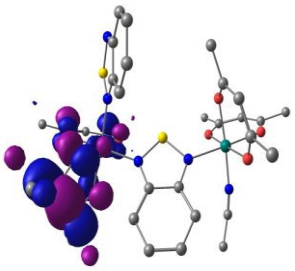
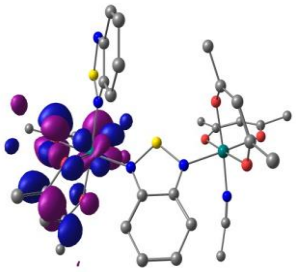
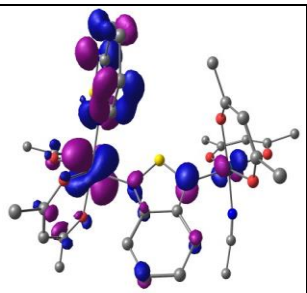
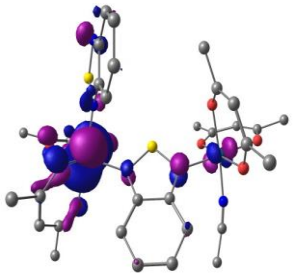
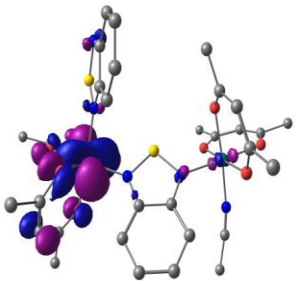
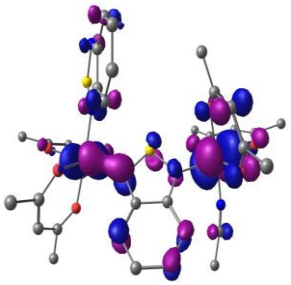
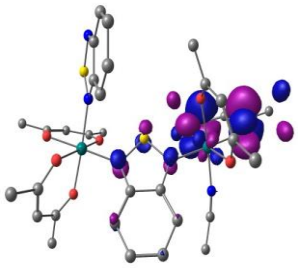
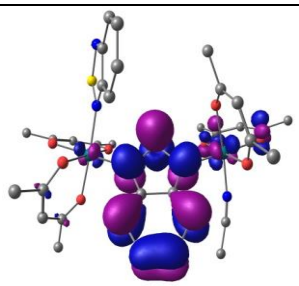
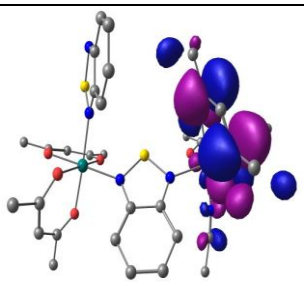
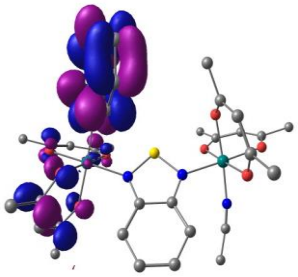
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 Composition and energies of selected molecular orbitals of $\mathbf{3}^{2+}$ (*S*=1)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
	α-spin			
LUMO+5	-6.095	26	64	10
LUMO+4	-6.141	8	59	33
LUMO+3	-6.197	44	22	34
LUMO+2	-7.544	3	1	96
LUMO+1	-7.555	3	1	96
LUMO	-8.196	7	2	91
SOMO 1	-10.899	28	59	13
SOMO 2	-11.017	17	73	10
HOMO-2	-11.096	24	68	7
HOMO-3	-11.135	18	76	5
HOMO-4	-11.433	18	22	60
HOMO-5	-11.449	14	20	66
	β-spin			
LUMO+5	-6.113	3	57	40
LUMO+4	-7.336	14	3	83
LUMO+3	-7.376	10	3	87
LUMO+2	-7.960	15	3	81
LUMO+1	-8.816	60	21	18
LUMO	-9.214	45	22	32
HOMO	-10.828	35	57	7
HOMO-1	-10.907	22	72	5
HOMO-2	-11.180	31	49	21
HOMO-3	-11.184	21	57	22
HOMO-4	-11.325	21	63	17
HOMO-5	-11.359	59	23	18

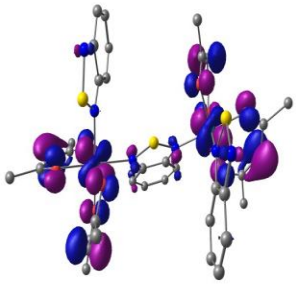
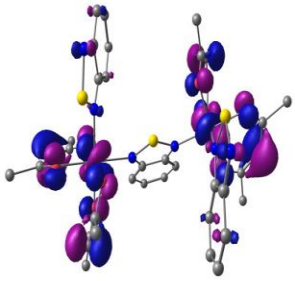
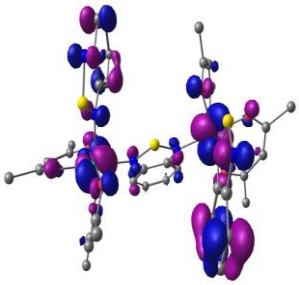
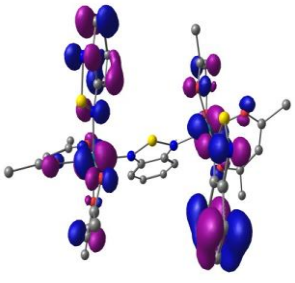
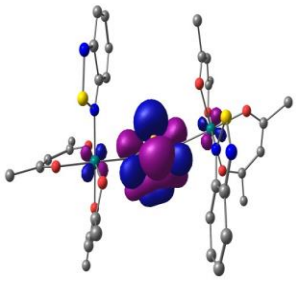
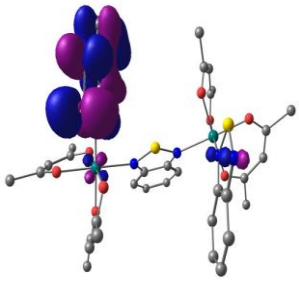
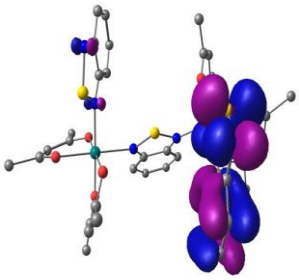
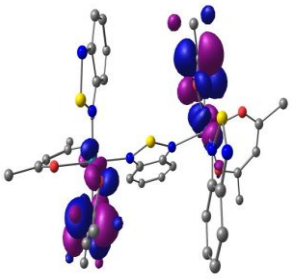
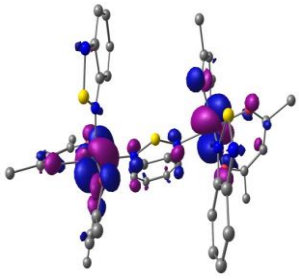
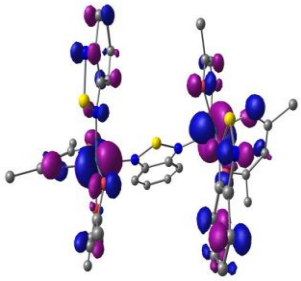
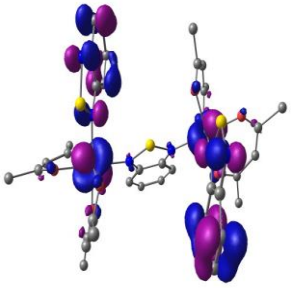
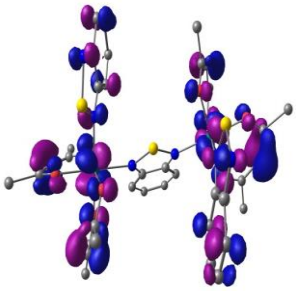
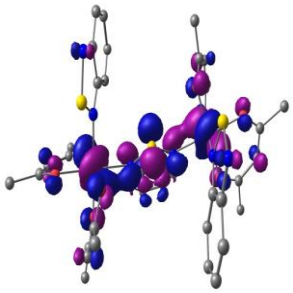
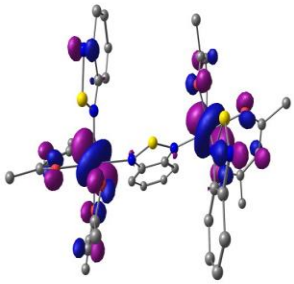
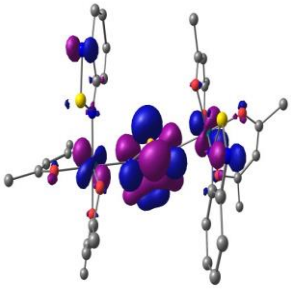
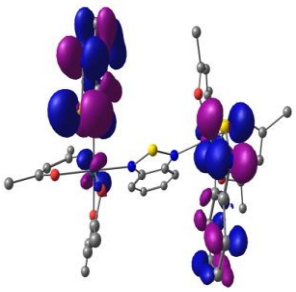
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 Composition and energies of selected molecular orbitals of $\mathbf{3}^{+}$ (S=1/2)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
	α-spin			
LUMO+5	-3.330	6	85	9
LUMO+4	-3.373	3	93	4
LUMO+3	-3.422	3	80	17
LUMO+2	-4.929	5	1	93
LUMO+1	-4.947	4	1	95
LUMO	-5.169	6	1	93
SOMO	-7.984	39	47	14
HOMO-1	-8.060	41	48	11
HOMO-2	-8.236	48	41	11
HOMO-3	-8.372	29	66	5
HOMO-4	-8.640	71	19	11
HOMO-5	-8.646	52	36	12
	β-spin			
LUMO+5	-3.357	3	93	4
LUMO+4	-3.413	3	78	19
LUMO+3	-4.773	18	4	78
LUMO+2	-4.875	9	2	89
LUMO+1	-5.157	12	3	85
LUMO	-6.243	64	18	18
HOMO	-7.423	42	25	33
HOMO-1	-8.019	54	36	10
HOMO-2	-8.046	54	36	10
HOMO-3	-8.436	73	18	9
HOMO-4	-8.468	71	18	10
HOMO-5	-8.549	16	72	11

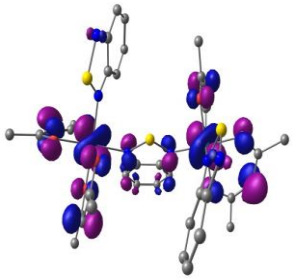
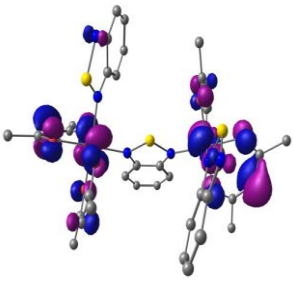
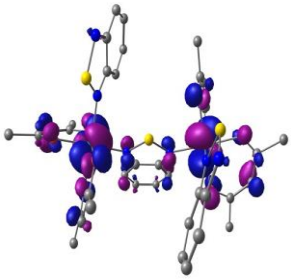
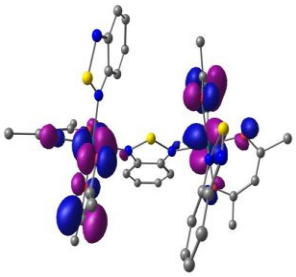
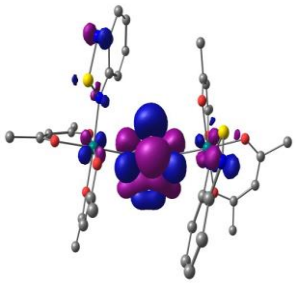
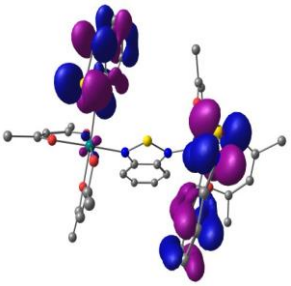
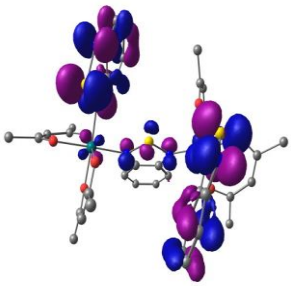
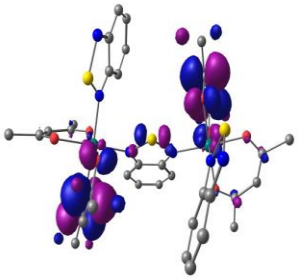
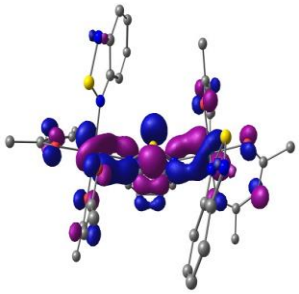
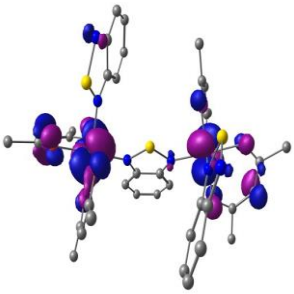
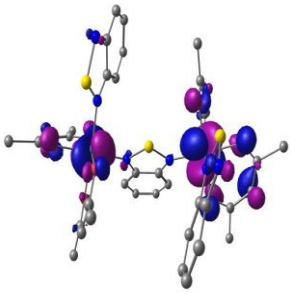
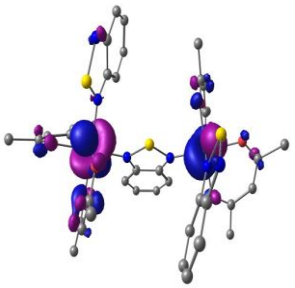
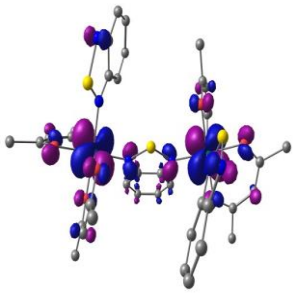
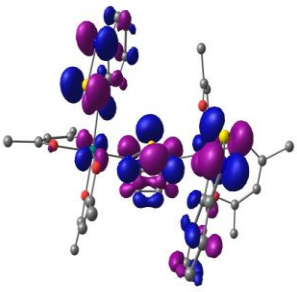
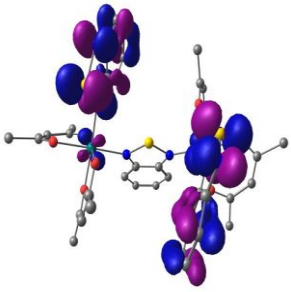
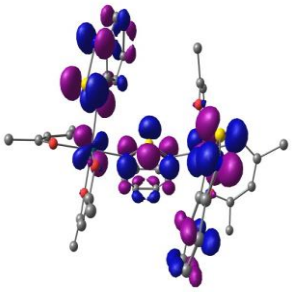
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 Composition and energies of selected molecular orbitals of **3** (*S*=0)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
LUMO+5	-0.887	11	72	17
LUMO+4	-1.033	19	65	16
LUMO+3	-1.235	44	40	16
LUMO+2	-1.809	3	9	88
LUMO+1	-2.432	4	3	94
LUMO	-2.569	3	4	93
HOMO	-4.588	65	21	14
HOMO-1	-4.600	66	18	15
HOMO-2	-4.712	72	17	11
HOMO-3	-4.935	72	21	6
HOMO-4	-5.075	73	21	6
HOMO-5	-5.443	75	16	10

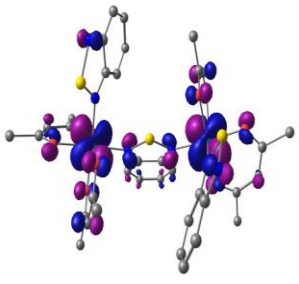
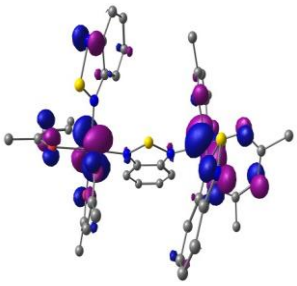
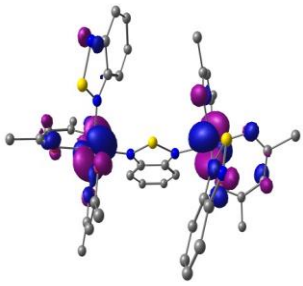
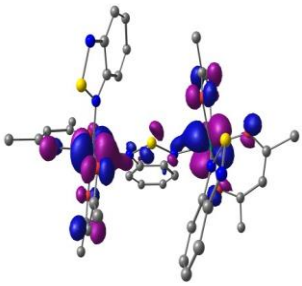
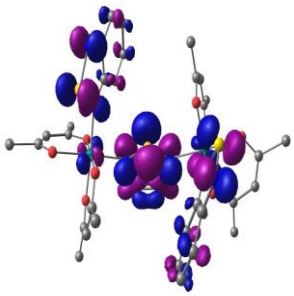
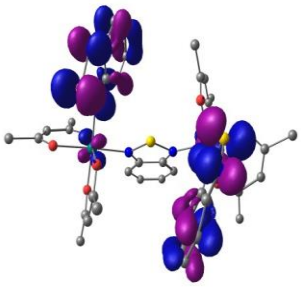
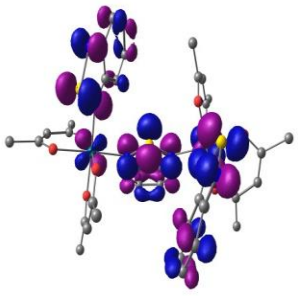
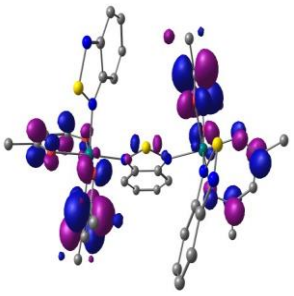
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18 Composition and energies of selected molecular orbitals of $\mathbf{3}^{-}$ (*S*=1/2)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
	α-spin			
LUMO+5	1.776	5	91	4
LUMO+4	1.749	5	86	9
LUMO+3	1.624	3	93	4
LUMO+2	1.622	3	93	4
LUMO+1	0.483	17	4	79
LUMO	0.251	11	3	86
SOMO	-0.391	6	2	93
HOMO-1	-1.805	62	16	22
HOMO-2	-2.191	60	20	21
HOMO-3	-2.353	72	18	11
HOMO-4	-2.448	72	19	8
HOMO-5	-2.607	73	16	11
	β-spin			
LUMO+5	1.750	5	86	9
LUMO+4	1.626	3	92	4
LUMO+3	1.625	3	93	4
LUMO+2	0.954	10	3	86
LUMO+1	0.650	6	2	92
LUMO	0.623	5	2	94
HOMO	-1.871	64	16	20
HOMO-1	-2.243	64	20	15
HOMO-2	-2.320	70	18	12
HOMO-3	-2.423	71	22	7
HOMO-4	-2.619	75	15	10
HOMO-5	-2.636	77	14	9

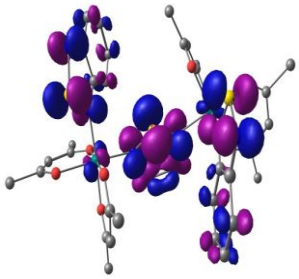
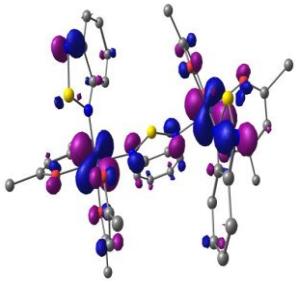
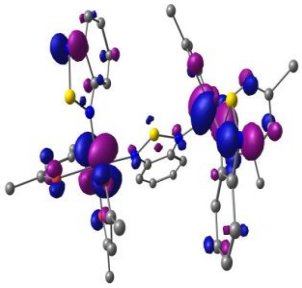
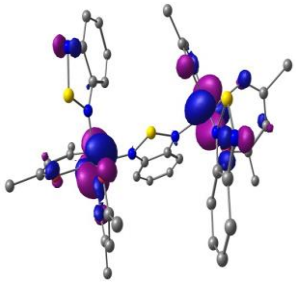
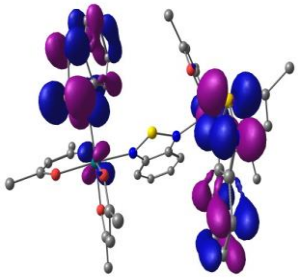
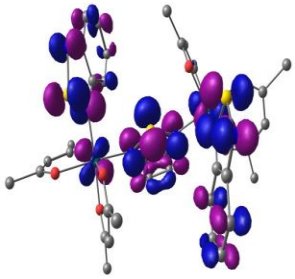
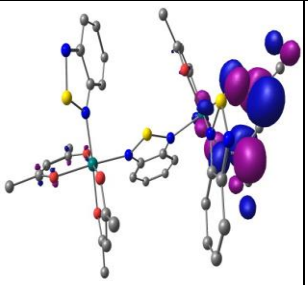
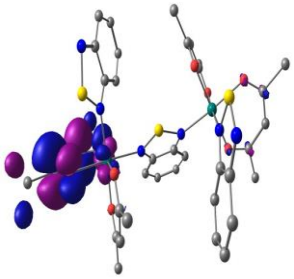
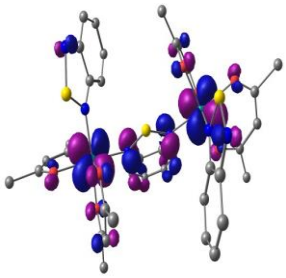
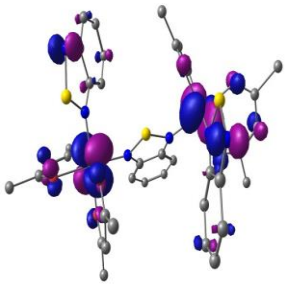
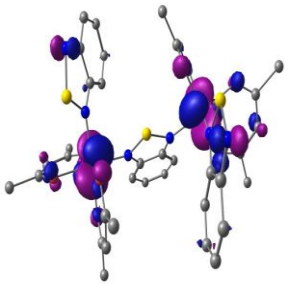
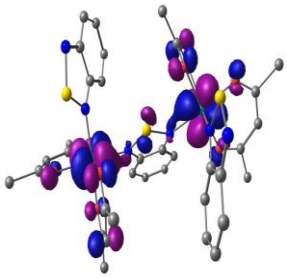
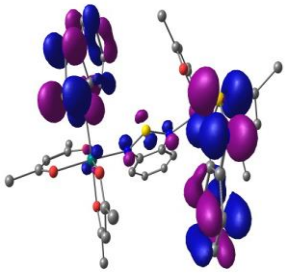
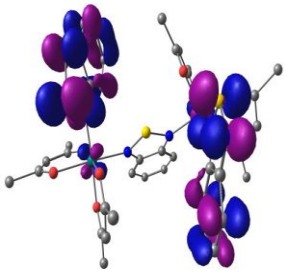
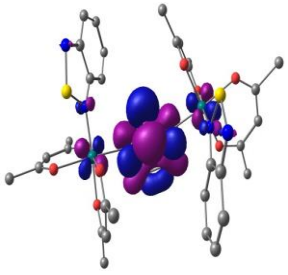
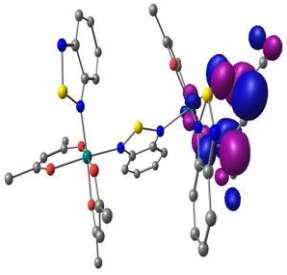
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19 Composition and energies of selected molecular orbitals of $\mathbf{3}^{2-}$ (*S*=1)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
	α-spin			
LUMO+5	5.195	67	28	5
LUMO+4	4.157	5	92	3
LUMO+3	4.129	7	86	7
LUMO+2	3.915	4	92	4
LUMO+1	3.909	4	92	4
LUMO	2.960	15	4	81
SOMO 1	2.387	9	3	88
SOMO 2	2.153	6	2	92
HOMO-2	0.732	66	15	19
HOMO-3	0.367	64	17	19
HOMO-4	0.254	73	16	11
HOMO-5	0.134	75	14	8
	β-spin			
LUMO+5	4.139	7	86	7
LUMO+4	3.929	5	83	12
LUMO+3	3.917	4	91	5
LUMO+2	3.842	6	15	79
LUMO+1	3.821	5	9	87
LUMO	3.444	8	5	87
HOMO	0.810	66	14	20
HOMO-1	0.500	64	15	20
HOMO-2	0.369	71	15	14
HOMO-3	0.181	73	19	8
HOMO-4	0.049	75	15	10
HOMO-5	0.023	76	14	9

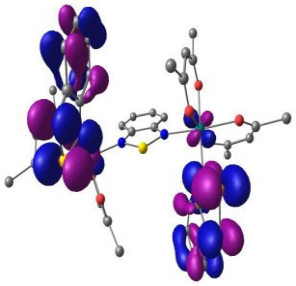
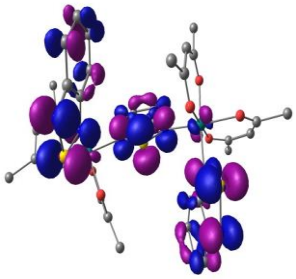
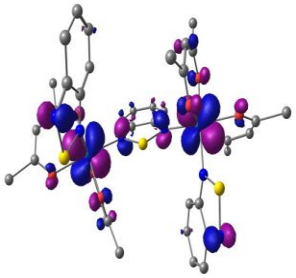
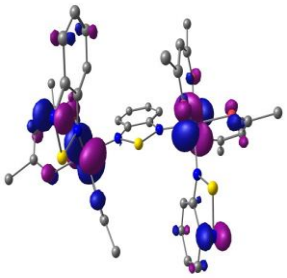
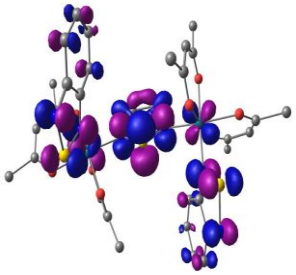
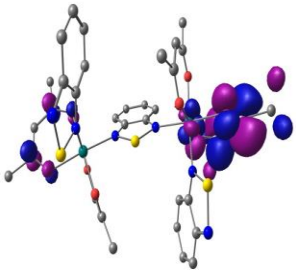
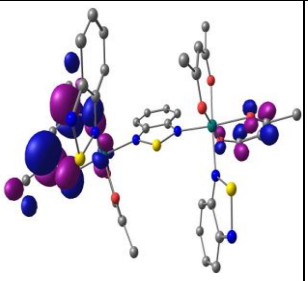
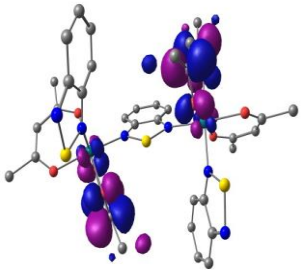
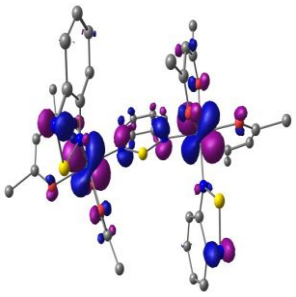
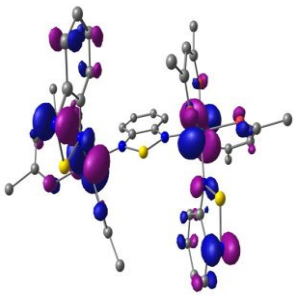
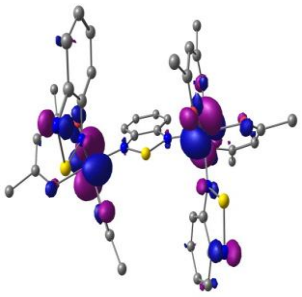
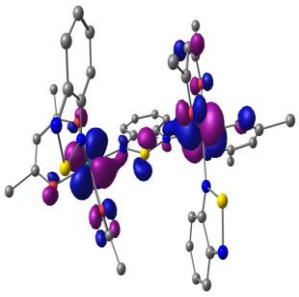
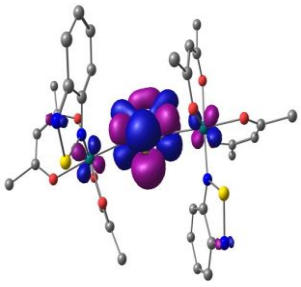
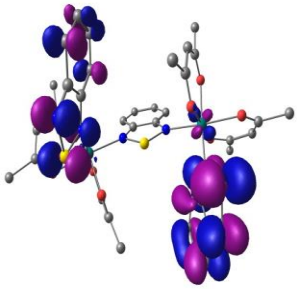
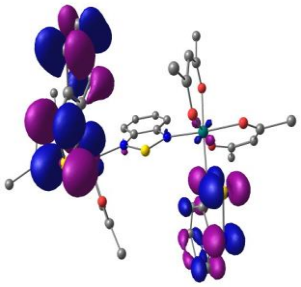
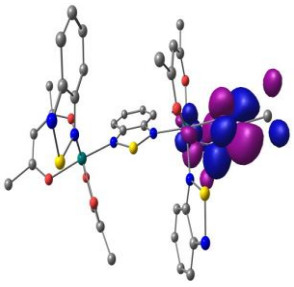
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 Composition and energies of selected molecular orbitals of $\mathbf{4}^{3+}$ (*S*=3/2)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
		α-spin		
LUMO+5	-7.838	32	42	27
LUMO+4	-7.909	42	21	38
LUMO+3	-9.050	3	1	96
LUMO+2	-9.197	3	1	96
LUMO+1	-9.769	8	2	90
LUMO	-9.851	6	2	92
SOMO	-12.328	22	70	8
HOMO-1	-12.497	24	64	12
HOMO-2	-12.513	17	76	6
HOMO-3	-12.641	22	70	8
HOMO-4	-12.710	17	77	6
HOMO-5	-12.800	21	73	7
		β-spin		
LUMO+5	-8.979	13	3	83
LUMO+4	-9.406	23	5	72
LUMO+3	-9.686	14	4	82
LUMO+2	-10.366	60	22	18
LUMO+1	-10.585	49	22	30
LUMO	-10.975	44	24	31
HOMO	-12.218	25	69	6
HOMO-1	-12.410	26	67	6
HOMO-2	-12.536	26	68	6
HOMO-3	-12.567	24	64	11
HOMO-4	-12.676	32	50	18
HOMO-5	-12.796	42	44	15

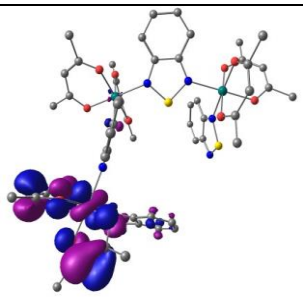
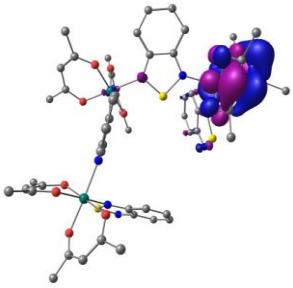
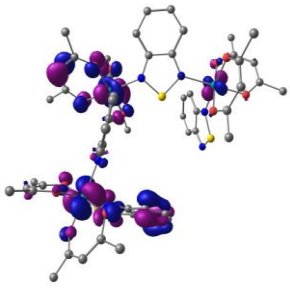
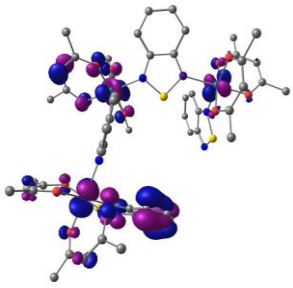
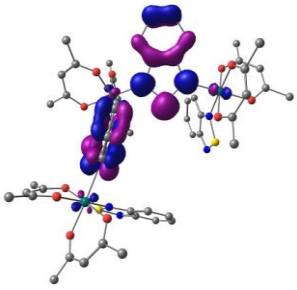
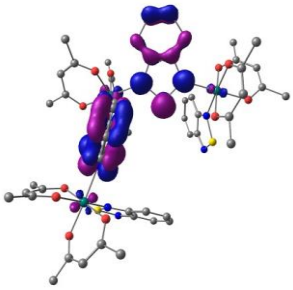
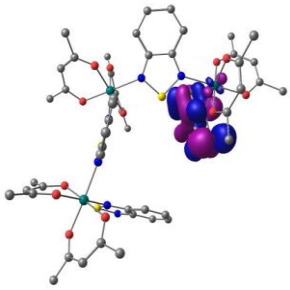
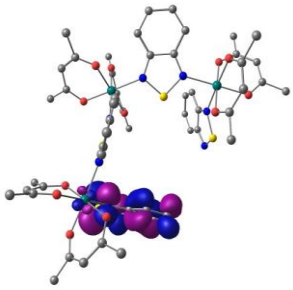
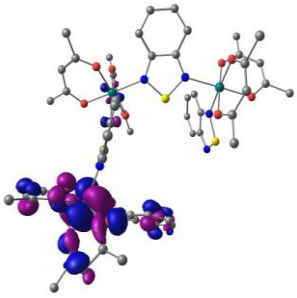
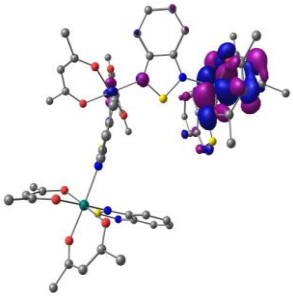
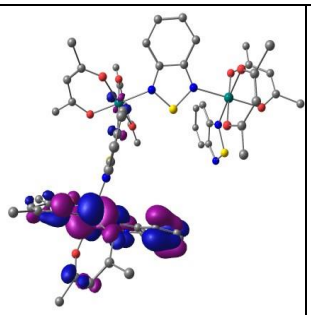
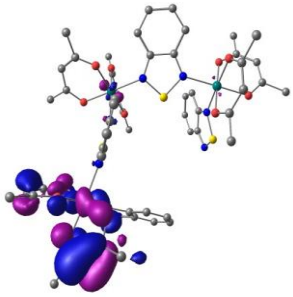
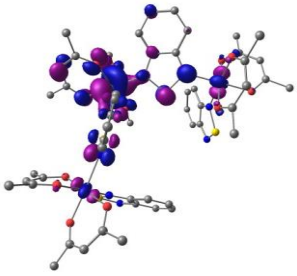
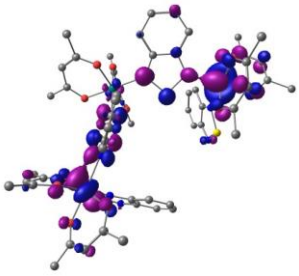
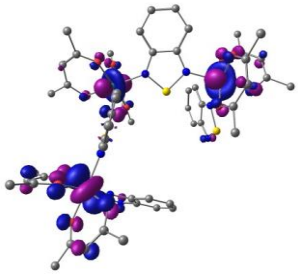
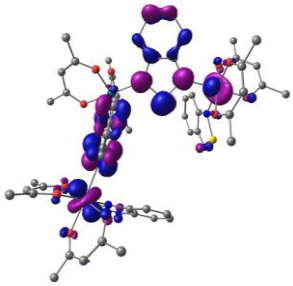
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 Composition and energies of selected molecular orbitals of $\mathbf{4}^{2+}$ (*S*=1)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
		α-spin		
LUMO+5	-5.329	33	41	25
LUMO+4	-5.461	4	82	14
LUMO+3	-6.897	3	1	96
LUMO+2	-6.993	4	1	95
LUMO+1	-7.136	9	2	89
LUMO	-7.271	6	2	92
SOMO 1	-9.758	36	51	12
SOMO 2	-9.965	43	48	9
HOMO-2	-10.196	24	66	10
HOMO-3	-10.198	24	66	10
HOMO-4	-10.323	31	61	8
HOMO-5	-10.369	56	33	11
		β-spin		
LUMO+5	-6.725	16	3	81
LUMO+4	-6.779	19	4	77
LUMO+3	-6.995	15	3	82
LUMO+2	-7.209	12	3	85
LUMO+1	-8.120	63	19	19
LUMO	-8.386	53	19	28
HOMO	-9.393	39	31	30
HOMO-1	-9.766	51	38	11
HOMO-2	-10.101	38	54	7
HOMO-3	-10.138	44	48	8
HOMO-4	-10.255	66	27	7
HOMO-5	-10.337	27	64	9

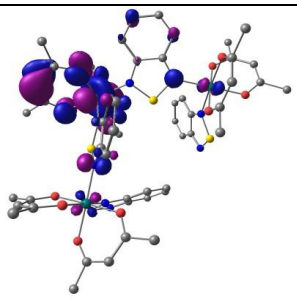
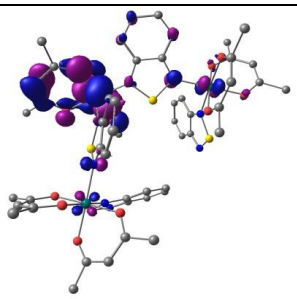
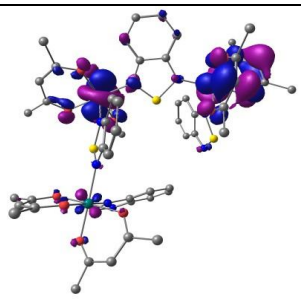
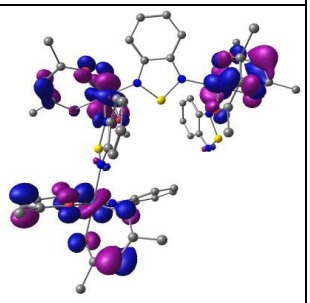
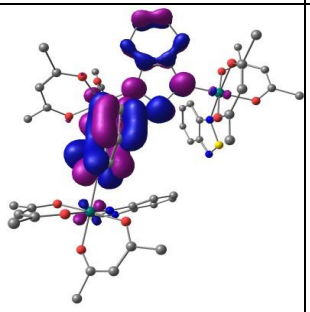
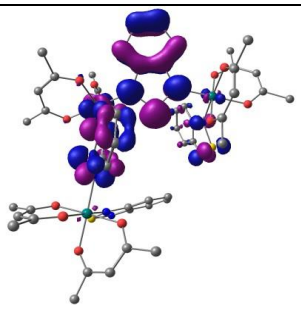
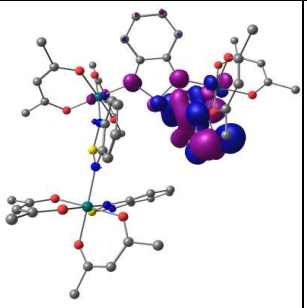
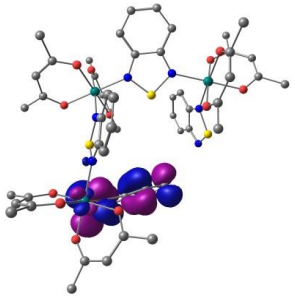
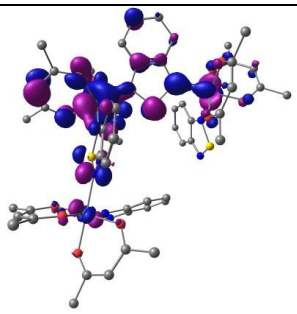
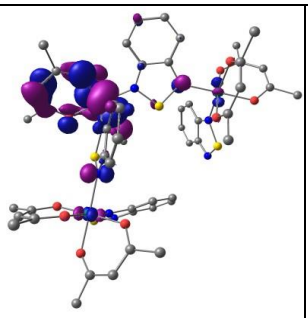
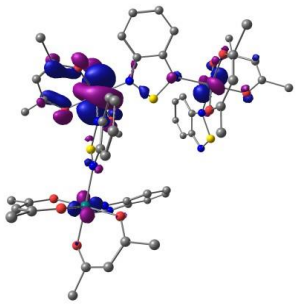
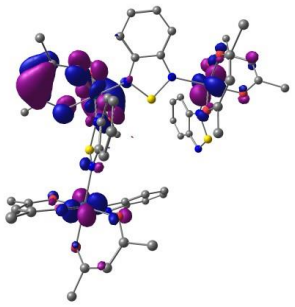
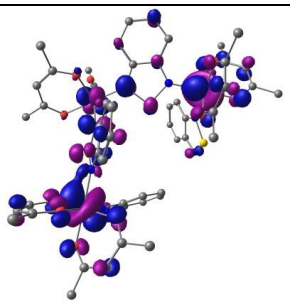
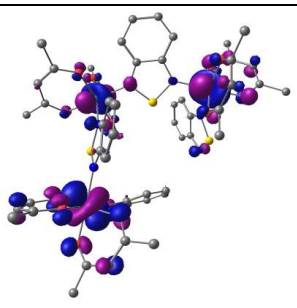
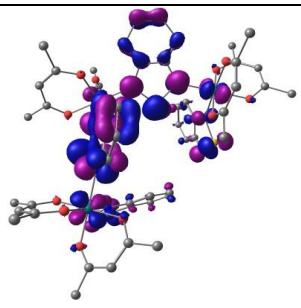
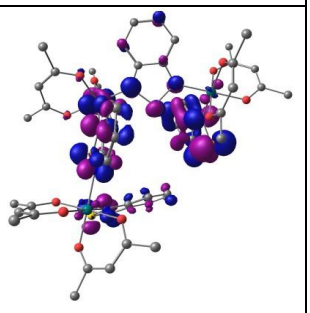
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22 Composition and energies of selected molecular orbitals of $\mathbf{4}^{+}$ (S=1/2)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
	α-spin			
LUMO+5	-3.167	3	89	9
LUMO+4	-3.207	4	84	13
LUMO+3	-4.511	7	2	91
LUMO+2	-4.528	5	1	93
LUMO+1	-4.776	9	2	89
LUMO	-4.872	7	2	91
SOMO	-7.262	49	35	16
HOMO-1	-7.503	57	31	12
HOMO-2	-7.536	49	38	13
HOMO-3	-7.739	52	37	11
HOMO-4	-7.813	73	18	9
HOMO-5	-7.974	33	58	9
	β-spin			
LUMO+5	-3.193	3	84	13
LUMO+4	-4.444	15	3	81
LUMO+3	-4.456	11	2	86
LUMO+2	-4.660	17	4	79
LUMO+1	-4.917	14	3	82
LUMO	-5.967	66	17	16
HOMO	-6.831	51	22	28
HOMO-1	-7.206	45	28	27
HOMO-2	-7.399	60	27	13
HOMO-3	-7.554	58	31	11
HOMO-4	-7.725	74	17	9
HOMO-5	-7.871	58	33	9

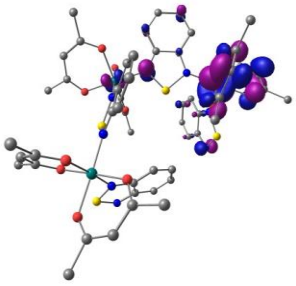
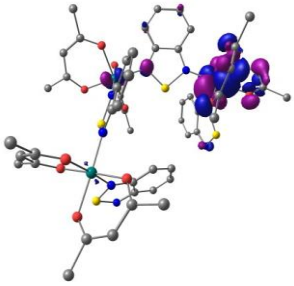
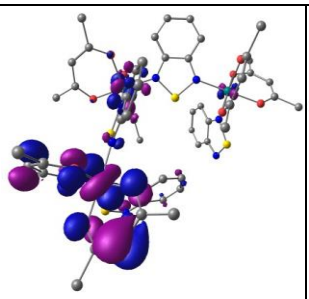
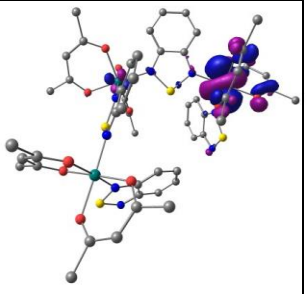
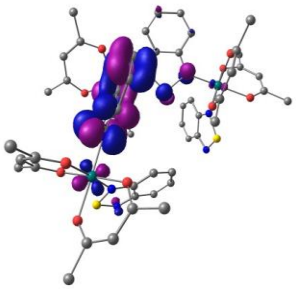
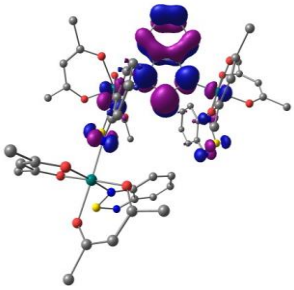
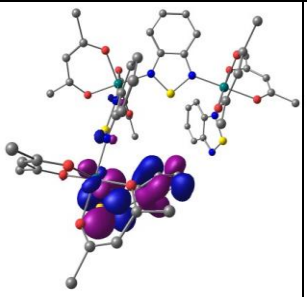
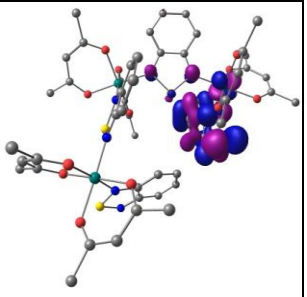
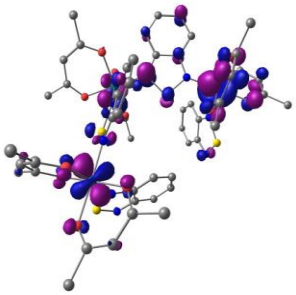
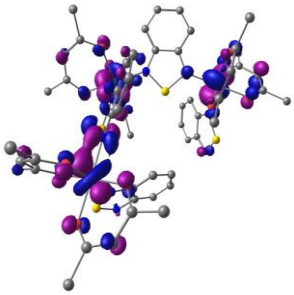
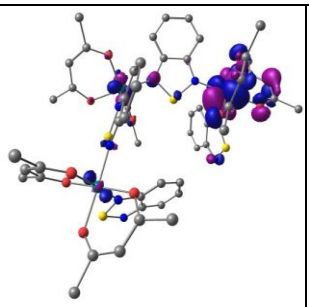
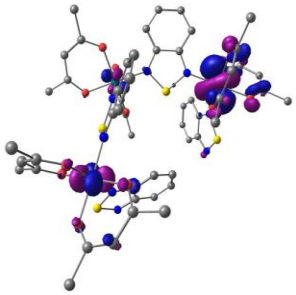
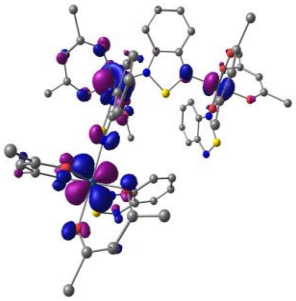
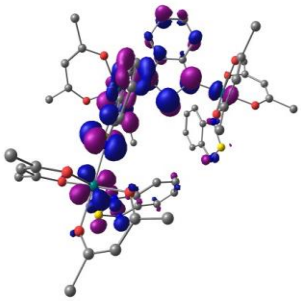
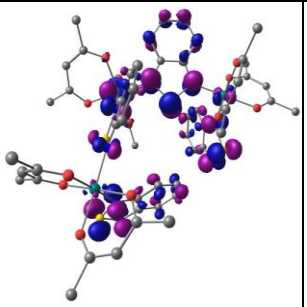
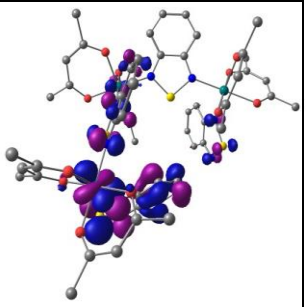
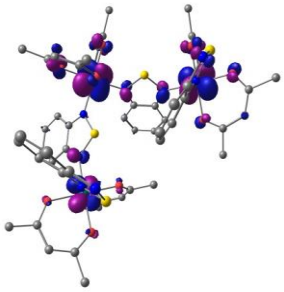
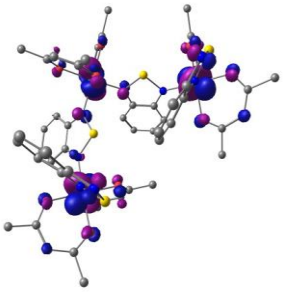
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 Composition and energies of selected molecularo of **4** (*S*=0)

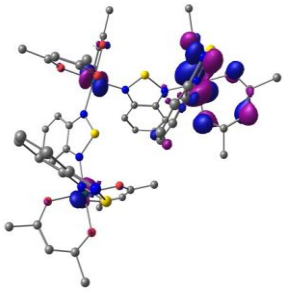
MO	Energy (eV)	% Composition		
		Ru	acac	BTD
LUMO+5	-0.733	4	86	10
LUMO+4	-0.770	3	94	4
LUMO+3	-2.097	13	3	84
LUMO+2	-2.199	12	3	85
LUMO+1	-2.305	10	3	87
LUMO	-2.444	7	2	91
HOMO	-4.452	65	20	15
HOMO-1	-4.683	64	20	16
HOMO-2	-4.912	64	22	14
HOMO-3	-4.961	64	23	13
HOMO-4	-5.087	62	26	11
HOMO-5	-5.118	64	25	11



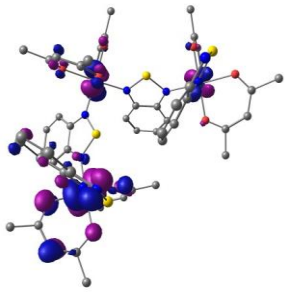
HOMO



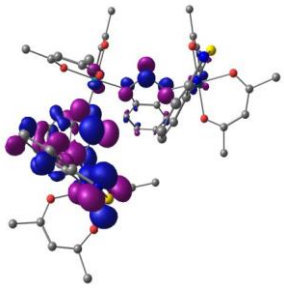
HOMO-1



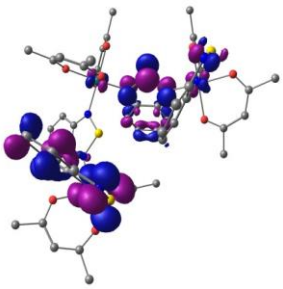
HOMO-2



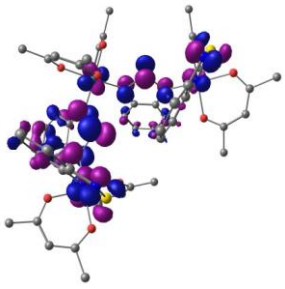
HOMO-3



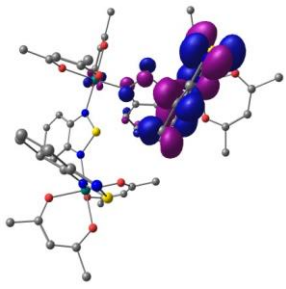
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S24 Composition and energies of selected molecular orbitals of **4**$^{-}$ (*S*=1/2)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
		α-spin		
LUMO+5	1.355	3	92	5
LUMO+4	1.353	5	87	8
LUMO+3	1.296	2	94	3
LUMO+2	0.222	18	4	78
LUMO+1	0.053	13	3	85
LUMO	-0.087	10	3	87
SOMO	-0.666	7	2	91
HOMO-1	-2.011	64	16	20
HOMO-2	-2.327	64	18	18
HOMO-3	-2.565	62	20	18
HOMO-4	-2.659	66	20	14
HOMO-5	-2.700	74	19	8
		β-spin		
LUMO+5	1.353	5	87	8
LUMO+4	1.298	2	94	3
LUMO+3	0.607	11	3	86
LUMO+2	0.417	10	3	87
LUMO+1	0.271	6	2	93
LUMO	0.096	6	2	92
HOMO	-2.103	65	16	19
HOMO-1	-2.318	67	17	16
HOMO-2	-2.579	65	20	15
HOMO-3	-2.657	66	20	14
HOMO-4	-2.688	71	22	8
HOMO-5	-2.750	73	19	8

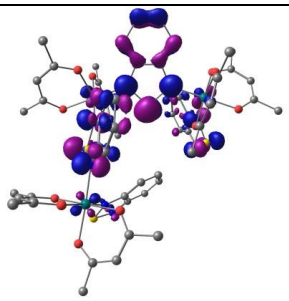
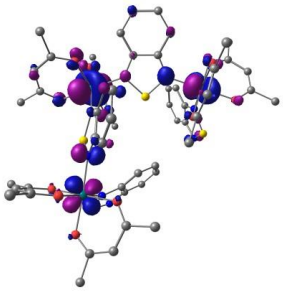
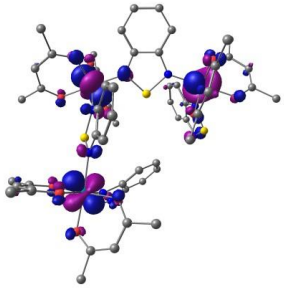
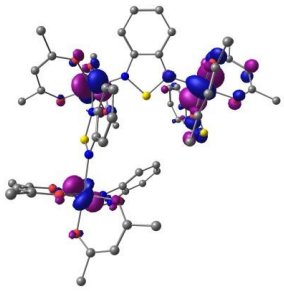
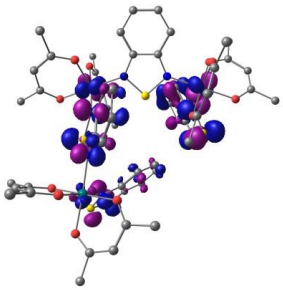
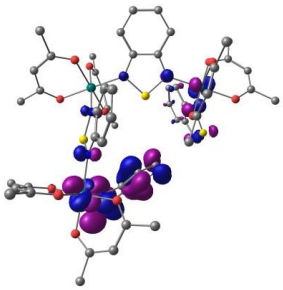
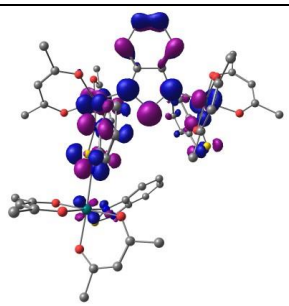
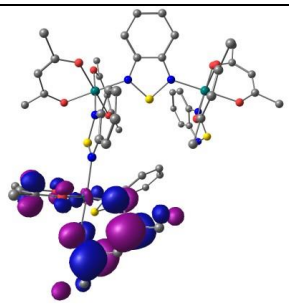
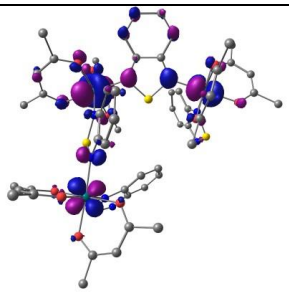
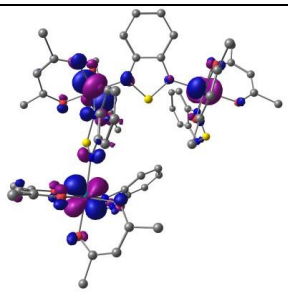
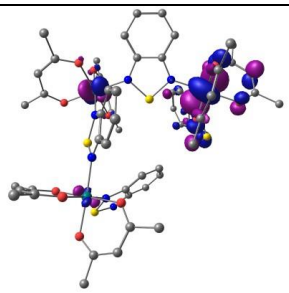
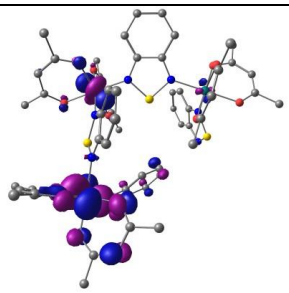
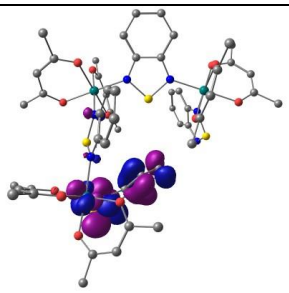
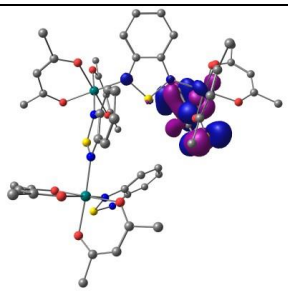
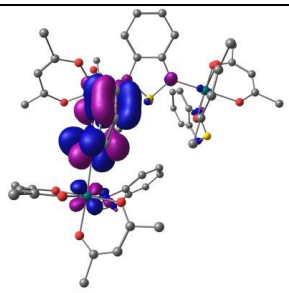
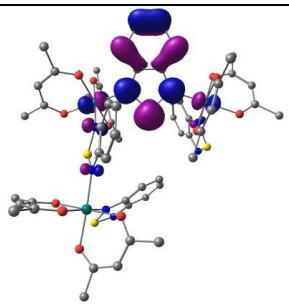
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25 Composition and energies of selected molecular orbitals of $\mathbf{4}^{2-}$ (*S*=1)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
	α-spin			
LUMO+5	3.563	4	92	4
LUMO+4	3.435	6	87	6
LUMO+3	3.393	4	92	4
LUMO+2	3.357	3	95	3
LUMO+1	2.476	16	4	81
LUMO	2.402	14	3	83
SOMO 1	1.748	10	3	87
SOMO 2	1.602	7	2	91
HOMO-2	0.251	66	15	19
HOMO-3	0.024	67	15	18
HOMO-4	-0.268	64	18	18
HOMO-5	-0.319	67	17	15
	β-spin			
LUMO+5	3.397	4	91	5
LUMO+4	3.364	3	93	4
LUMO+3	3.109	10	7	83
LUMO+2	3.065	6	4	91
LUMO+1	2.881	7	3	90
LUMO	2.283	6	3	91
HOMO	0.328	66	14	20
HOMO-1	0.055	68	15	17
HOMO-2	-0.202	66	17	18
HOMO-3	-0.289	66	17	17
HOMO-4	-0.336	76	17	7
HOMO-5	-0.391	73	18	9

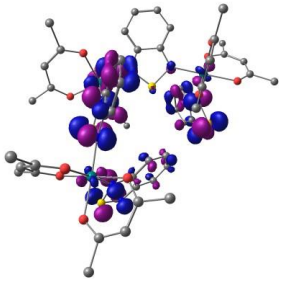
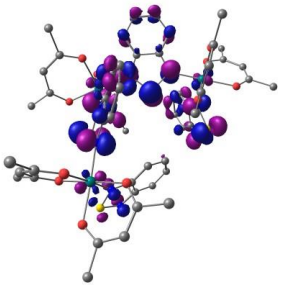
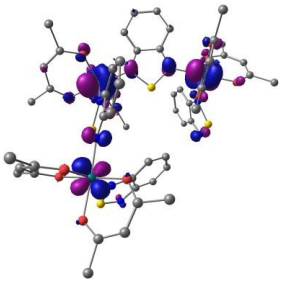
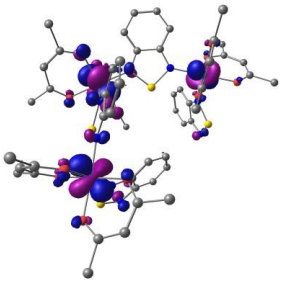
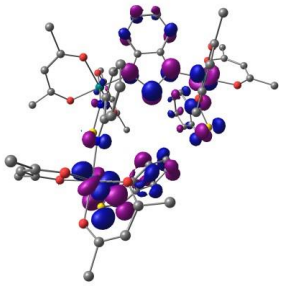
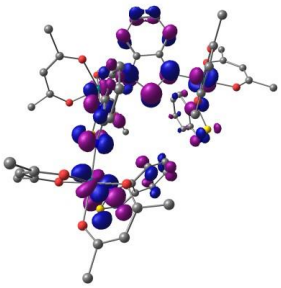
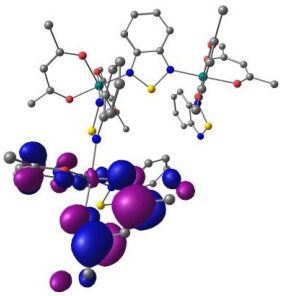
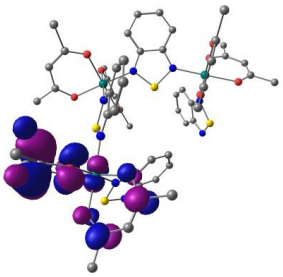
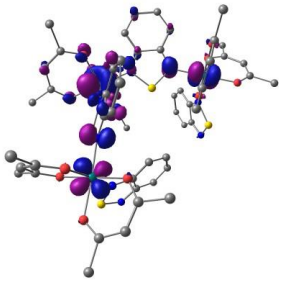
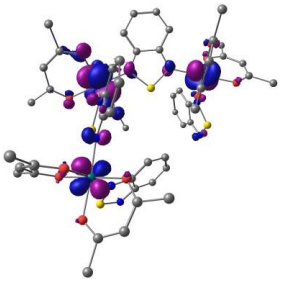
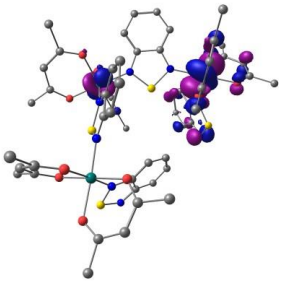
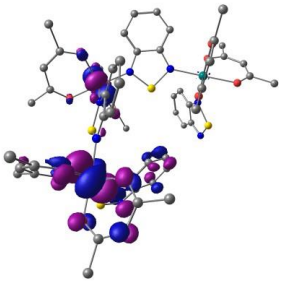
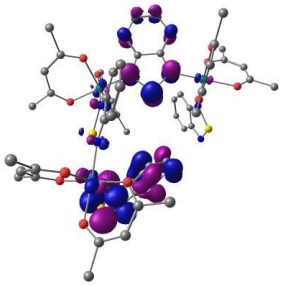
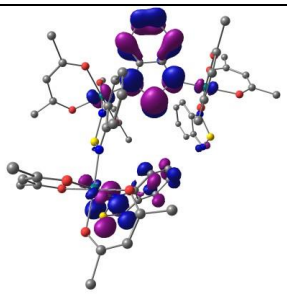
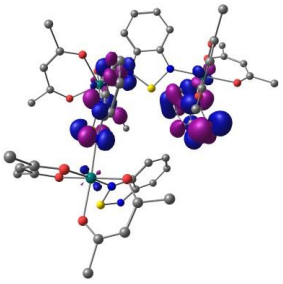
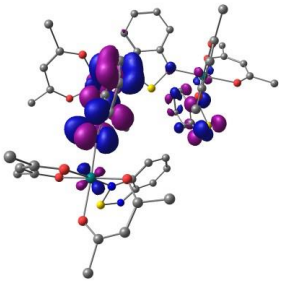
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26 Composition and energies of selected molecular orbitals of $\mathbf{4}^{3-}$ (*S*=3/2)

MO	Energy (eV)	% Composition		
		Ru	acac	BTD
		α-spin		
LUMO+5	5.881	8	86	6
LUMO+4	5.575	5	91	4
LUMO+3	5.560	5	91	4
LUMO+2	5.456	8	86	6
LUMO+1	5.359	3	95	2
LUMO	4.663	14	4	82
SOMO	4.231	11	3	86
HOMO-1	4.077	9	3	88
HOMO-2	3.878	8	3	89
HOMO-3	2.520	68	14	18
HOMO-4	2.271	67	15	18
HOMO-5	2.117	71	15	13
		β-spin		
LUMO+5	5.582	9	38	53
LUMO+4	5.574	6	76	18
LUMO+3	5.486	6	45	50
LUMO+2	5.435	6	73	21
LUMO+1	5.401	6	55	39
LUMO	5.327	3	55	41
HOMO	2.714	65	12	22
HOMO-1	2.464	65	13	22
HOMO-2	2.275	68	14	18
HOMO-3	2.070	65	15	21
HOMO-4	2.041	75	18	7
HOMO-5	1.899	77	16	8

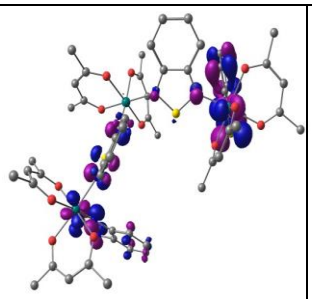
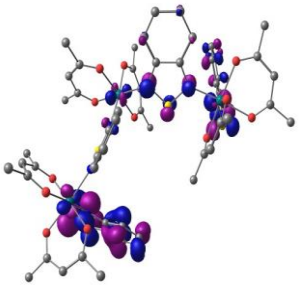
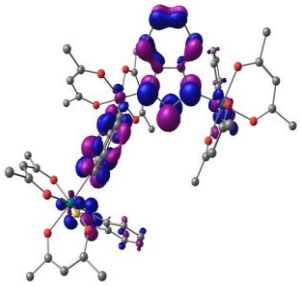
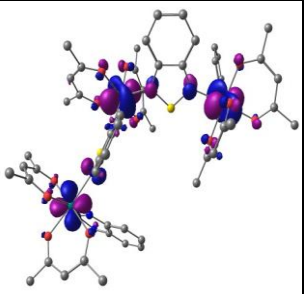
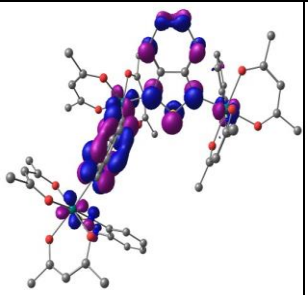
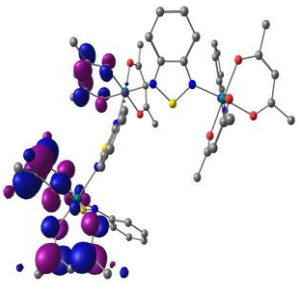
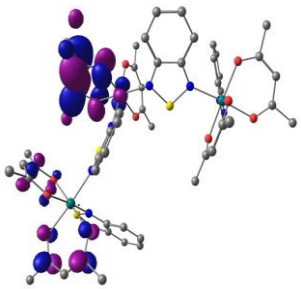
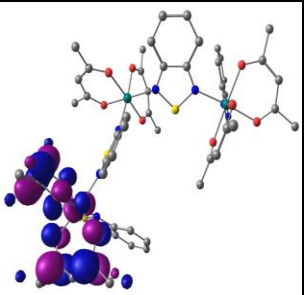
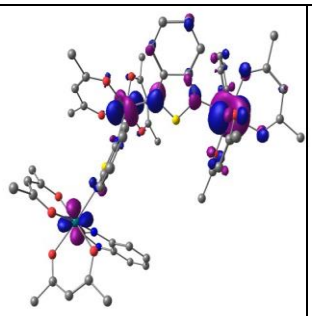
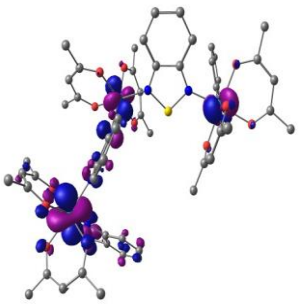
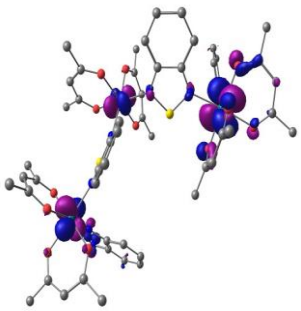
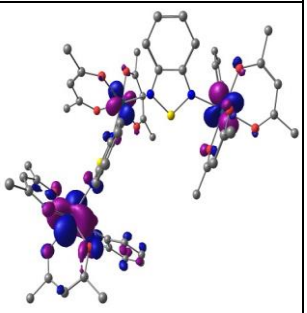
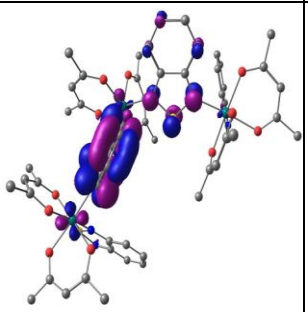
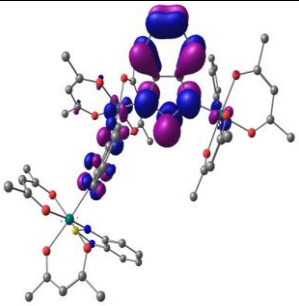
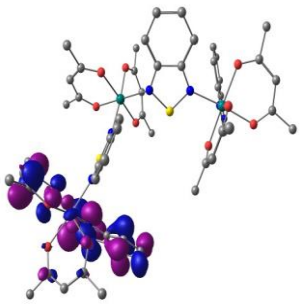
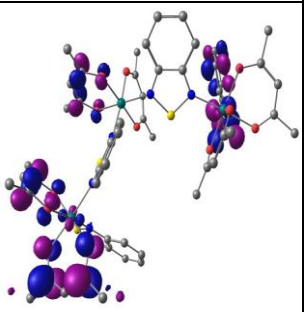
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S27 DFT (UB3LYP) calculated Mulliken spin density distributions for cations and anions

Complex	Ru1	Ru2	Ru3	μ-BTD	η^1-BTD	acac	CH_3CN
$\mathbf{1}^{2+}$(*S*=1)	0.710	0.714	-	0.009		0.563	0.006
$\mathbf{1}^{+}$(*S*=1/2)	0.538	0.467	-	-0.200		0.199	-0.002
$\mathbf{2}^{2+}$(*S*=1)	0.744	0.710	-	-0.011	-0.006	0.563	0.005
$\mathbf{2}^{+}$(*S*=1/2)	0.583	0.434	-	-0.172	-0.006	0.164	0.001
$\mathbf{3}^{2+}$(*S*=1)	0.732	0.732	-	0.014	0.013/0/014	0.502	-
$\mathbf{3}^{+}$(*S*=1/2)	0.523	0.523	-	-0.218	0.000/-0.001	0.177	-
$\mathbf{4}^{3+}$(*S*=3/2)	0.725	0.720	0.719	0.010/0.017	0.010/0.011	0.797	-
$\mathbf{4}^{2+}$(*S*=1)	0.720	0.308	0.685	-0.058/-0.097	0.004/0.006	0.431	-
$\mathbf{4}^{+}$(*S*=1/2)	0.436	0.533	0.171	-0.205/-0.096	-0.007/-0.003	0.180	-
$\mathbf{1}^{-}$(*S*=1/2)	0.023	0.023	-	0.950	-	0.003	0.000
$\mathbf{2}^{-}$(*S*=1/2)	0.018	-0.069	-	0.628	0.420	0.005	0.000
$\mathbf{2}^{2-}$(*S*=1)	0.048	0.014	-	0.950	0.975	0.016	-0.002
$\mathbf{3}^{-}$(*S*=1/2)	-0.075	-0.075	-	0.558	0.301/0.295	-0.002	-
$\mathbf{3}^{2-}$(*S*=1)	-0.013	-0.016	-	0.425	0.801/0.798	0.005	-
$\mathbf{4}^{-}$(*S*=1/2)	-0.085	-0.067	-0.001	0.484/0.354	0.266/0.052	-0.002	-
$\mathbf{4}^{2-}$(*S*=1)	-0.076	-0.059	0.046	0.676/0.400	0.671/0.333	0.003	-
$\mathbf{4}^{3-}$(*S*=3/2)	-0.036	0.026	0.024	0.644/0.511	0.910/0.901	0.023	-

Table S28 Experimental and TD-DFT (UB3LYP/6-31G**/LANL2DZ) calculated electronic transitions for $\mathbf{1}^n$- $\mathbf{3}^n$ (n = +2, +1, 0) and 4^m (m = +3, +2, +1, 0) in CH_3CN

λ [nm] expt (DFT)	ε /dm^3 mol^{-1}cm^{-1} (f)	Transitions	Character
		$\mathbf{1}^{2+}$ (S=1/2)	
575(621)	9940 (0.040)	HOMO-2(β)→LUMO(β)(0.38)	acac(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
		HOMO-6(β)→LUMO(β)(0.36)	acac(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
(615)	(0.038)	HOMO-6(β)→LUMO(β)(0.47)	acac(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
452(452)	10620(0.049)	HOMO-1(β)→LUMO+2(β)(0.58)	acac(π)/Ru(dπ)→BTD(π*)/acac(π*)
290(299)	40070(0.040)	HOMO-13(α)→LUMO(α)(0.77)	acac(π)/BTD(π)→BTD(π*)
(288)	(0.089)	HOMO-11(β)→LUMO+2(β)(0.48)	BTD(π)→BTD(π*)/Ru(dπ)
217(265)	55080(0.031)	HOMO-3(β)→LUMO+5(β)(0.27)	acac(π)/Ru(dπ)→acac(π*)
		HOMO-4(β)→LUMO+4(β)(0.23)	acac(π)/Ru(dπ)→acac(π*)
		$\mathbf{1}^{+}$ (S=1/2)	
1890			
(1986)	3800 (0.056)	HOMO-1(β)→LUMO(β)(0.80)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ)
(1638)	(0.034)	HOMO-2(β)→LUMO(β)(0.52)	acac(π)/Ru(dπ)→Ru(dπ)
(1373)	(0.091)	HOMO-4(β)→LUMO(β)(0.86)	Ru(dπ)→Ru(dπ)
736(621)	18740(0.149)	HOMO(α)→LUMO(α)(0.66)	acac(π)/Ru(dπ)→BTD(π*)
555(564)	6250(0.042)	HOMO-8(β)→LUMO(β)(0.74)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ)
337(294)	15120(0.054)	HOMO-4(α)→LUMO+3(α)(0.70)	acac(π)/BTD(π)→acac(π*)
272(290)	41050(0.068)	HOMO-12(β)→LUMO+1(β)(0.57)	BTD(π)→BTD(π*)/Ru(dπ)
(290)	(0.035)	HOMO-1(β)→LUMO+3(β)(0.42)	acac(π)/Ru(dπ)→acac(π*)
220(264)	24670(0.39)	HOMO-7(α)→LUMO+3(α)(0.42)	acac(π)→acac(π*)
		1 (S=0)	
788(692)	22920(0.1932)	HOMO-2→LUMO(0.59)	acac(π)/Ru(dπ)→BTD(π*)/Ru(dπ)
540(648)	5210(0.1663)	HOMO-2→LUMO(0.59)	acac(π)/Ru(dπ)→BTD(π*)/Ru(dπ)
(515)	(0.049)	HOMO-4→LUMO(0.47)	acac(π)/Ru(dπ)→BTD(π*)/Ru(dπ)
375(339)	13360(0.040)	HOMO-5→LUMO+3(0.34)	BTD(π)→acac(π*)
		HOMO-3→LUMO+3(0.26)	acac(π)/Ru(dπ)→acac(π*)
(338)	(0.060)	HOMO-4→LUMO+2(0.30)	acac(π)/Ru(dπ)→acac(π*)

		HOMO-5→LUMO+2(0.21)	BTD(π)→acac(π*)
272(337)	46020(0.037)	HOMO-10→LUMO(0.44)	acac(π)/Ru(dπ)→BTD(π*)/Ru(dπ)
		HOMO-3→LUMO+4(0.14)	acac(π)/Ru(dπ)→acac(π*)
(333)	(0.059)	HOMO-3→LUMO+1(0.39)	acac(π)/Ru(dπ)→acac(π*)
		HOMO-10→LUMO(0.28)	acac(π)/Ru(dπ)→BTD(π*)/Ru(dπ)
225(256)	31490(0.030)	HOMO-16→LUMO(0.44)	acac(π)/BTD(π)→BTD(π*)/Ru(dπ)
(252)	(0.061)	HOMO-8→LUMO+2(0.44)	acac(π)→acac(π*)
		1^{-} (*S*=1/2)	
720(617)	21720(0.110)	HOMO(β)→LUMO(β)(0.94)	acac(π)/BTD(π)/Ru(dπ)→acac(π*)/ BTD(π*)
528(480)	8010 (0.012)	HOMO-1(β)→LUMO(β)(0.61)	acac(π)/BTD(π)/Ru(dπ)→acac(π*)/ BTD(π*)
351(364)	13360(0.079)	HOMO-2(α)→LUMO(α)(0.30)	Ru(dπ)→acac(π*)/BTD(π*)
		HOMO-2(α)→LUMO(α)(0.28)	Ru(dπ)→acac(π*)/BTD(π*)
277(316)	59220(0.050)	HOMO-11(β)→LUMO(β)(0.52)	acac(π)→acac(π*)/BTD(π*)
		2^{2+} (*S*=1)	
563(666)	8130(0.041)	HOMO-4(β)→LUMO(β)(0.77)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ)
(635)	(0.044)	HOMO-5(β)→LUMO+1(β)(0.93)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ)
465(477)	9900(0.025)	HOMO-2(β)→LUMO+2(β)(0.50)	acac(π)/Ru(dπ)→BTD(π*)
403(405)	20670(0.024)	HOMO-1(α)→LUMO+2(α)(0.46)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ)
293(289)	34990(0.045)	HOMO-13(β)→LUMO+2(β)(0.62)	acac(π)/BTD(π)→BTD(π*)
220(287)	45890(0.163)	HOMO-10(α)→LUMO+1(α)(0.53)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
		2^{+} (*S*=1/2)	
1866			
(1720)	3430(0.043)	HOMO-5(β)→LUMO(β)(0.52)	Ru(dπ)→Ru(dπ)
(1374)	(0.109)	HOMO-5(β)→LUMO(β)(0.58)	Ru(dπ)→Ru(dπ)
775(744)	19460(0.037)	HOMO(β)→LUMO+1(β)(0.55)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
525(582)	7610(0.091)	HOMO-1(α)→LUMO(α)(0.57)	acac(π)/Ru(dπ)→BTD(π*)
(480)	(0.063)	HOMO-3(β)→LUMO+1(β)(0.70)	acac(π)/Ru(dπ)→BTD(π*)
333(298)	17670(0.019)	HOMO(β)→LUMO+9(β)(0.47)	BTD(π)/Ru(dπ)→BTD(π*)/Ru(dπ)
311(288)	21330(0.030)	HOMO-13(α)→LUMO+1(α)(0.45)	acac(π)/BTD(π)→BTD(π*)
276(285)	34890(0.133)	HOMO-12(β)→LUMO+2(β)(0.57)	BTD(π)→BTD(π*)
218(281)	34720(0.053)	HOMO-6(α)→LUMO+3(α)(0.53)	acac(π)/Ru(dπ)→acac(π*)
		2 (*S*=0)	
845(733)	24650(0.076)	HOMO→LUMO(0.61)	acac(π)/Ru(dπ)→BTD(π*)
610(658)	11060(0.181)	HOMO→LUMO+1(0.40)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-2→LUMO(0.30)	acac(π)/Ru(dπ)→BTD(π*)

(573)	(0.031)	HOMO-2→LUMO+1(0.35)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO→LUMO+1(0.34)	acac(π)/Ru(dπ)→BTD(π*)
373(367)	11960(0.025)	HOMO→LUMO+3(0.52)	acac(π)/Ru(dπ)→acac(π*)
330(337)	12440(0.058)	HOMO-4→LUMO+4(0.40)	Ru(dπ)→acac(π*)
273(296)	46260(0.033)	HOMO-15→LUMO(0.48)	acac(π)→BTD(π*)
218(265)	30140(0.038)	HOMO-6→LUMO+5(0.44)	acac(π)→acac(π*)
		HOMO-8→LUMO+4(0.25)	acac(π)/Ru(dπ)→acac(π*)
		2^{-} (*S*=1/2)	
731(678)	29120(0.044)	HOMO(β)→LUMO(β)(0.72)	BTD(π)/Ru(dπ)→BTD(π*)
556(559)	18010(0.043)	HOMO-6(α)→LUMO(α)(0.64)	Ru(dπ)→BTD(π*)
(543)	(0.095)	HOMO-3(β)→LUMO(β)(0.60)	acac(π)/Ru(dπ)→BTD(π*)
485(465)	13380(0.016)	HOMO-4(β)→LUMO+1(β)(0.52)	acac(π)/Ru(dπ)→BTD(π*)
(446)	(0.018)	HOMO-5(β)→LUMO+1(β)(0.46)	acac(π)/Ru(dπ)→BTD(π*)
335(356)	19400(0.077)	HOMO-4(β)→LUMO+4(β)(0.48)	acac(π)/Ru(dπ)→acac(π*)
		HOMO-5(α)→LUMO+2(α)(0.46)	acac(π)/Ru(dπ)→acac(π*)
228(293)	46500(0.043)	HOMO-13(β)→LUMO(β)(0.56)	BTD(π)→BTD(π*)
		2^{2-} (*S*=1)	
703(639)	23280(0.097)	HOMO(β)→LUMO(β)(0.85)	BTD(π)/Ru(dπ)→acac(π*)
550(565)	19280(0.044)	HOMO(β)→LUMO+1(β)(0.74)	BTD(π)/Ru(dπ)→acac(π*)
332(363)	20720(0.063)	HOMO-5(β)→LUMO+2(β)(0.52)	acac(π)/Ru(dπ)→BTD(π*)
(317)	(0.030)	HOMO-6(α)→LUMO+3(α)(0.46)	acac(π)/Ru(dπ)→acac(π*)
260(313)	50470(0.031)	HOMO-7(β)→LUMO+2(β)(0.42)	BTD(π)→acac(π*)
		HOMO-8(β)→LUMO(β)(0.36)	BTD(π)/Ru(dπ)→acac(π*)
(310)	(0.093)	HOMO-10(β)→LUMO+1(β)(0.55)	acac(π)→acac(π*)
		3^{2+} (*S*=1)	
560(625)	8380(0.044)	HOMO-1(β)→LUMO+1(β)(0.54)	acac(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
(536)	(0.054)	HOMO-5(β)→LUMO+1(β)(0.50)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
475(464)	9960(0.061)	HOMO-2(α)→LUMO+1(α)(0.69)	acac(π)/Ru(dπ)→BTD(π*)
402(394)	14270(0.036)	HOMO-2(β)→LUMO+4(β)(0.39)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
		HOMO-1(β)→LUMO+3(β)(0.35)	acac(π)/Ru(dπ)→BTD(π*)
297(291)	43340(0.069)	HOMO-13(β)→LUMO+2(β)(0.49)	acac(π)→BTD(π*)
		HOMO-13(α)→LUMO(α)(0.37)	acac(π)→BTD(π*)
222(286)	51890(0.171)	HOMO-11(β)→LUMO+3(β)(0.52)	BTD(π)→BTD(π*)
		HOMO-12(α)→LUMO+2(α)(0.36)	BTD(π)→BTD(π*)
		3^{+} (*S*=1/2)	

1838 (1930) (1627)	2890(0.059) (0.097)	HOMO-2(β)→LUMO(β)(0.70) HOMO-3(β)→LUMO(β)(0.76)	acac(π)/Ru(dπ)→Ru(dπ) Ru(dπ)→Ru(dπ)
782(776) (633)	19630(0.025) (0.128)	HOMO(β)→LUMO+1(β)(0.91) HOMO-2(α)→LUMO+1(α)(0.66)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*)
525(598) (578)	12050(0.043) (0.38)	HOMO(β)→LUMO+2(β)(0.58) HOMO-8(β)→LUMO(β)(0.81)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*) acac(π)/BTD(π)→BTD(π*)/Ru(dπ)
307(297)	34300(0.030)	HOMO-2(β)→LUMO+5(β)(0.34) HOMO-4(α)→LUMO+4(α)(0.27)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ) acac(π)/Ru(dπ)→acac(π*)
275(290)	48600(0.048)	HOMO-16(β)→LUMO+2(β)(0.43) HOMO-12(β)→LUMO+2(β)(0.42)	BTD(π)→BTD(π*) acac(π)/BTD(π)→BTD(π*)
220(281)	41980(0.082)	HOMO-13(β)→LUMO+3(β)(0.41) HOMO-3(β)→LUMO+6(β)(0.18)	acac(π)/BTD(π)→BTD(π*) acac(π)→acac(π*)
		3 (*S*=0)	
875(784) (651)	21670(0.170) (0.081)	HOMO→LUMO(0.69) HOMO-2→LUMO+2(0.44) HOMO-2→LUMO(0.39)	acac(π)/Ru(dπ)→BTD(π*) Ru(dπ)→BTD(π*) Ru(dπ)→BTD(π*)
582(585) (550)	14480(0.033) (0.064)	HOMO-5→LUMO(0.48) HOMO-4→LUMO+1(0.31) HOMO-4→LUMO(0.31) HOMO-1→LUMO(0.25)	Ru(dπ)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*)
382(418) (400)	13550(0.021) (0.021)	HOMO-2→LUMO+1(0.57) HOMO-2→LUMO+2(0.29)	Ru(dπ)→acac(π*) Ru(dπ)→acac(π*)
330(336)	11940(0.124)	HOMO-3→LUMO+4(0.37) HOMO-5→LUMO+4(0.23)	acac(π)/Ru(dπ)→acac(π*)/Ru(dπ) Ru(dπ)→acac(π*)/Ru(dπ)
273(287)	47850(0.093)	HOMO-17→LUMO+1(0.44) HOMO→LUMO+15(0.15)	acac(π)/BTD(π)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*)
215(253)	28710(0.059)	HOMO-3→LUMO+13(0.41) HOMO-8→LUMO+5(0.20)	acac(π)/Ru(dπ)→BTD(π*) acac(π)/BTD(π)→acac(π*)
		3^{-} (*S*=1/2)	
1022 (1050)	3960(0.011)	HOMO-1(α)→LUMO+1(α)(0.63)	BTD(π)/Ru(dπ)→BTD(π*)
692(728) (634)	16350(0.047) (0.091)	HOMO(β)→LUMO(β)(0.84) HOMO(β)→LUMO+2(β)(0.62)	BTD(π)/Ru(dπ)→BTD(π*) BTD(π)/Ru(dπ)→BTD(π*)
540(580) (541) (530) (516)	21980(0.057) (0.153) (0.050) (0.050)	HOMO-2(α)→LUMO+1(α)(0.50) HOMO(β)→LUMO+2(β)(0.51) HOMO-1(β)→LUMO+2(β)(0.51) HOMO-3(β)→LUMO+1(β)(0.51)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*) BTD(π)/Ru(dπ)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*) acac(π)/Ru(dπ)→BTD(π*)

345(351)	15350(0.126)	HOMO-3(β)→LUMO+4(β)(0.37)	acac(π)/Ru(dπ)→acac(π*)
		HOMO-4(α)→LUMO+3(α)(0.33)	acac(π)/Ru(dπ)→acac(π*)
220(291)	50470(0.094)	HOMO-18(α)→LUMO(α)(0.38)	acac(π)/BTD(π)→BTD(π*)
		HOMO-19(β)→LUMO(β)(0.28)	acac(π)→BTD(π*)
		3^{2-} (*S*=1)	
767(727)	17240(0.147)	HOMO(β)→LUMO(β)(0.69)	BTD(π)/Ru(dπ)→BTD(π*)
(722)	(0.032)	HOMO-5(α)→LUMO(α)(0.58)	Ru(dπ)→BTD(π*)
562(556)	15060(0.073)	HOMO(β)→LUMO+2(β)(0.67)	BTD(π)/Ru(dπ)→BTD(π*)
(540)	(0.085)	HOMO(β)→LUMO+2(β)(0.75)	BTD(π)/Ru(dπ)→BTD(π*)
396(364)	12670(0.161)	HOMO-5(α)→LUMO+2(α)(0.34)	Ru(dπ)→acac(π*)
		HOMO-3(β)→LUMO+4(β)(0.28)	Ru(dπ)→acac(π*)
308(301)	38380(0.172)	HOMO-12(β)→LUMO+2(β)(0.48)	acac(π)/BTD(π)→BTD(π*)
		HOMO-8(β)→LUMO+2(β)(0.48)	BTD(π)→BTD(π*)
240(297)	50470(0.020)	HOMO(β)→LUMO+9(β)(0.50)	BTD(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
		HOMO-2(α)→LUMO+6(α)(0.44)	Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
		4^{3+} (*S*=1/2)	
570(642)	8460(0.053)	HOMO-10(β)→LUMO+1(β)(0.37)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)/
		HOMO-9(β)→LUMO+2(β)(0.24)	acac(π*)/Ru(dπ)
			acac(π)/Ru(dπ)→BTD(π*)/acac(π*)/Ru(dπ)
489(463)	9310(0.037)	HOMO-4(α)→LUMO(α)(0.38)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-3(β)→LUMO+3(β)(0.25)	acac(π)/Ru(dπ)→BTD(π*)
402(394)	11270(0.016)	HOMO-3(β)→LUMO+5(β)(0.35)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-9(β)→LUMO+3(β)(0.21)	acac(π)/Ru(dπ)→BTD(π*)
298(363)	36690(0.010)	HOMO(β)→LUMO+6(β)(0.52)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-12(β)→LUMO+3(β)(0.26)	BTD(π)/Ru(dπ)→BTD(π*)
		4^{2+} (*S*=1)	
1735	2400		
(1839)	……(0.050)	HOMO(β)→LUMO(β)(0.54)	acac(π)/BTD(π)/Ru(dπ)→Ru(dπ)
(1601)	……(0.031)	HOMO(β)→LUMO(β)(0.51)	acac(π)/BTD(π)/Ru(dπ)→Ru(dπ)
825(835)	10960(0.030)	HOMO(β)→LUMO+2(β)(0.67)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
(698)	……..(0.096)	HOMO(α)→LUMO(α)(0.66)	acac(π)/Ru(dπ)→BTD(π*)
550(555)	8460(0.029)	HOMO-2(α)→LUMO+1(α)(0.49)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO(β)→LUMO+5(β)(0.34)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
(500)	(0.042)	HOMO-2(β)→LUMO+3(β)(0.51)	acac(π)/Ru(dπ)→BTD(π*)
398(442)	8690(0.015)	HOMO-3(α)→LUMO+2(α)(0.51)	acac(π)/Ru(dπ)→BTD(π*)
(405)	(0.015)	HOMO-7(α)→LUMO+3(α)(0.25)	acac(π)/Ru(dπ)→BTD(π*)

		HOMO-18(β)→LUMO(β)(0.23)	acac(π)/BTD(π)→BTD(π*)/Ru(dπ)
280(376)	33850(0.022)	HOMO-12(β)→LUMO+2(β)(0.41)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-10(α)→LUMO+3(α)(0.20)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
		4^{+} (*S*=1/2)	
1860			
(1746)	2840(0.027)	HOMO-1(β)→LUMO(β)(0.56)	acac(π)/Ru(dπ)→Ru(dπ)
(1595)	(0.038)	HOMO-5(β)→LUMO(β)(0.63)	acac(π)/Ru(dπ)→Ru(dπ)
(1255)	(0.045)	HOMO-8(β)→LUMO(β)(0.49)	acac(π)/Ru(dπ)→Ru(dπ)
		HOMO-6(β)→LUMO(β)(0.27)	acac(π)/Ru(dπ)→Ru(dπ)
938	9120		
(1011)	(0.012)	HOMO(β)→LUMO+1(β)(0.58)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
810(824)	12560(0.025)	HOMO-1(β)→LUMO+1(β)(0.43)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
		HOMO(β)→LUMO+1(β)(0.43)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
745(716)	12140(0.035)	HOMO(α)→LUMO+1(α)(0.44)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO(β)→LUMO+3(β)(0.33)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
540(572)	9600(0.061)	HOMO-1(α)→LUMO+3(α)(0.38)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-4(β)→LUMO+1(β)(0.29)	acac(π)/Ru(dπ)→BTD(π*)
(540)	(0.053)	HOMO-3(α)→LUMO+3(α)(0.47)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO(α)→LUMO+3(α)(0.29)	acac(π)/Ru(dπ)→BTD(π*)
275(380)	36870(0.011)	HOMO-12(α)→LUMO+1(α)(0.43)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
		HOMO-11(β)→LUMO+2(β)(0.19)	acac(π)→BTD(π*)
		4 (*S*=0)	
975	22010		
(845)	(0.1709)	HOMO→LUMO(0.69)	acac(π)/Ru(dπ)→BTD(π*)
746(731)	12210(0.080)	HOMO→LUMO+1(0.54)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-1→LUMO(0.32)	acac(π)/Ru(dπ)→BTD(π*)
590(637)	12440(0.172)	HOMO→LUMO+3(0.30)	acac(π)/Ru(dπ)→BTD(π*)
		HOMO-2→LUMO+3(0.27)	acac(π)/Ru(dπ)→BTD(π*)
371(397)	10650(0.042)	HOMO-13→LUMO(0.36)	acac(π)→BTD(π*)
		HOMO-12→LUMO+1(0.24)	acac(π)→BTD(π*)
275(334)	47540(0.091)	HOMO-7→LUMO+6(0.30)	Ru(dπ)→acac(π*)
		HOMO-4→LUMO+6(0.19)	acac(π)/Ru(dπ)→acac(π*)
		4^{-} (*S*=1/2)	
846(759)	25200(0.025)	HOMO(β)→LUMO+1(β)(0.73)	BTD(π)/Ru(dπ)→BTD(π*)
643(702)	24340(0.099)	HOMO(β)→LUMO+2(β)(0.64)	BTD(π)/Ru(dπ)→BTD(π*)
(625)	(0.159)	HOMO-3(α)→LUMO+2(α)(0.47)	acac(π)/BTD(π)/Ru(dπ)→BTD(π*)
		HOMO-2(β)→LUMO+1(β)(0.26)	acac(π)/Ru(dπ)→BTD(π*)
476(533)	19320(0.103)	HOMO-4(β)→LUMO(β)(0.57)	acac(π)/Ru(dπ)→BTD(π*)

		HOMO-4(α)→LUMO+1(α)(0.31)	acac(π)/Ru(dπ)→BTD(π*)
277(350)	18320(0.049)	HOMO-5(α)→LUMO+6(α)(0.28)	acac(π)/Ru(dπ)→acac(π*)
		HOMO-5(β)→LUMO+7(β)(0.27)	acac(π)/Ru(dπ)→acac(π*)
		4^{2-} (*S*=1)	
747(768)	22080(0.091)	HOMO(β)→LUMO+1(β)(0.57)	BTD(π)/Ru(dπ)→BTD(π*)
		HOMO-7(α)→LUMO+1(α)(0.33)	Ru(dπ)→BTD(π*)
680(681)	22720(0.036)	HOMO-1(β)→LUMO+1(β)(0.69)	Ru(dπ)→BTD(π*)
(658)	(0.051)	HOMO(β)→LUMO+2(β)(0.45)	BTD(π)/Ru(dπ)→BTD(π*)
		HOMO(β)→LUMO+3(β)(0.36)	BTD(π)/Ru(dπ)→BTD(π*)
504(536)	19010(0.077)	HOMO-2(β)→LUMO+2(β)(0.42)	Ru(dπ)→BTD(π*)
		HOMO-6(β)→LUMO+1(β)(0.23)	acac(π)/Ru(dπ)→BTD(π*)
248(356)	55080(0.066)	HOMO-7(β)→LUMO+6(β)(0.35)	Ru(dπ)→acac(π*)
		HOMO-9(α)→LUMO+3(α)(0.26)	Ru(dπ)→acac(π*)
		4^{3-} (*S*=3/2)	
820(764)	24320(0.133)	HOMO(β)→LUMO(β)(0.51)	BTD(π)/Ru(dπ)→BTD(π*)/ acac(π*)
630(647)	23190(0.032)	HOMO-10(α)→LUMO(α)(0.50)	Ru(dπ)→BTD(π*)
		HOMO-9(α)→LUMO(α)(0.24)	Ru(dπ)→BTD(π*)
(631)	(0.033)	HOMO-2(β)→LUMO+1(β)(0.51)	Ru(dπ)→BTD(π*)/acac(π*)
482(542)	22980(0.038)	HOMO-1(β)→LUMO+2(β)(0.43)	BTD(π)/Ru(dπ)→BTD(π*)/ acac(π*)
		HOMO-1(α)→LUMO+11(α)(0.24)	BTD(π)→BTD(π*)/acac(π*)/ Ru(dπ)
284(389)	19420(0.055)	HOMO-7(α)→LUMO+5(α)(0.39)	Ru(dπ)→acac(π*)
		HOMO-4(β)→LUMO+8(β)(0.36)	Ru(dπ)→acac(π*)