Supporting Information

Evidence for Bidirectional Noninnocent Behavior of a Formazanate Ligand in Ruthenium Complexes

Abhishek Mandal,[§] Brigitte Schwederski,[†] Jan Fiedler,[‡] Wolfgang Kaim,[*,†] and Goutam Kumar Lahiri[*,§]

Table S1. Selected Crystallographic Data for 1, [2]ClO_4 and [3]ClO_4

	1	2x{[**2**]ClO_4}	[**3**]ClO_4
empirical formula	$C_{30}H_{31}N_4O_4Ru$	$C_{80}H_{66}Cl_2N_{16}O_8Ru_2$	$C_{42}H_{35}ClN_{10}O_4Ru$
formula weight	612.66	1652.52	880.32
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	10.871(2)	12.886(6)	14.021(9)
b (Å)	11.507(2)	17.921(8)	18.008(9)
c (Å)	11.956(2)	22.418(11)	16.026(9)
α (deg)	100.775(2)	97.35(2)	90
β (deg)	100.271(2)	105.30(3)	107.634(11)
γ (deg)	106.4560(10)	109.36(2)	90
V (Å^3)	1365.9(4)	4577(4)	3856(4)
Z	2	4	4
μ (mm^{-1})	0.617	0.444	0.534
T (K)	100(2)	100(2)	100(2)
ρ_{calcd} (g cm^{-3})	1.490	1.199	1.516
F (000)	630	1688	1800
θ range (deg)	3.15 to 25.00	3.00 to 25.00	3.23 to 25.00
data / restraints / parameters	4794 / 0 / 352	16078 / 0 / 975	6732 / 24 / 523
R_1, wR_2 [$I > 2\sigma(I)$]	0.0278, 0.0675	0.0905, 0.2318	0.0686, 0.1526
R_1, wR_2(all data)	0.0314, 0.0691	0.1107, 0.2493	0.0771, 0.1581
GOF on F^2	1.044	1.036	1.093
largest difference in peak and hole (e Å^{-3})	0.732 and –1.020	2.221 and –1.144	1.911 and –0.653

Table S2. Selected Experimental Bond Lengths and Bond Angles (deg) (Å) for [2]ClO_4 (Molecule B)

bond length (Å)	[**2**]ClO_4	bond angles (deg)	[**2**]ClO_4
Ru2-N10	2.042(5)	N10-Ru2-N12	87.4(2)
Ru2-N12	2.034(5)	N10-Ru2-N13	175.2(2)
Ru2-N13	2.087(5)	N10-Ru2-N14	97.4(2)
Ru2-N14	2.076(5)	N10-Ru2-N15	88.4(2)
Ru2-N15	2.063(5)	N10-Ru2-N16	93.9(2)
Ru2-N16	2.089(6)	N12-Ru2-N13	94.9(2)
N9-N10	1.291(7)	N12-Ru2-N14	95.1(2)
N11-N12	1.300(8)	N12-Ru2-N15	86.9(2)
C48-N9	1.355(8)	N12-Ru2-N16	177.3(2)
C48-N11	1.373(9)	N13-Ru2-N14	78.8(2)
C49-N12	1.456(9)	N13-Ru2-N15	95.2(2)
C55-N10	1.418(9)	N13-Ru2-N16	83.7(2)
C41-C42	1.522(10)	N14-Ru2-N15	171.5(2)
C42-C43	1.386(12)	N14-Ru2-N16	95.2(2)
C42-C47	1.386(11)	N15-Ru2-N16	78.1(2)
C43-C44	1.392(10)		
C44-C45	1.398(10)		
C45-C46	1.398(10)		
C45-C48	1.490(9)		
C46-C47	1.414(10)		

Table S3. Selected Experimental and DFT Calculated Bond Angles [deg] for 1^n

bond angle [deg]	X-ray	DFT		
	1	$\mathbf{1}^+$ (S=0)	**1** (S=1/2)	$\mathbf{1}^-$ (S=0)
N2-Ru1-N4	88.13(9)	84.47	87.32	87.96
N2-Ru1-O1	94.92(8)	92.43	96.00	92.360
N2-Ru1-O2	173.73(7)	174.06	174.98	175.71
N2-Ru1-O3	87.27(8)	89.59	87.34	88.65
N2-Ru1-O4	90.03(8)	98.72	93.50	93.60
N4-Ru1-O1	98.41(8)	99.98	98.21	96.72
N4-Ru1-O2	92.11(8)	89.63	92.64	95.15
N4-Ru1-O3	84.70(8)	83.44	84.87	85.12
N4-Ru1-O4	175.80(7)	173.22	175.51	175.76
O1-Ru1-O2	91.25(7)	89.27	88.98	90.26
O1-Ru1-O3	176.24(7)	176.18	175.55	177.96
O1-Ru1-O4	85.51(7)	85.91	86.11	87.17
O2-Ru1-O3	86.52(7)	89.05	87.66	88.68
O2-Ru1-O4	89.30(7)	87.08	86.17	83.10
O3-Ru1-O4	91.44(7)	90.58	90.76	90.97

Table S4. Selected Experimental and DFT Calculated Bond Angles [deg] for 2^n (Molecule A)

bond angle [deg]	X-ray	DFT			
	$\mathbf{2}^+$	$\mathbf{2}^{2+}$ (S=1/2)	$\mathbf{2}^+$ (S=0)	**2** (S=1/2)	$\mathbf{2}^-$ (S=1)
N2-Ru1-N4	86.2(2)	86.69	86.71	87.06	86.81
N2-Ru1-N5	176.7(2)	174.59	172.03	172.07	173.81
N2-Ru1-N6	97.7(2)	98.64	95.64	95.58	96.59
N2-Ru1-N7	89.3(2)	85.74	85.77	86.64	87.40
N2-Ru1-N8	95.5(2)	95.14	95.51	96.19	95.69
N4-Ru1-N5	94.2(2)	96.17	95.53	96.28	96.01
N4-Ru1-N6	85.8(2)	86.47	85.57	86.51	87.82
N4-Ru1-N7	100.9(2)	97.40	95.72	95.54	96.10
N4-Ru1-N8	178.3(2)	173.86	172.09	172.03	173.48
N5-Ru1-N6	79.1(2)	77.00	76.95	77.50	78.06
N5-Ru1-N7	93.9(2)	98.42	101.58	100.16	97.75
N5-Ru1-N8	84.2(2)	82.50	83.31	81.44	82.10
N6-Ru1-N7	170.7(2)	174.35	178.15	177.07	174.58
N6-Ru1-N8	94.5(2)	99.02	101.73	100.38	97.85
N7-Ru1-N8	78.7(2)	76.93	76.91	77.44	78.04

Table S5. Selected Experimental and DFT Calculated Bond Angles [deg] for 3^n

bond angle [deg]	X-ray	DFT			
	$\mathbf{3}^{+}$	$\mathbf{3}^{2+}$ (S=1/2)	$\mathbf{3}^{+}$ (S=0)	**3** (S=1/2)	$\mathbf{3}^{-}$ (S=1)
N2-Ru1-N4	90.4(2)	86.23	86.71	87.28	87.13
N2-Ru1-N5	85.2(2)	83.73	83.27	84.05	84.36
N2-Ru1-N7	92.7(2)	98.63	95.26	96.57	94.36
N2-Ru1-N8	171.9(2)	169.71	167.66	167.70	169.01
N2-Ru1-N9	99.1(2)	94.91	93.41	93.31	93.81
N4-Ru1-N5	94.9(2)	97.96	93.31	93.27	94.03
N4-Ru1-N7	170.5(2)	170.84	167.51	167.50	169.12
N4-Ru1-N8	95.5(2)	93.65	95.19	96.34	94.03
N4-Ru1-N9	85.9(2)	82.91	83.46	84.21	84.13
N5-Ru1-N7	76.46(18)	75.00	74.72	75.39	74.43
N5-Ru1-N8	99.82(16)	106.46	108.74	107.40	106.44
N5-Ru1-N9	175.65(16)	178.32	175.51	176.44	177.48
N7-Ru1-N8	82.41(17)	82.95	85.52	82.40	86.57
N7-Ru1-N9	102.49(17)	104.28	108.69	107.35	106.49
N8-Ru1-N9	75.83(16)	74.88	74.74	75.44	75.46

Table S6. Deviations (Å) from Least-Square Plane (Best Plane)

atom	**1**	[**2**]ClO_4	[**3**]ClO_4
N2*	0.0167 (9)	–0.0527 (27)	0.0270 (31)
N1*	–0.0519 (13)	0.0724 (41)	–0.0112 (44)
C8*	0.0696 (14)	–0.0277 (41)	–0.0396 (40)
N3*	–0.0476 (14)	–0.0320 (39)	0.0661 (41)
N4*	0.0133 (9)	0.0402 (26)	–0.0423 (29)
Ru1	0.7492 (24)	–0.3080 (79)	–0.4523 (87)
Rms deviation of fitted atoms	0.0453	0.0478	0.0414

(* indicates atom used to define plane**)**

Table S7. Dihedral Angles [deg] between the Planes

	1	[**2**]ClO_4	[**3**]ClO_4
N1-C8-N3-N4 / N1-N2-Ru1-N4	20.95	14.06	8.18
N1-C8-N3-N4 / C4-C5-C6-C7	9.55	12.11	25.55
N1-C8-N3-N4 / C11-C10-C9-C14	28.04	50.93	89.47
N1-C8-N3-N4 / C18-C17-C16-C20	85.80	64.61	23.64

Table S8. Experimental and TD-DFT ((U)B3LYP/CPCM/CH_3CN) Calculated Electronic Transitions for 1^n

λ /nm (expt.) (ε/$M^{-1}cm^{-1}$)	λ/nm (DFT) (f)	transitions	Character
$\mathbf{1}^+$ (S=0)			
1445(sh)	1537(0.006)	HOMO→LUMO(0.66)	acac(π)/Ru(dπ)→L(π^*)/Ru(dπ)
1090(440)	1007(0.008)	HOMO-2→LUMO(0.43)	L(π)/Ru(dπ)/acac(π)→L(π^*)/Ru(dπ)
		HOMO-1→LUMO+1(0.41)	acac(π)/L(π)→L(π^*)/Ru(dπ)
638(6000)	654(0.083)	HOMO-3→LUMO(0.41)	Ru(dπ)/acac(π)→L(π^*)/Ru(dπ)
		HOMO-3→LUMO+1(0.21)	acac(π)/Ru(dπ)→L(π^*)/Ru(dπ)
521(20820)	533(0.142)	HOMO-4→LUMO+1(0.47)	L(π)→L(π^*)/Ru(dπ)
		HOMO-6→LUMO+1(0.30)	L(π)→L(π^*)/Ru(dπ)
445(24940)	463(0.202)	HOMO-10→LUMO(0.40)	Ru(dπ)/acac(π)→L(π^*)/Ru(dπ)
		HOMO→LUMO+1(0.25)	acac(π)/Ru(dπ)→L(π^*)
317(21460)	372(0.249)	HOMO-5→LUMO+1(0.48)	L(π)→L(π^*)
242(23260)	275(0.121)	HOMO-2→LUMO+2(0.38)	L(π)/Ru(dπ)/acac(π)→acac(π^*)
		HOMO-1→LUMO+4(0.27)	acac(π)/L(π)→L(π^*)/acac(π^*)
1 (S=1/2)			
990(sh)	837(0.015)	SOMO(α)→LUMO(α)(0.89)	L(π)/Ru(dπ)→L(π^*)
740(2540)	777(0.077)	HOMO-1(β)→LUMO(β)(0.80)	L(π)/Ru(dπ)→Ru(dπ)/L(π^*)
490(sh)	513(0.017)	HOMO-4(β)→LUMO(β)(0.58)	L(π)→Ru(dπ)/L(π^*)
		HOMO-1(β)→LUMO+1(β)(0.42)	L(π)/Ru(dπ)→L(π^*)
415(13580)	446(0.048)	HOMO-5(β)→LUMO(β)(0.71)	L(π)→Ru(dπ)/L(π^*)
		HOMO-7(β)→LUMO(β)(0.26)	L(π)/acac(π)→Ru(dπ)/L(π^*)
393(sh)	404(0.041)	HOMO-9(β)→LUMO(β)(0.60)	L(π)→Ru(dπ)/L(π^*)
355(18880)	365(0.094)	SOMO(α)→LUMO+4(α)(0.48)	L(π)/Ru(dπ)→L(π^*)
		SOMO(α)→LUMO+1(α)(0.44)	L(π)/Ru(dπ)→acac(π^*)
293(sh)	329(0.046)	HOMO-13(β)→LUMO(β)(0.38)	L(π)/acac(π)→Ru(dπ)/L(π^*)
		HOMO-10(α)→LUMO(α)(0.37)	L(π)/Ru(dπ)→L(π^*)

264(27630)	300(0.097)	SOMO(α)→LUMO+3(α)(0.36)	L(π)/Ru(dπ)→L(π^*)
		HOMO-2(α)→LUMO+1(α)(0.32)	Ru(dπ)/acac(π)→acac(π^*)
1$^-$ (*S*=0)			
947(1790)	798(0.043)	HOMO→LUMO(0.69)	Ru(dπ)/L(π)→L(π^*)
513(6690)	491(0.058)	HOMO→LUMO+1(0.57)	Ru(dπ)/L(π)→acac(π^*)
		HOMO-2→LUMO(0.27)	Ru(dπ)/L(π)→L(π^*)
411(20230)	397(0.179)	HOMO-3→LUMO(0.51)	L(π)/Ru(dπ)→L(π^*)
		HOMO-1→LUMO+1(0.23)	Ru(dπ)/acac(π)→acac(π^*)
370(19150)	379(0.370)	HOMO→LUMO+3(0.68)	Ru(dπ)/L(π)→L(π^*)
273(34250)	272(0.193)	HOMO-3→LUMO+3(0.55)	L(π)/Ru(dπ)→L(π^*)
		HOMO-13→LUMO(0.28)	L(π)→L(π^*)

Table S9. Experimental and TD-DFT ((U)B3LYP/CPCM/CH_3CN) Calculated Electronic Transitions for 2^n

λ /nm (expt.) (ε/$M^{-1}cm^{-1}$)	λ/nm (DFT) (f)	transitions	Character
$\mathbf{2}^{2+}$ (S=1/2)			
815(6880)	917(0.167)	HOMO(β)→LUMO(β)(0.92)	L(π)/Ru(dπ)→L(π^*)
515(sh)	551(0.018)	HOMO-6(β)→LUMO+11(β)(0.70)	L(π)→L(π^*)
		HOMO-2(β)→LUMO(β)(0.15)	Ru(dπ)→L(π^*)
464(5710)	437(0.040)	HOMO-11(β)→LUMO(β)(0.73)	L(π)→L(π^*)
		HOMO-1(β)→LUMO+1(β)(0.52)	L(π)→bpy(π^*)
358(17970)	359(0.122)	SOMO(α)→LUMO+7(α)(0.47)	L(π)→Ru(dπ)/bpy(π^*)
		HOMO-5(α)→LUMO(α)(0.33)	L(π)→L(π^*)
300(sh)	345(0.087)	HOMO-2(α)→LUMO+2(α)(0.76)	Ru(dπ)/L(π)→bpy(π^*)
		HOMO-2(β)→LUMO+3(β)(0.42)	Ru(dπ)→L(π^*)
265(22340)	285(0.136)	HOMO-5(α)→LUMO+2(α)(0.32)	L(π)→bpy(π^*)
		SOMO(α)→LUMO+7(α)(0.29)	L(π)→Ru(dπ)/bpy(π^*)
$\mathbf{2}^{+}$ (S=0)			
675(3900)	631(0.019)	HOMO→LUMO(0.69)	L(π)/Ru(dπ)→bpy(π^*)
650(3900)	609(0.008)	HOMO→LUMO+1(0.70)	L(π)/Ru(dπ)→bpy(π^*)/L(π^*)
450(9600)	410(0.055)	HOMO-2→LUMO+1(0.60)	Ru(dπ)/bpy(π)→bpy(π^*)/L(π^*)
353(15640)	379(0.095)	HOMO-3→LUMO+2(0.39)	L(π)→L(π^*)/bpy(π^*)
298(28430)	316(0.171)	HOMO-2→LUMO+3(0.45)	Ru(dπ)/bpy(π)→bpy(π^*)
		HOMO-6→LUMO+2(0.40)	L(π)/bpy(π)→L(π^*)/bpy(π^*)
241(23950)	277(0.123)	HOMO-13→LUMO+2(0.49)	L(π)/bpy(π)→L(π^*)/bpy(π^*)
2 (S=1/2)			
960(sh)	898(0.007)	SOMO(α)→LUMO+5(α)(0.98)	bpy(π)→bpy(π^*)
765(4580)	724(0.007)	HOMO-1(α)→LUMO(α)(0.97)	L(π)/Ru(dπ)→bpy(π^*)
550(sh)	552(0.009)	HOMO(β)→LUMO+2(β)(0.58)	L(π)/Ru(dπ)→bpy(π^*)/L(π^*)
		SOMO(α)→LUMO+10(α)(0.39)	bpy(π)→L(π^*)

476(12420)	465(0.073)	SOMO(α)→LUMO+13(α)(0.94)	bpy(π)→L(π^*)
366(22620)	333(0.132)	HOMO-2(α)→LUMO+3(α)(0.51)	Ru(dπ)→bpy(π^*)
		HOMO-1(β)→LUMO+4(β)(0.41)	Ru(dπ)→bpy(π^*)
296(30640)	286(0.151)	HOMO-2(β)→LUMO+6(β)(0.34)	Ru(dπ)→bpy(π^*)
		HOMO-5(β)→LUMO+2(β)(0.26)	L(π)→bpy(π^*)/L(π^*)
241(26650)	280(0.185)	HOMO-3(β)→LUMO+4(β)(0.61)	Ru(dπ)/L(π)→bpy(π^*)
		HOMO-4(α)→LUMO+3(α)(0.50)	Ru(dπ)/L(π)→bpy(π^*)
2$^-$ (S=1)			
847(5000)	809(0.016)	SOMO2(α)→LUMO+4(α)(0.78)	bpy(π)→bpy(π^*)
		SOMO2(α)→LUMO+5(α)(0.32)	bpy(π)→bpy(π^*)
505(sh)	458(0.020)	HOMO-1(β)→LUMO+1(β)(0.62)	Ru(dπ)→bpy(π^*)
		HOMO-6(β)→LUMO(β)(0.30)	L(π)/bpy(π)→L(π^*)
465(sh)	445(0.095)	HOMO-1(β)→LUMO+1(β)(0.52)	Ru(dπ)→bpy(π^*)
		SOMO1(α)→LUMO+12(α)(0.37)	bpy(π)→Ru(dπ)/bpy(π^*)
351(26110)	379(0.137)	HOMO-3(β)→LUMO(β)(0.50)	L(π)/Ru(dπ)→L(π^*)
		HOMO-5(α)→LUMO(α)(0.45)	L(π)/Ru(dπ)→L(π^*)
297(30720)	285(0.210)	HOMO-2(β)→LUMO+8(β)(0.58)	Ru(dπ)→L(π^*)
		HOMO-4(α)→LUMO+5(α)(0.41)	Ru(dπ)→bpy(π^*)

Table S10. Experimental and TD-DFT ((U)B3LYP/CPCM/CH_3CN) Calculated Electronic Transitions for 3^n

λ /nm (expt.) (ε/$M^{-1}cm^{-1}$)	λ/nm (DFT) (f)	transitions	Character
$\mathbf{3}^{2+}$ (S=1/2)			
815(3120)	770(0.037)	HOMO-4(β)→LUMO(β)(0.69)	L(π)/Ru(dπ)→L(π^*)
500(13500)	567(0.048)	HOMO-11(β)→LUMO(β)(0.69)	L(π)→L(π^*)
		HOMO-8(β)→LUMO(β)(0.47)	pap(π)→L(π^*)
366(26210),	347(0.168)	SOMO(α)→LUMO+5(α)(0.47)	L(π)→Ru(dπ)/L(π^*)
		HOMO(β)→LUMO+7(β)(0.27)	L(π)/Ru(dπ)→Ru(dπ)/pap(π^*)
$\mathbf{3}^{+}$ (S=0)			
845(1180)	913(0.022)	HOMO→LUMO+1(0.70)	L(π)→pap(π^*)
605(sh)	555(0.019)	HOMO-2→LUMO(0.65)	L(π)/Ru(dπ)→pap(π^*)
515(10300)	526(0.149)	HOMO→LUMO+2(0.68)	L(π)→pap(π^*)
355(26000)	377(0.268)	HOMO-11→LUMO+1(0.48)	pap(π)→pap(π^*)
3 (S=1/2)			
1060(1390)	1148(0.016)	HOMO-1(α)→LUMO(α)(0.94)	L(π)→pap(π^*)
538(10060)	547(0.130)	HOMO-1(α)→LUMO+1(α)(0.66)	L(π)→L(π^*)
		HOMO(β)→LUMO+2(β)(0.66)	L(π)→L(π^*)
347(28920)	306(0.370)	SOMO(α)→LUMO+16(α)(0.39)	pap(π)→pap(π^*)
		HOMO-11(α)→LUMO+1(α)(0.30)	L(π)→L(π^*)
$\mathbf{3}^{-}$ (S=1)			
1072(4630)	916(0.004)	SOMO1(α)→LUMO(α)(0.67)	pap(π)→L(π^*)
		HOMO(β)→LUMO+2(β)(0.55)	L(π)/Ru(dπ)→pap(π^*)
522(14320)	517(0.039)	HOMO-2(β)→LUMO(β)(0.90)	Ru(dπ)→pap(π^*)/L(π^*)
361(36680)	361(0.126)	SOMO1(α)→LUMO+8(α)(0.49)	pap(π)→pap(π^*)
		HOMO-2(α)→LUMO2(α)(0.44)	L(π)/Ru(dπ)→pap(π^*)

Table S11. Composition and Energies of Selected Molecular Orbitals of 1 (*S*=1/2)

MO	energy (eV)	composition		
		Ru	L	$acac^-$
		α-spin		
HOMO–5	–6.404	0.07	0.84	0.09
HOMO–4	–6.269	0.10	0.64	0.26
HOMO–3	–5.955	0.48	0.16	0.36
HOMO–2	–5.830	0.45	0.17	0.37
HOMO–2	–5.388	0.44	0.09	0.46
SOMO	–4.654	0.25	0.65	0.10
LUMO	–2.133	0.08	0.91	0.01
LUMO+1	–0.869	0.03	0.04	0.92
LUMO+2	–0.812	0.04	0.05	0.90
LUMO+3	–0.243	0.03	0.95	0.02
LUMO+4	0.114	0.12	0.82	0.06
LUMO+5	0.183	0.07	0.87	0.06
		β-spin		
HOMO–5	–6.413	0.06	0.83	0.11
HOMO–4	–6.362	0.10	0.70	0.19
HOMO–3	–6.122	0.06	0.26	0.67
HOMO–2	–5.666	0.69	0.14	0.17
HOMO–1	–5.389	0.28	0.54	0.18
HOMO	–5.219	0.48	0.14	0.38
LUMO	–2.613	0.50	0.35	0.14
LUMO+1	–2.002	0.11	0.88	0.02
LUMO+2	–0.833	0.04	0.04	0.92
LUMO+3	–0.747	0.06	0.07	0.88
LUMO+4	–0.173	0.03	0.96	0.01
LUMO+5	0.141	0.08	0.90	0.02

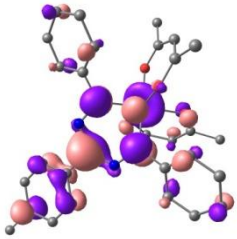
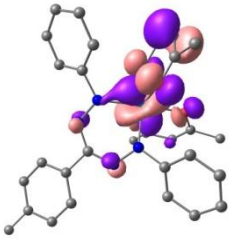
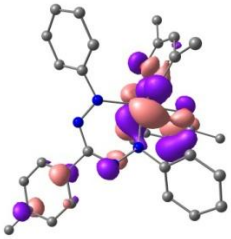
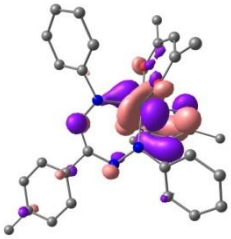
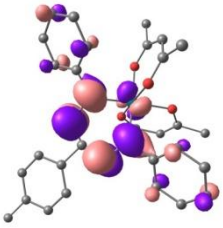
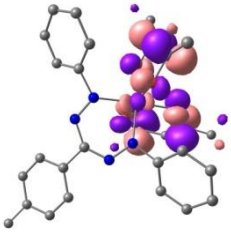
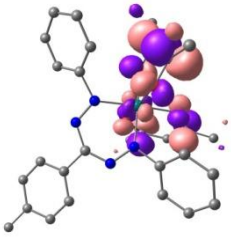
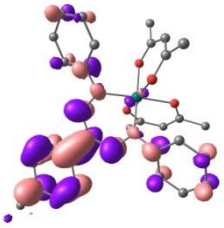
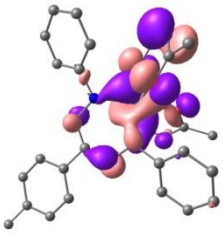
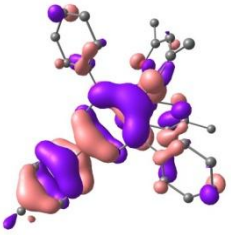
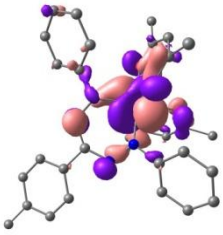
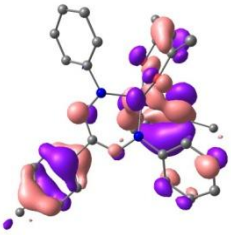
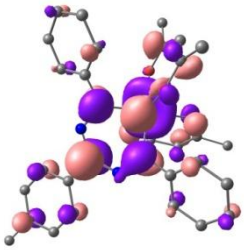
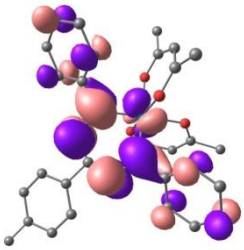
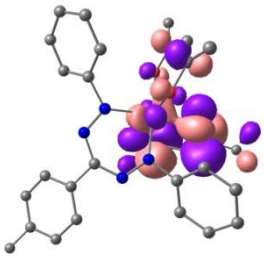
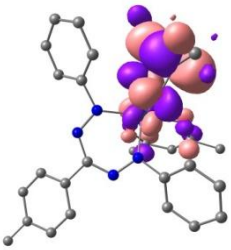
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12. Composition and Energies of Selected Molecular Orbitals of 1^+ (*S*=0)

MO	energy (eV)	composition		
		Ru	L	$acac^-$
HOMO–5	–9.575	0.01	0.88	0.11
HOMO–4	–9.550	0.09	0.80	0.11
HOMO–3	–9.396	0.64	0.15	0.21
HOMO–2	–9.296	0.28	0.44	0.28
HOMO–2	–8.863	0.14	0.32	0.54
HOMO	–8.526	0.25	0.09	0.67
LUMO	–6.997	0.37	0.51	0.12
LUMO+1	–5.610	0.09	0.90	0.01
LUMO+2	–3.955	0.10	0.04	0.86
LUMO+3	–3.819	0.25	0.11	0.64
LUMO+4	–3.610	0.14	0.46	0.40
LUMO+5	–3.522	0.22	0.48	0.29

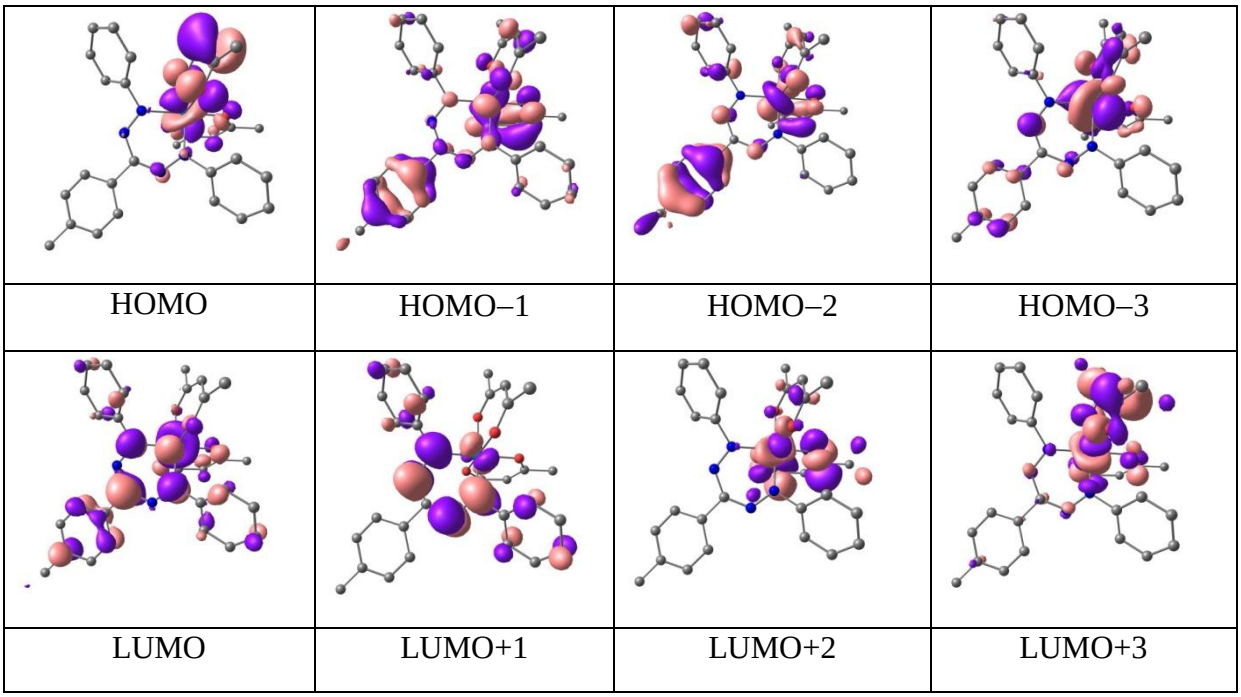


Table S13. Composition and Energies of Selected Molecular Orbitals of 1^- (*S*=0)

MO	energy (eV)	composition		
		Ru	L	$acac^-$
HOMO–5	–2.966	0.08	0.40	0.52
HOMO–4	–2.810	0.08	0.60	0.33
HOMO–3	–2.341	0.24	0.55	0.21
HOMO–2	–1.751	0.76	0.10	0.14
HOMO–2	–1.476	0.64	0.13	0.23
HOMO	–0.723	0.49	0.39	0.12
LUMO	1.473	0.10	0.87	0.02
LUMO+1	2.243	0.03	0.06	0.91
LUMO+2	2.395	0.05	0.06	0.89
LUMO+3	2.615	0.02	0.96	0.01
LUMO+4	2.824	0.05	0.93	0.01
LUMO+5	2.993	0.05	0.92	0.03

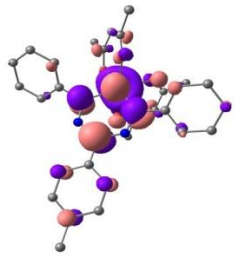
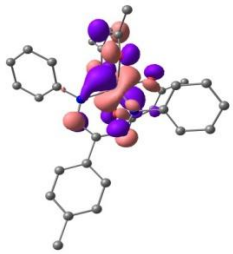
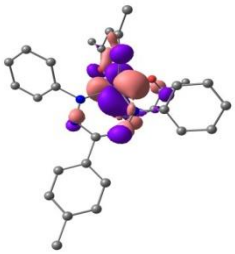
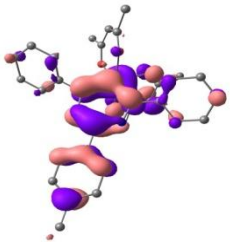
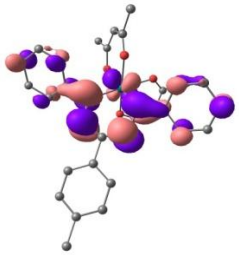
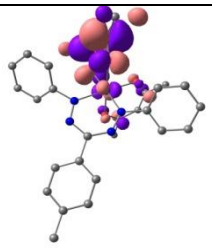
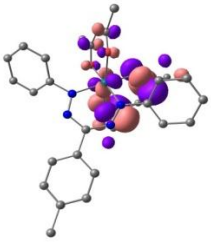
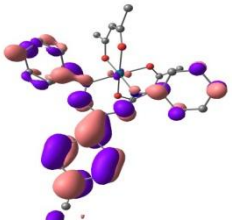
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14. Composition and Energies of Selected Molecular Orbitals of 2^+ (*S*=0)

MO	energy (eV)	composition		
		Ru	L	bpy
HOMO–5	–8.501	0.11	0.64	0.25
HOMO–4	–8.445	0.46	0.35	0.18
HOMO–3	–8.302	0.07	0.91	0.02
HOMO–2	–8.193	0.56	0.20	0.24
HOMO–2	–7.935	0.36	0.43	0.20
HOMO	–7.044	0.19	0.64	0.17
LUMO	–5.676	0.06	0.10	0.85
LUMO+1	–4.795	0.07	0.28	0.65
LUMO+2	–4.745	0.09	0.52	0.40
LUMO+3	–4.137	0.04	0.09	0.87
LUMO+4	–3.887	0.05	0.04	0.90
LUMO+5	–3.700	0.09	0.04	0.87

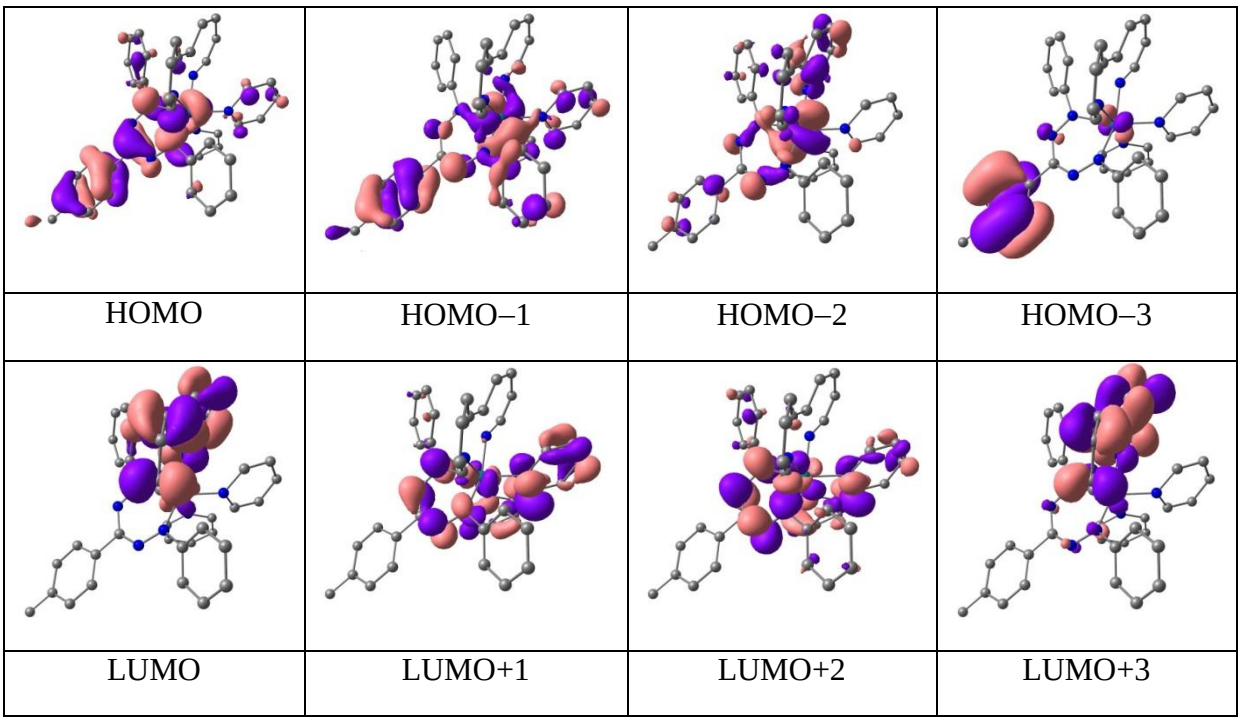


Table S15. Composition and Energies of Selected Molecular Orbitals of 2^{2+} (*S*=1/2)

MO	energy (eV)	composition		
		Ru	L	bpy
		α-spin		
HOMO–5	–11.546	0.07	0.85	0.08
HOMO–4	–11.470	0.62	0.26	0.12
HOMO–3	–11.384	0.18	0.78	0.04
HOMO–2	–11.329	0.66	0.25	0.09
HOMO–2	–11.262	0.17	0.80	0.02
SOMO	–10.391	0.14	0.83	0.03
LUMO	–7.661	0.08	0.89	0.04
LUMO+1	–7.353	0.06	0.02	0.92
LUMO+2	–7.317	0.04	0.02	0.95
LUMO+3	–6.484	0.03	0.06	0.91
LUMO+4	–6.356	0.04	0.04	0.92
LUMO+5	–6.213	0.00	0.01	0.99
		β-spin		
HOMO–5	–11.540	0.02	0.95	0.03
HOMO–4	–11.393	0.28	0.62	0.09
HOMO–3	–11.392	0.63	0.24	0.12
HOMO–2	–11.270	0.72	0.19	0.09
HOMO–1	–11.178	0.07	0.93	0.01
HOMO	–10.928	0.41	0.52	0.06
LUMO	–8.954	0.19	0.76	0.04
LUMO+1	–7.358	0.05	0.10	0.86
LUMO+2	–7.301	0.05	0.02	0.93
LUMO+3	–7.283	0.09	0.80	0.11
LUMO+4	–6.478	0.03	0.06	0.91
LUMO+5	–6.354	0.04	0.04	0.92

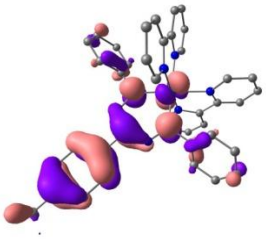
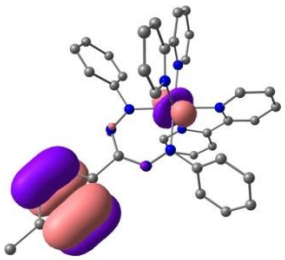
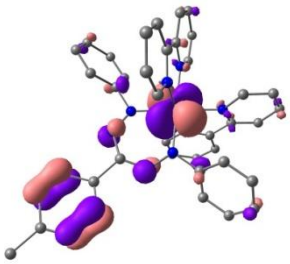
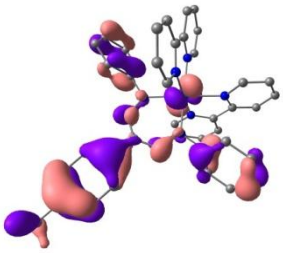
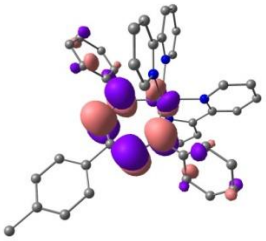
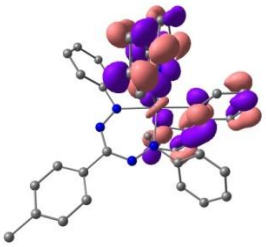
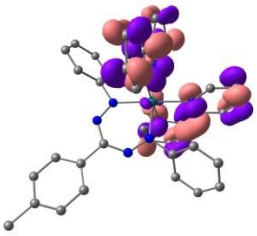
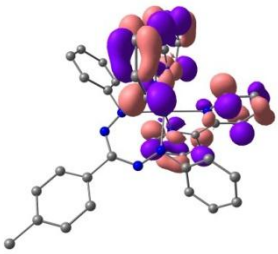
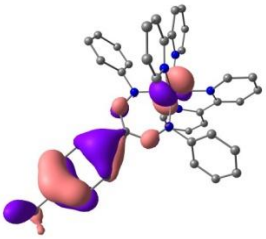
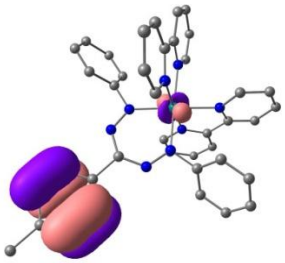
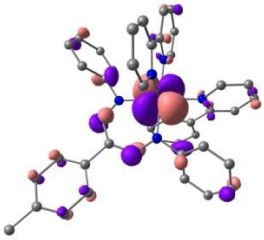
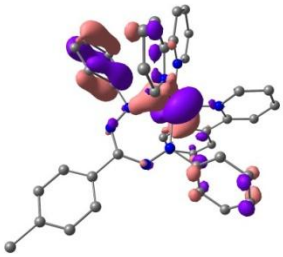
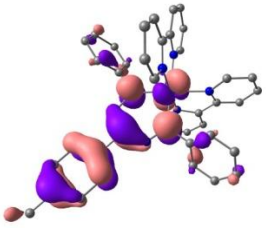
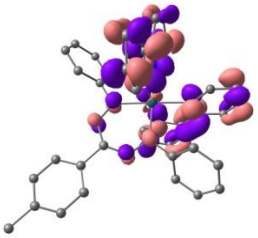
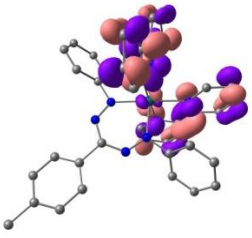
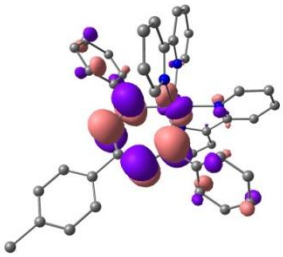
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16. Composition and Energies of Selected Molecular Orbitals of 2 (*S*=1/2)

MO	energy (eV)	composition		
		Ru	L	bpy
		α-spin		
HOMO–5	–5.771	0.09	0.86	0.05
HOMO–4	–5.395	0.49	0.39	0.12
HOMO–3	–5.382	0.80	0.08	0.12
HOMO–2	–5.057	0.80	0.10	0.10
HOMO–1	–4.213	0.29	0.65	0.06
SOMO	–2.511	0.06	0.02	0.92
LUMO	–1.905	0.05	0.02	0.93
LUMO+1	–1.435	0.09	0.87	0.05
LUMO+2	–0.850	0.04	0.07	0.89
LUMO+3	–0.705	0.05	0.03	0.91
LUMO+4	–0.600	-	0.01	0.98
LUMO+5	–0.571	0.03	0.04	0.93
		β-spin		
HOMO–5	–5.960	-	-	1.00
HOMO–4	–5.767	0.09	0.85	0.06
HOMO–3	–5.392	0.49	0.39	0.12
HOMO–2	–5.252	0.79	0.08	0.13
HOMO–1	–5.023	0.80	0.09	0.11
HOMO	–4.212	0.29	0.65	0.05
LUMO	–1.466	0.05	0.53	0.43
LUMO+1	–1.388	0.05	0.02	0.93
LUMO+2	–1.369	0.10	0.41	0.49
LUMO+3	–0.815	0.04	0.07	0.89
LUMO+4	–0.652	0.06	0.03	0.91
LUMO+5	–0.481	-	0.02	0.98

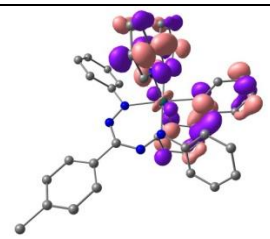
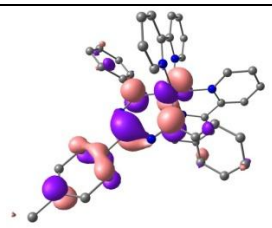
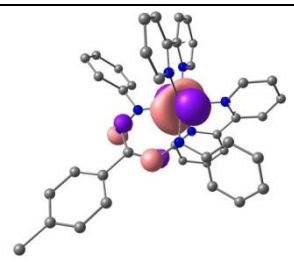
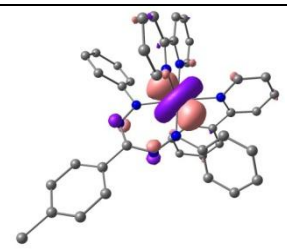
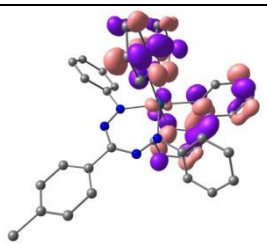
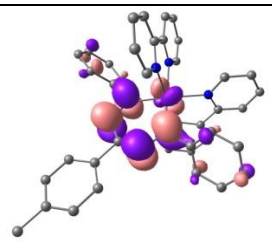
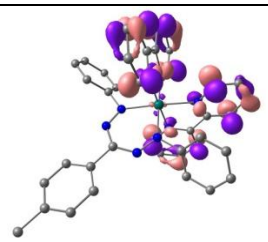
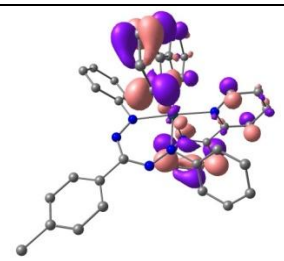
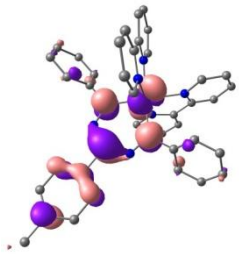
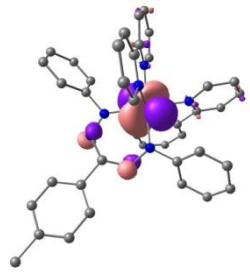
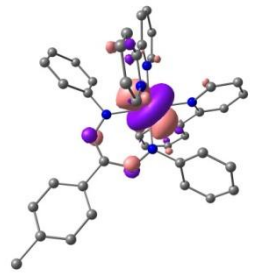
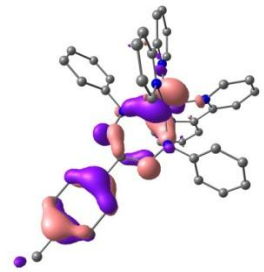
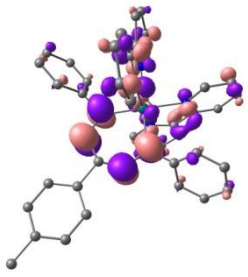
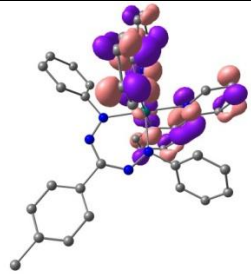
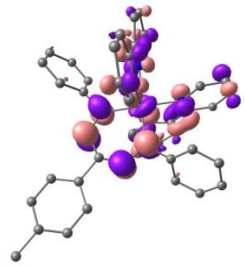
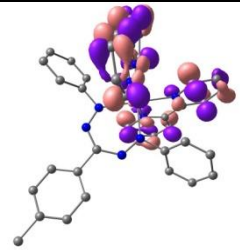
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17. Composition and Energies of Selected Molecular Orbitals of 2^{-} (*S*=1)

MO	energy (eV)	composition		
		Ru	L	bpy
		α-spin		
HOMO−5	−2.721	0.39	0.49	0.12
HOMO−4	−2.370	0.79	0.08	0.13
HOMO−3	−2.057	0.77	0.12	0.11
HOMO−2	−1.526	0.41	0.51	0.08
SOMO2	0.133	0.05	0.05	0.90
SOMO1	0.227	0.06	0.02	0.92
LUMO	1.203	0.12	0.83	0.06
LUMO+1	2.259	0.07	0.18	0.75
LUMO+2	2.421	0.06	0.06	0.88
LUMO+3	2.455	0.05	0.85	0.10
LUMO+4	2.509	-	0.03	0.97
LUMO+5	2.526	0.04	0.06	0.90
		β-spin		
HOMO−5	−3.124	0.07	0.03	0.91
HOMO−4	−3.061	0.02	0.31	0.67
HOMO−3	−2.632	0.34	0.51	0.15
HOMO−2	−2.260	0.78	0.09	0.13
HOMO−1	−1.983	0.75	0.10	0.15
HOMO	−1.442	0.46	0.47	0.08
LUMO	1.229	0.10	0.86	0.04
LUMO+1	1.750	0.07	0.05	0.88
LUMO+2	1.829	0.06	0.05	0.89
LUMO+3	2.327	0.07	0.26	0.67
LUMO+4	2.477	0.06	0.77	0.17
LUMO+5	2.518	0.06	0.06	0.87

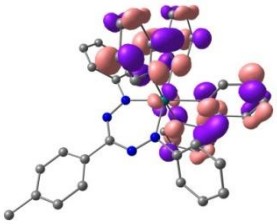
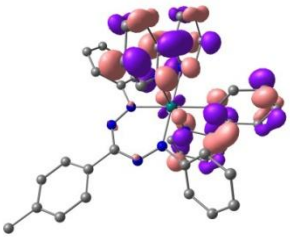
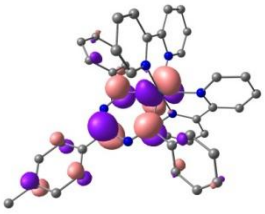
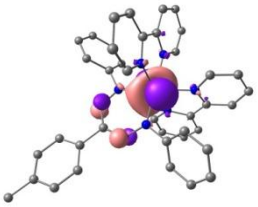
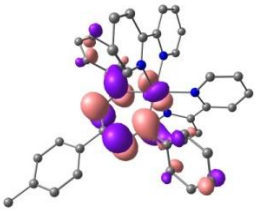
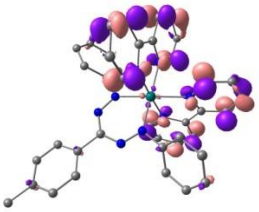
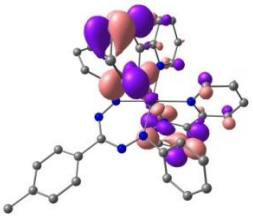
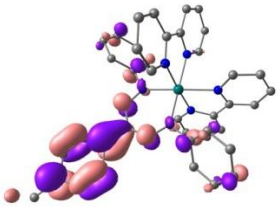
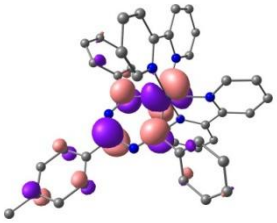
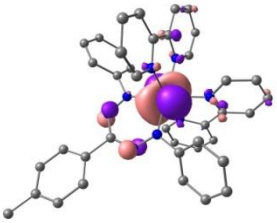
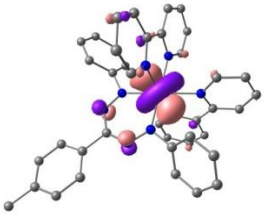
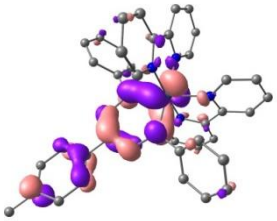
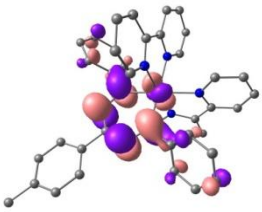
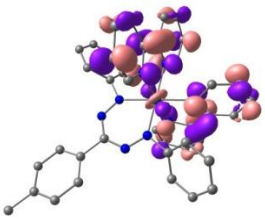
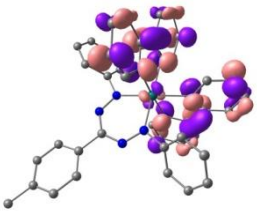
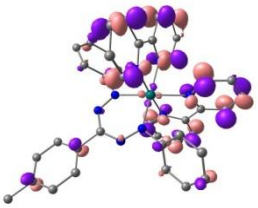
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18. Composition and Energies of Selected Molecular Orbitals of 3^+ (*S*=0)

MO	energy (eV)	composition		
		Ru	L	pap
HOMO–5	–9.074	0.17	0.73	0.10
HOMO–4	–9.000	0.13	0.70	0.17
HOMO–3	–8.813	0.62	0.15	0.23
HOMO–2	–8.530	0.27	0.64	0.08
HOMO–1	–8.081	0.01	0.99	-
HOMO	–6.963	0.06	0.86	0.09
LUMO	–5.770	0.13	0.03	0.84
LUMO+1	–5.697	0.14	0.05	0.81
LUMO+2	–4.321	0.05	0.81	0.14
LUMO+3	–4.129	0.04	0.13	0.83
LUMO+4	–3.980	0.03	0.03	0.93
LUMO+5	–3.112	0.12	0.10	0.78

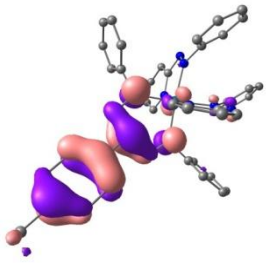
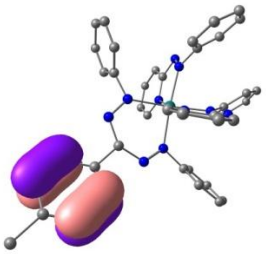
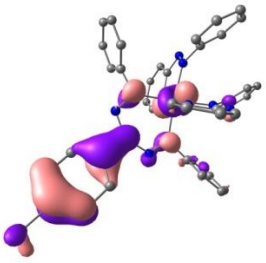
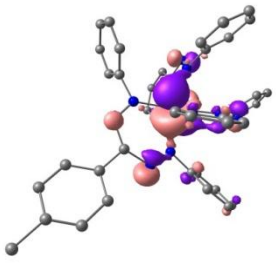
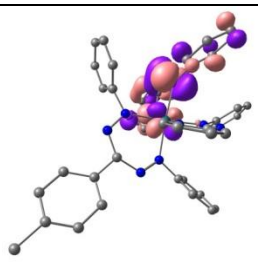
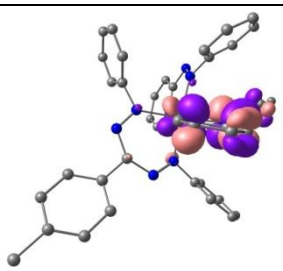
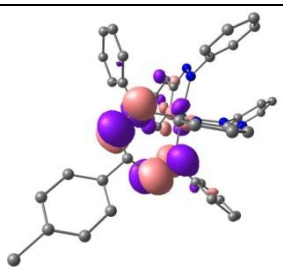
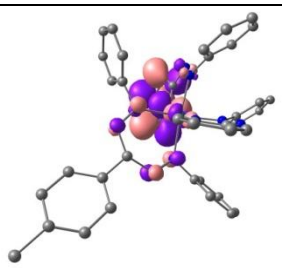
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19. Composition and Energies of Selected Molecular Orbitals of 3^{2+} (*S*=1/2)

MO	energy (eV)	composition		
		Ru	L	pap
		α-spin		
HOMO–5	–11.651	0.06	0.40	0.54
HOMO–4	–11.615	0.03	0.91	0.05
HOMO–3	–11.563	0.05	0.59	0.36
HOMO–2	–11.560	0.04	0.70	0.26
HOMO–2	–11.434	0.39	0.09	0.52
SOMO	–10.660	0.12	0.85	0.03
LUMO	–8.333	0.09	0.02	0.89
LUMO+1	–8.181	0.08	0.02	0.90
LUMO+2	–7.918	0.08	0.89	0.03
LUMO+3	–6.466	0.06	0.04	0.90
LUMO+4	–6.435	0.02	0.04	0.94
LUMO+5	–5.904	0.43	0.30	0.27
		β-spin		
HOMO–5	–11.608	0.13	0.18	0.69
HOMO–4	–11.592	0.29	0.67	0.04
HOMO–3	–11.503	0.23	0.47	0.29
HOMO–2	–11.470	0.04	0.86	0.10
HOMO–1	–11.420	0.38	0.15	0.47
HOMO	–11.268	0.26	0.68	0.06
LUMO	–9.281	0.11	0.83	0.06
LUMO+1	–8.329	0.09	0.02	0.89
LUMO+2	–8.145	0.10	0.03	0.87
LUMO+3	–7.532	0.08	0.88	0.04
LUMO+4	–6.465	0.06	0.04	0.90
LUMO+5	–6.428	0.02	0.03	0.95

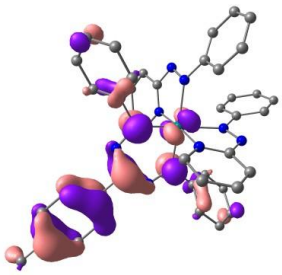
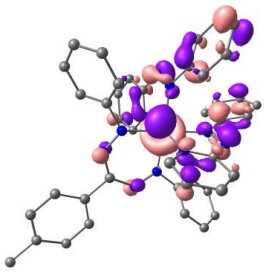
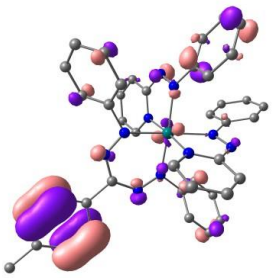
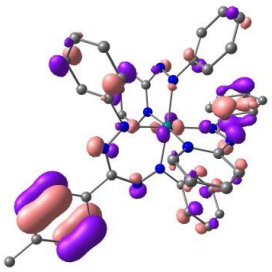
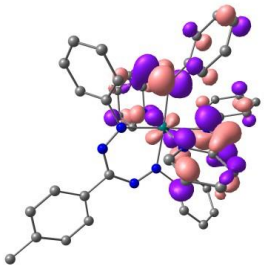
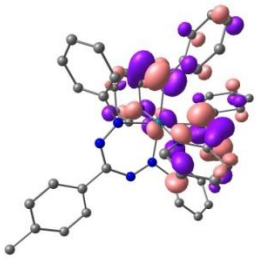
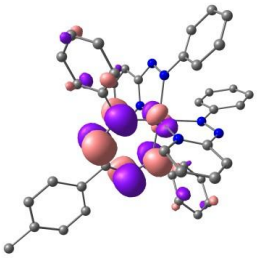
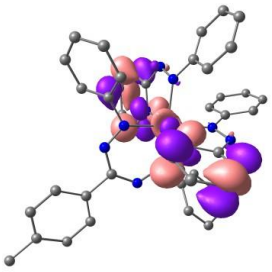
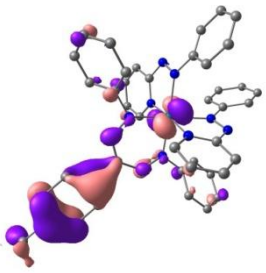
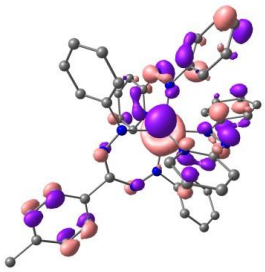
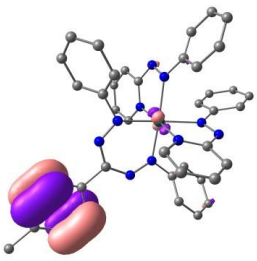
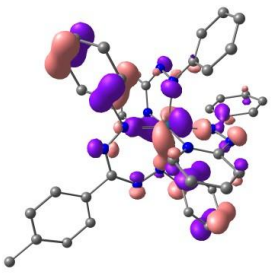
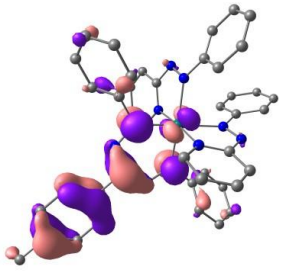
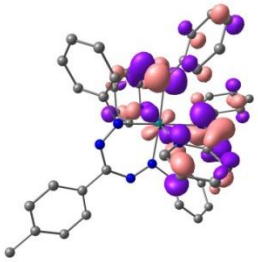
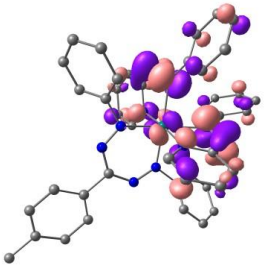
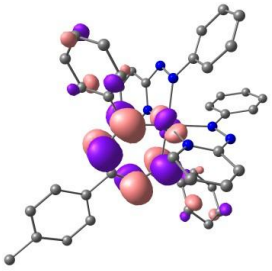
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20. Composition and Energies of Selected Molecular Orbitals of 3 (*S*=1/2)

MO	energy (eV)	composition		
		Ru	L	pap
		α-spin		
HOMO–5	–6.068	0.15	0.72	0.14
HOMO–4	–6.053	0.74	0.14	0.12
HOMO–3	–5.713	0.39	0.37	0.24
HOMO–2	–5.518	0.69	0.11	0.20
HOMO–1	–4.623	0.18	0.73	0.09
SOMO	–3.664	0.10	0.02	0.87
LUMO	–2.755	0.15	0.04	0.82
LUMO+1	–1.796	0.08	0.88	0.03
LUMO+2	–0.982	0.05	0.04	0.91
LUMO+3	–0.958	0.04	0.03	0.93
LUMO+4	–0.131	0.14	0.61	0.25
LUMO+5	–0.075	0.10	0.07	0.83
		β-spin		
HOMO–5	–6.197	-	0.04	0.96
HOMO–4	–6.082	0.20	0.65	0.15
HOMO–3	–5.833	0.77	0.10	0.13
HOMO–2	–5.732	0.34	0.42	0.25
HOMO–1	–5.460	0.67	0.10	0.23
HOMO	–4.646	0.19	0.76	0.05
LUMO	–2.363	0.10	0.03	0.87
LUMO+1	–2.190	0.10	0.03	0.87
LUMO+2	–1.796	0.08	0.88	0.04
LUMO+3	–0.905	0.05	0.04	0.91
LUMO+4	–0.885	0.03	0.03	0.93
LUMO+5	–0.112	0.14	0.71	0.15

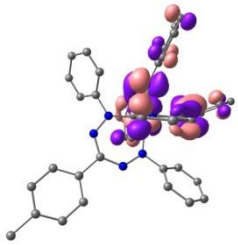
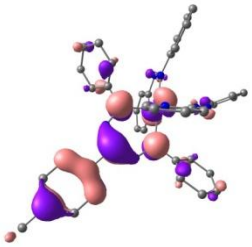
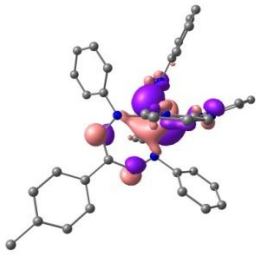
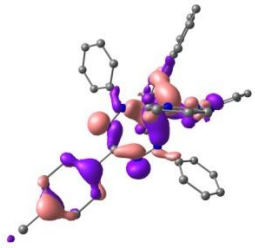
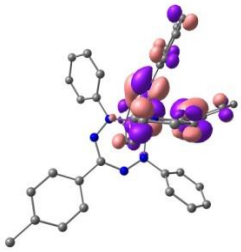
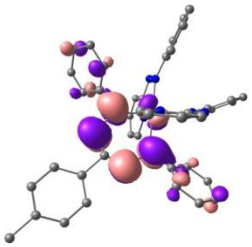
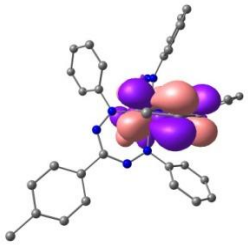
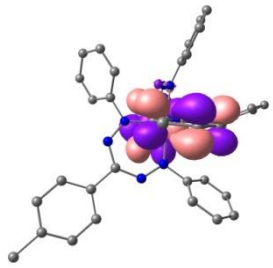
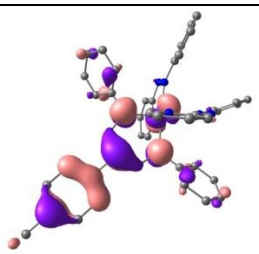
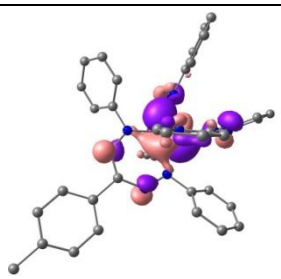
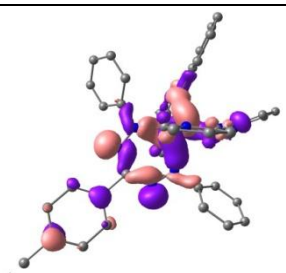
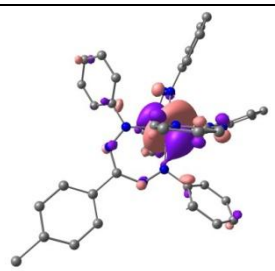
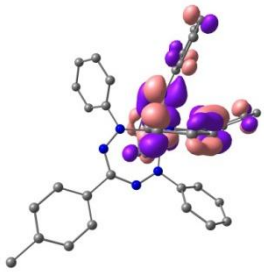
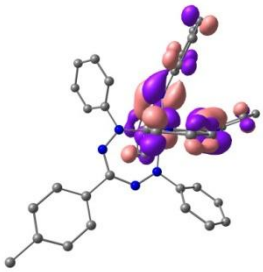
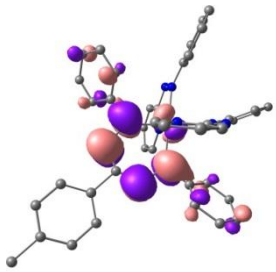
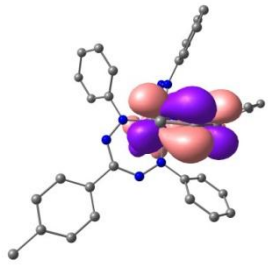
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21. Composition and Energies of Selected Molecular Orbitals of 3^{-} (*S*=1)

MO	energy (eV)	composition		
		Ru	L	pap
		α-spin		
HOMO−5	−2.992	0.76	0.07	0.17
HOMO−4	−2.945	0.25	0.42	0.33
HOMO−3	−2.368	0.66	0.12	0.21
HOMO−2	−1.989	0.27	0.62	0.11
SOMO2	−0.982	0.13	0.02	0.84
SOMO1	−0.724	0.14	0.04	0.82
LUMO	0.894	0.10	0.87	0.03
LUMO+1	2.045	0.05	0.08	0.87
LUMO+2	2.053	0.05	0.04	0.91
LUMO+3	2.213	0.04	0.90	0.07
LUMO+4	2.587	0.07	0.84	0.09
LUMO+5	2.595	0.03	0.92	0.06
		β-spin		
HOMO−5	−3.194	0.22	0.05	0.73
HOMO−4	−2.991	0.11	0.07	0.82
HOMO−3	−2.791	0.21	0.46	0.33
HOMO−2	−2.671	0.78	0.08	0.14
HOMO−1	−2.184	0.61	0.11	0.29
HOMO	−1.817	0.41	0.50	0.09
LUMO	0.751	0.08	0.24	0.69
LUMO+1	0.941	0.12	0.69	0.19
LUMO+2	1.095	0.12	0.04	0.84
LUMO+3	2.147	0.03	0.36	0.61
LUMO+4	2.169	0.06	0.05	0.90
LUMO+5	2.242	0.05	0.62	0.33

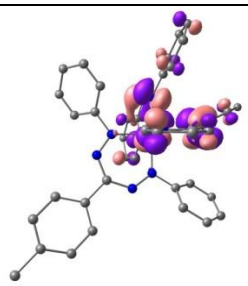
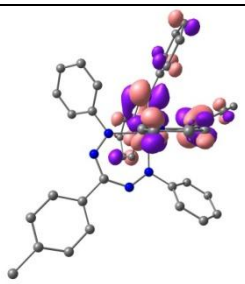
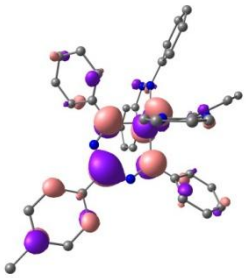
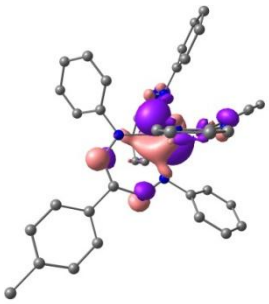
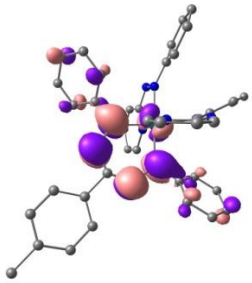
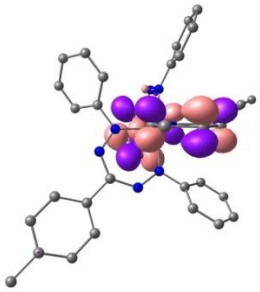
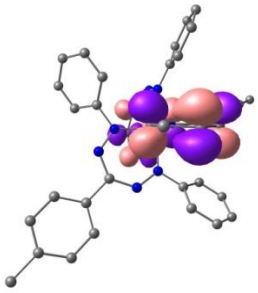
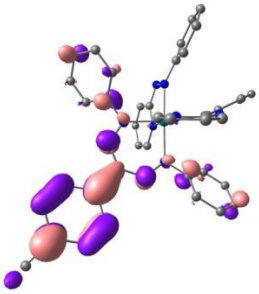
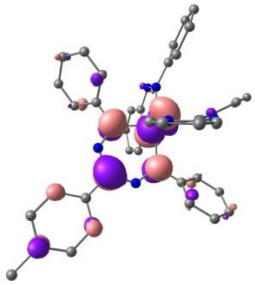
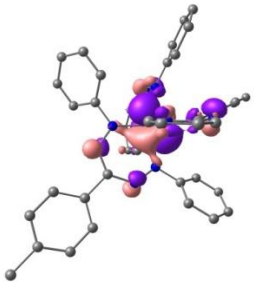
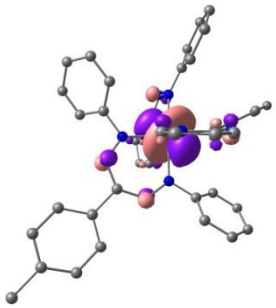
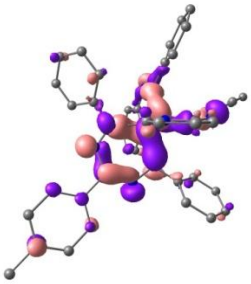
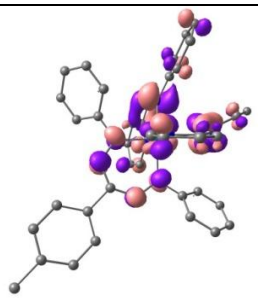
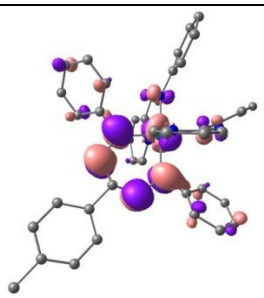
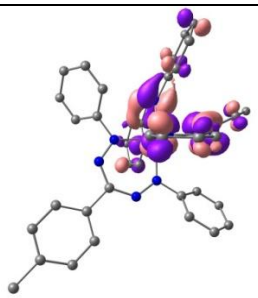
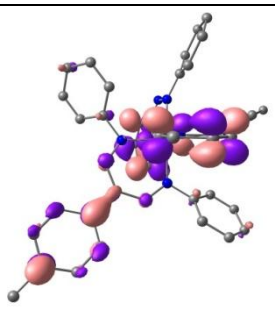
α-spin			
			
SOMO1	SOMO2	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22. Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) Optimized Structures of $\mathbf{1}^{n}$

compd	$E_{(S=0)}$ (Hartrees)	$E_{(S=1/2)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$E_{(S=3/2)}$ (Hartrees)	$\Delta E_{(\mathrm{HE-LE})}{}^{a}$
$\mathbf{1}^{+}$	−1775.4708		−1775.4607		0.0101 Hartrees 26.518 kJ mol^{-1} 2216 cm^{-1}
1		−1775.6829			
$\mathbf{1}^{-}$	−1775.7547		−1775.7320		0.0227 Hartrees 59.599 kJ mol^{-1} 4982 cm^{-1}

[a]HE = spin state higher in energy, LE = spin state lower in energy.

Table S23. Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) Optimized Structures of 2^n

compd	$E_{(S=0)}$ (Hartrees)	$E_{(S=1/2)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$E_{(S=3/2)}$ (Hartrees)	$\Delta E_{(\mathrm{HE-LE})}{}^{a}$
$\mathbf{2}^{2+}$		–2075.6039			
$\mathbf{2}^{+}$	–2075.8896		–2075.8529		0.0367 Hartrees 96.356 kJ mol^{-1} 8055 cm^{-1}
2		–2076.0280			
$\mathbf{2}^{-}$	–2076.0516		–2076.0658		0.0142 Hartrees 37.282 kJ mol^{-1} 3116 cm^{-1}

[a]HE = spin state higher in energy, LE = spin state lower in energy.

Table S24. Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) Optimized Structures of $\mathbf{3}^{n}$

compd	$E_{(S=0)}$ (Hartrees)	$E_{(S=1/2)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$E_{(S=3/2)}$ (Hartrees)	$\Delta E_{(\mathrm{HE-LE})}{}^{a}$
$\mathbf{3}^{2+}$		–2262.4148			
$\mathbf{3}^{+}$	–2262.7127		–2262.6873		0.0254 Hartrees 66.688 kJ mol^{-1} 5575 cm^{-1}
3		–2262.8911			
$\mathbf{3}^{-}$	–2262.9511		–2262.9627		0.0116 Hartrees 30.456 kJ mol^{-1} 2546 cm^{-1}

[a]HE = spin state higher in energy, LE = spin state lower in energy.

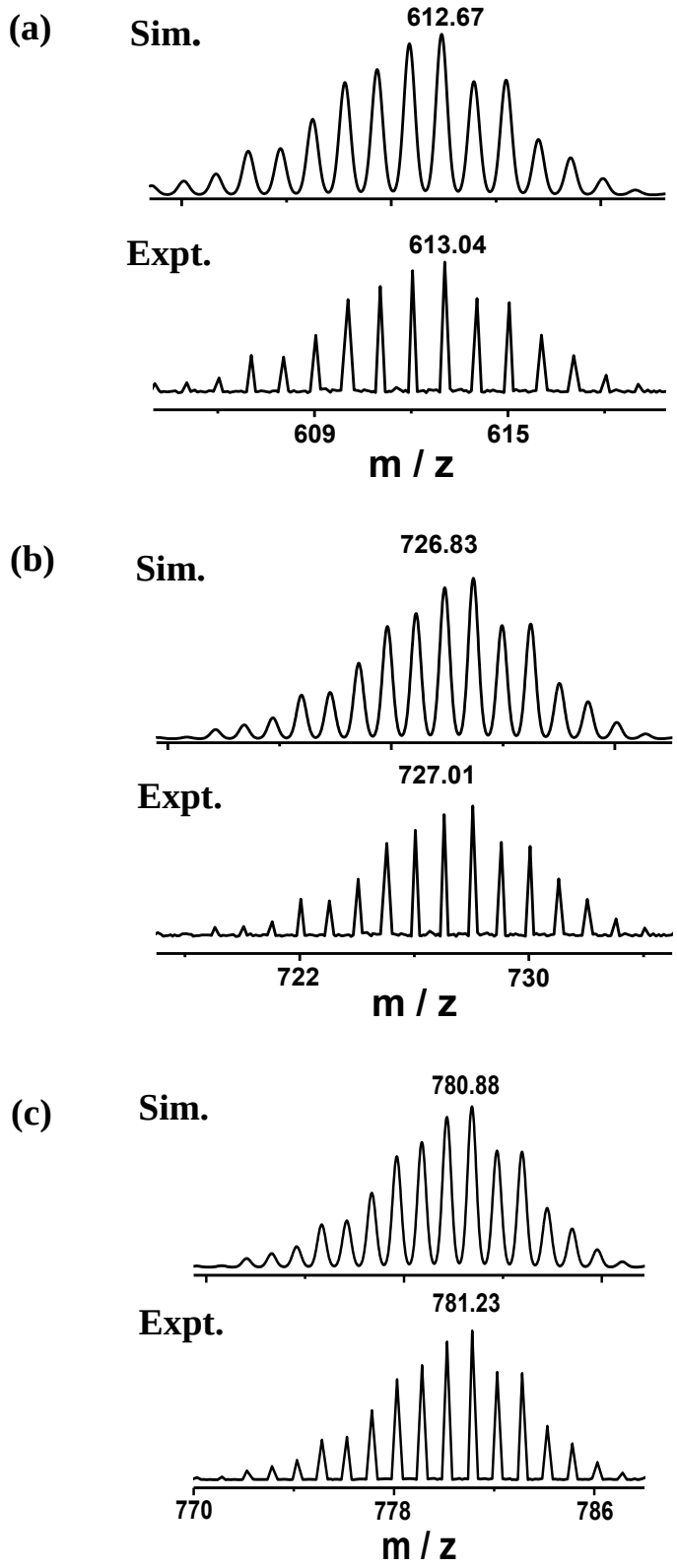


Figure S1. ESI-MS(+) spectra of (a) [**1**]$^{+}$, (b) [**2**]$^{+}$ and (c) [**3**]$^{+}$ in CH_3CN.

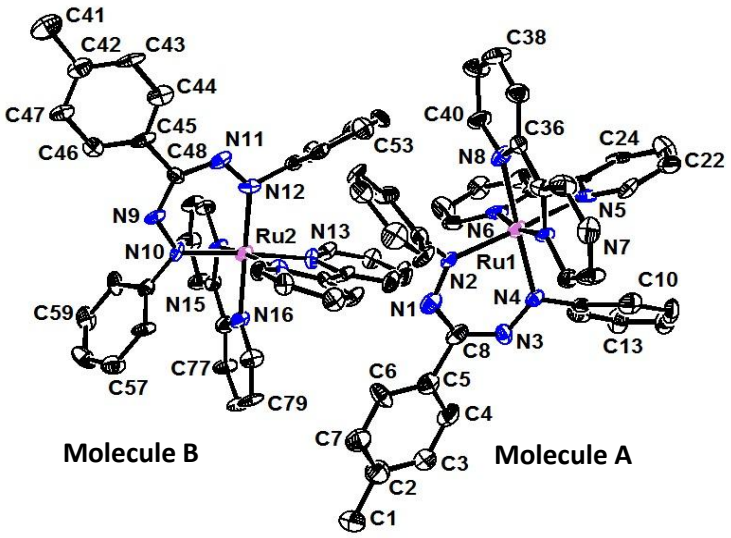


Figure S2. Cationic parts of [**2**]ClO_4 in the crystal. The asymmetric unit exhibits two independent molecules. Ellipsoids are drawn at 50% probability level. Hydrogen atoms are removed for clarity.

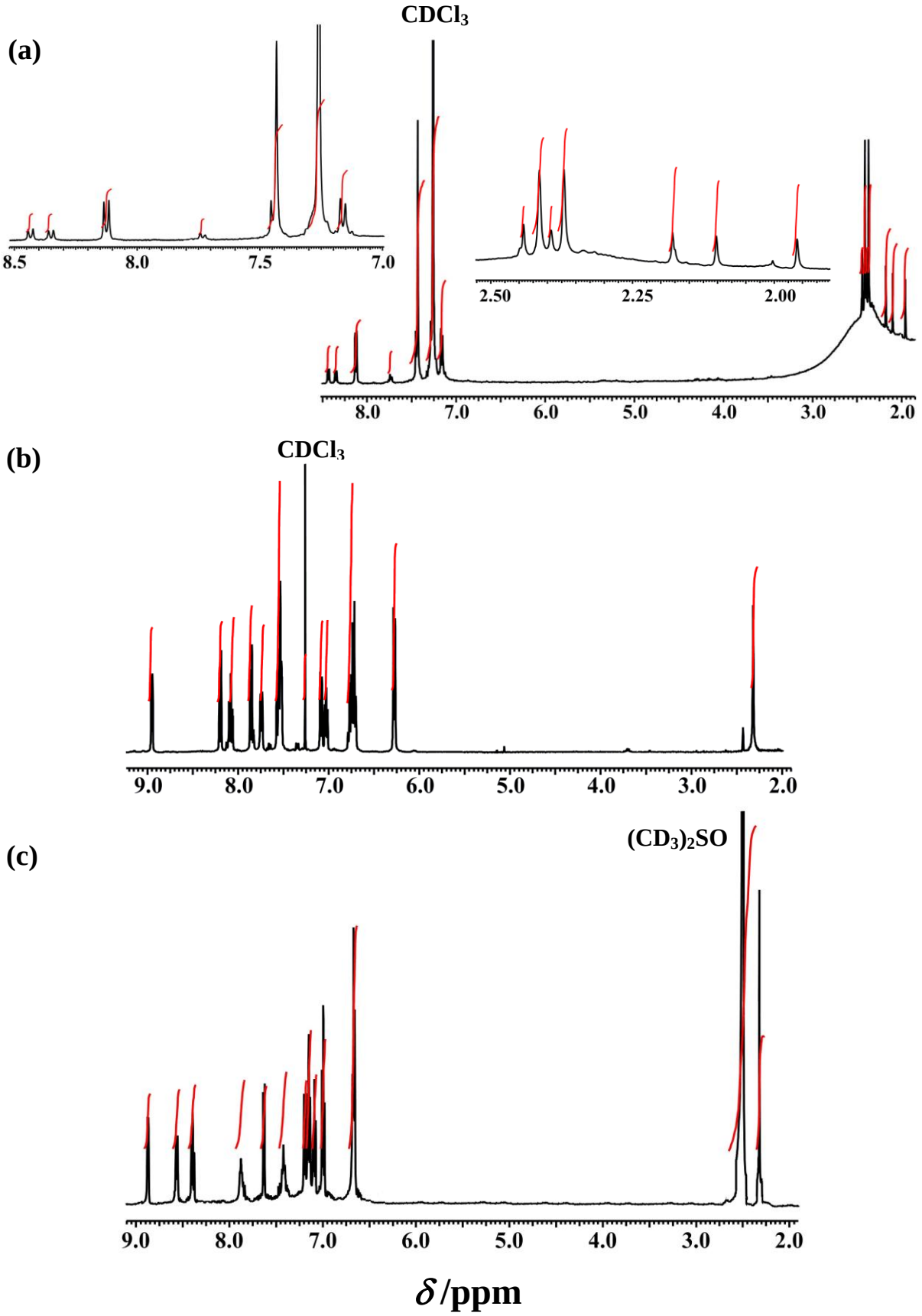


Figure S3. ^{1}H NMR spectra of (a) **1** in $CDCl_3$ (insets show the expanded parts), (b)[**2**]ClO_4 in $CDCl_3$ and (b) [**3**]ClO_4 in $(CD_3)_2SO$.

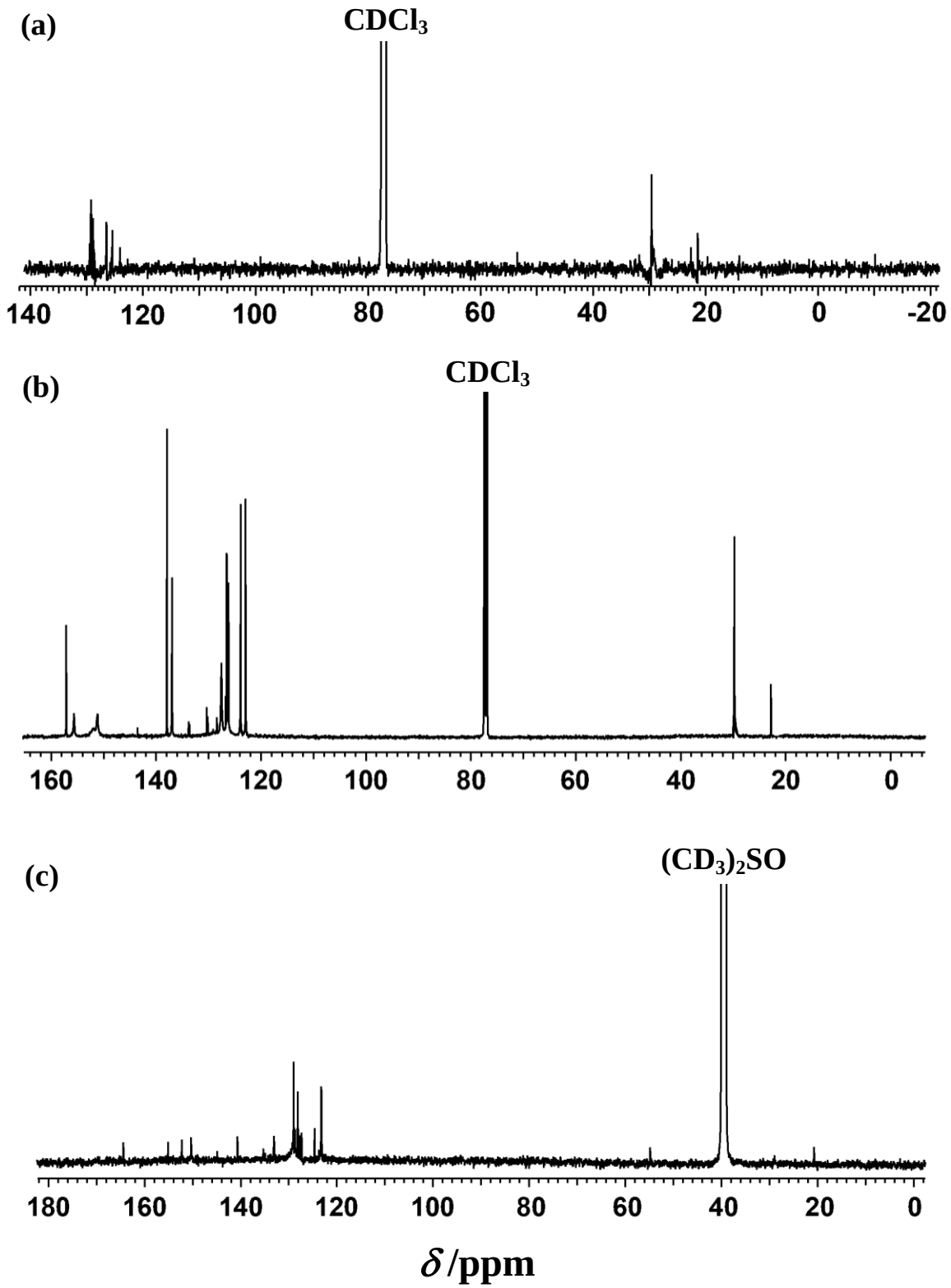


Figure S4. ^{13}C NMR spectra of (a) **1** in $CDCl_3$, (b)[**2**]ClO_4 in $CDCl_3$ and (b) [**3**]ClO_4 in $(CD_3)_2SO$.

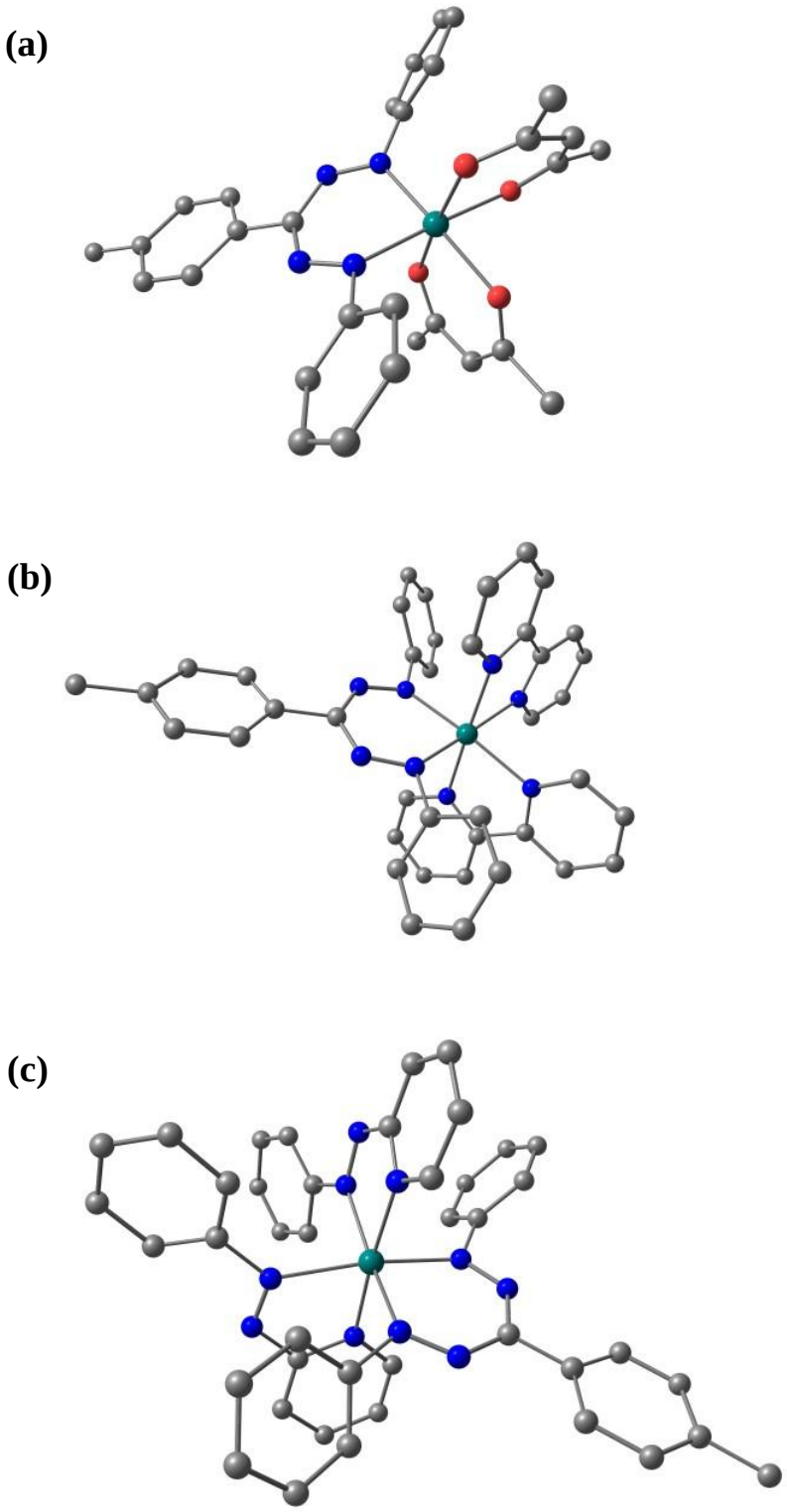


Figure S5. DFT ((U)B3LYP/LanL2DZ/6-31G*) optimized structures of (a) **1** (*S*=1/2), (b) $\mathbf{2}^{+}$ (*S*=0) and (c) $\mathbf{3}^{+}$ (*S*=0).

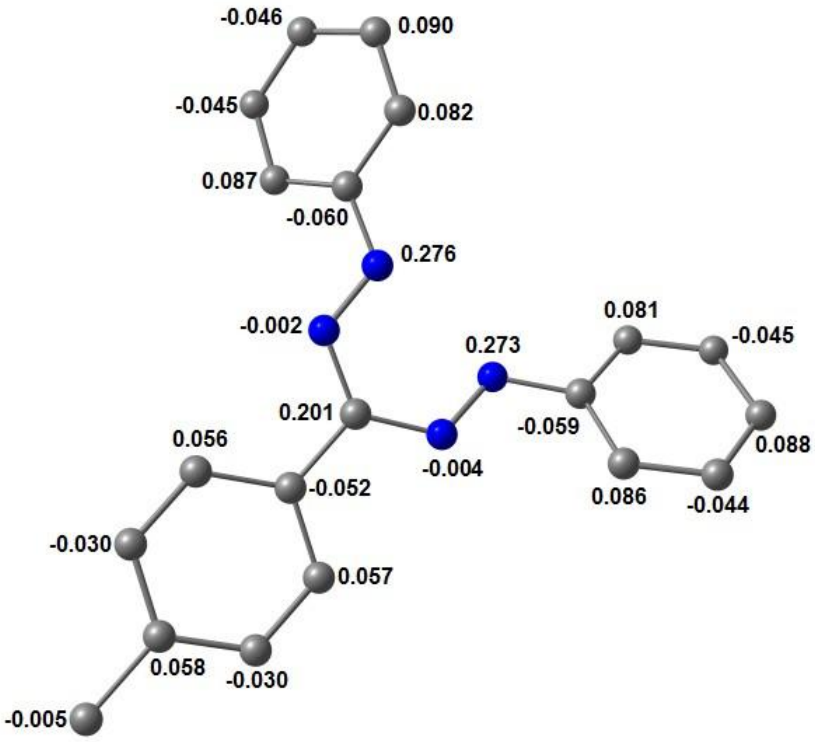


Figure S6. DFT calculated (UB3LYP/6-31G*) Mulliken spin densities on specific atoms of $\mathbf{L}^{\bullet}$ (S=1/2).

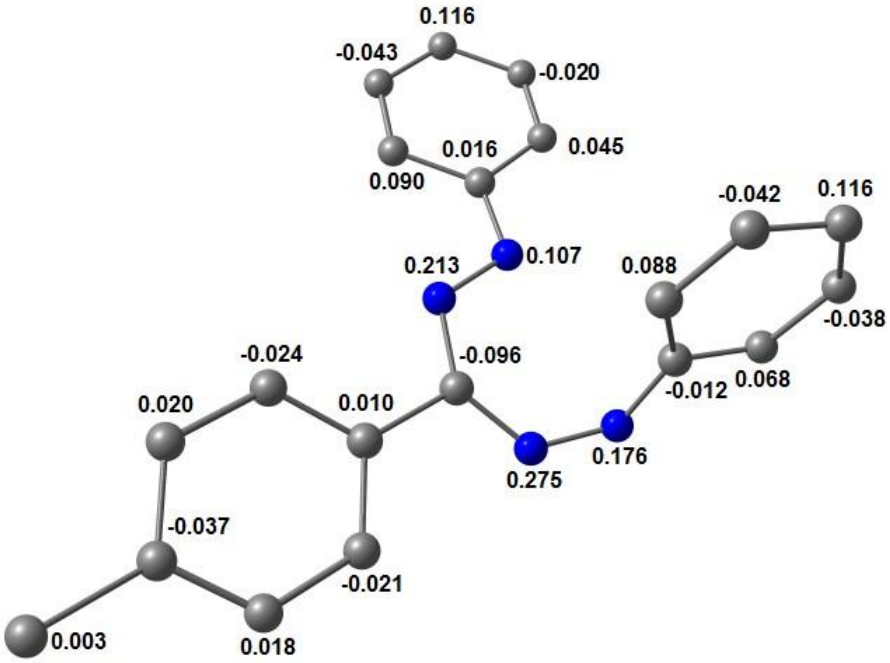


Figure S7. DFT calculated (UB3LYP/6-31G*) Mulliken spin densities on specific atoms of $\mathbf{L}^{\bullet 2-}$ (S=1/2).

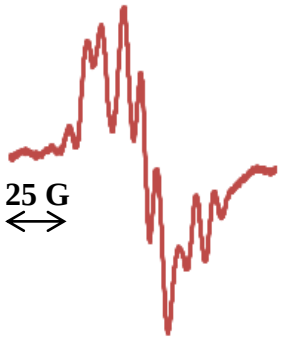


Figure S8. EPR spectrum of reduced [**2**](ClO_4) at 298 K in CH_2Cl_2/0.1 M Bu_4NPF_6.

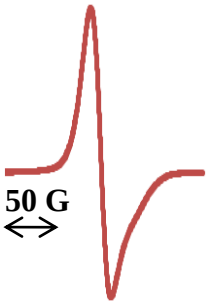


Figure S9. EPR signal of oxidized [**3**](ClO_4) at 120 K in CH_2Cl_2/0.1 M Bu_4NPF_6.

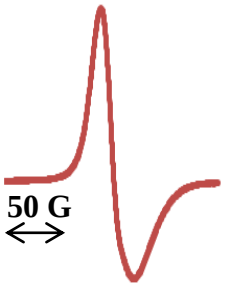


Figure S10. EPR signal of reduced [**3**](ClO_4) at 120 K CH_2Cl_2/0.1 M Bu_4NPF_6.

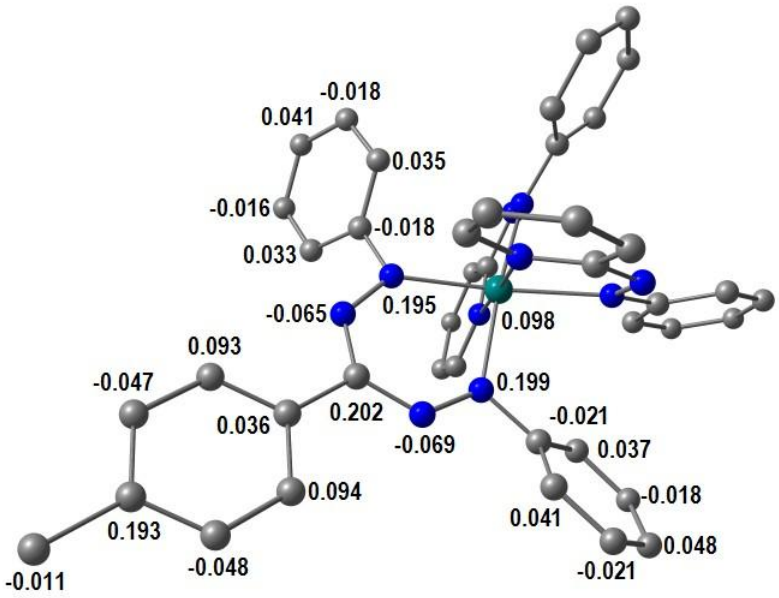


Figure S11. DFT calculated (UB3LYP/LanL2DZ/6-31G*) Mulliken spin densities on specific atoms of $\mathbf{3}^{2+}$ (S=1/2).