On the non-innocence and reactive *versus* non-reactive nature of α-diketones in a set of diruthenium frameworks

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Table S1 Selected crystallographic data

	[2]$(ClO4)_2$•C_6H_6	**[3]**$(ClO4)_2$
empirical formula	$C_{60}H_{46}Cl_2N_8O_{12}Ru_2$	$C_{58}H_{44}Cl_2N_{12}O_{12}Ru_2$
formula weight	1344.09	1374.09
crystal system	Triclinic	monoclinic
space group	*P*ī	*P*2/n
a (Å)	15.5752(6)	13.6797(7)
b (Å)	15.6427(5)	10.7866(6)
c (Å)	16.7119(7)	19.9547(14)
α (deg)	102.235(3)	90
β (deg)	103.995(3)	95.896(6)
γ (deg)	115.029(3)	90
V (Å^3)	3343.3(2)	2928.9(3)
Z	2	2
μ (mm^{-1})	0.592	0.680
T (K)	150(2)	150(2)
ρ_{calcd} (g cm^{-3})	1.335	1.558
F (000)	1360	1388
θ range (deg)	25.252 to 2.028	26.370 to 2.409
data / restraints / parameters	12099/2140/1012	5993/58/435
R_1, wR_2 [$I > 2\sigma(I)$]	0.0914, 0.2169	0.0797, 0.1737
R_1, wR_2(all data)	0.1410, 0.2586	0.1279, 0.2082
GOF on F^2	1.041	1.049
largest difference in peak and hole (e Å^{-3})	1.383, -0.919	1.329, -0.777

Table S2 Selected DFT calculated bond lengths [Å] for **1a**^{n}

Bond	DFT				
	1a	**1a**$^{+}$	**1a**$^{2+}$	**1a**$^{-}$	**1a**$^{2-}$
Ru1-O1	2.001	2.000	1.966	2.012	2.065
Ru1-O2	2.074	2.073	2.090	2.070	2.073
Ru1-O5	2.040	2.016	1.993	2.071	2.098
Ru1-O6	2.057	2.036	2.022	2.074	2.097
Ru1-O7	2.041	2.030	2.016	2.047	2.080
Ru1-O8	2.035	2.012	1.990	2.065	2.088
Ru2-O3	2.076	2.068	1.967	2.036	2.068
Ru2-O4	2.001	1.987	2.085	2.066	2.067
Ru2-O9	2.036	2.008	1.989	2.073	2.099
Ru2-O10	2.030	2.018	2.015	2.072	2.085
Ru2-O11	2.063	2.034	2.017	2.068	2.087
Ru2-O12	2.041	2.013	1.991	2.063	2.088
C7-O2	1.254	1.256	1.257	1.257	1.258
C8-O3	1.254	1.256	1.535	1.529	1.536
C7-C8	1.531	1.530	1.257	1.257	1.257

Table S3 Selected DFT calculated bond angles [deg] for **1a**^{n}

Bond	DFT				
	1a	**1a**$^{+}$	**1a**$^{2+}$	**1a**$^{-}$	**1a**$^{2-}$
O1-Ru1-O2	89.39	88.51	87.37	90.27	90.15
O5-Ru1-O6	89.81	89.31	88.10	90.40	91.57
O7-Ru1-O8	93.40	92.61	91.55	92.75	91.87
O1-Ru1-O5	179.84	179.55	179.19	178.79	178.19
O2-Ru1-O8	179.51	178.47	177.33	179.13	178.64
O6-Ru1-O7	178.01	178.31	177.19	178.16	178.35
O3-Ru2-O4	89.23	88.26	87.35	90.08	90.36
O9-Ru2-O10	93.31	92.02	88.21	91.22	91.69
O11-Ru2-O12	89.53	88.93	91.52	91.21	92.08
O3-Ru2-O9	178.83	178.32	179.62	178.71	178.26
O4-Ru2-O12	179.50	179.55	177.38	179.12	179.12
O10-Ru2-O11	177.98	178.04	176.99	178.21	178.08

Table S4 Selected experimental and DFT calculated bond lengths [Å] for $\mathbf{2}^{n}$ ¥

Bond	X-ray	DFT					
	$\mathbf{2}^{2+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$	$\mathbf{2}^{4+}$	$\mathbf{2}^{+}$	**2**	$\mathbf{2}^{-}$
Ru1-O1	2.047(6)	2.073	2.031	1.982	2.087	2.103	2.107
Ru1-O2	2.042(5)	2.105	2.120	2.150	2.091	2.110	2.111
Ru1-N1A	2.025(16)	2.093	2.109	2.126	2.086	2.071	2.079
Ru1-N2A	2.147(12)	2.097	2.115	2.136	2.092	2.095	2.099
Ru1-N3	2.067(6)	2.091	2.097	2.097	2.095	2.095	2.097
Ru1-N4	2.038(6)	2.078	2.084	2.080	2.067	2.055	2.062
Ru2-O3	2.035(5)	2.115	2.134	2.159	2.107	2.120	2.128
Ru2-O4	2.053(6)	2.073	2.034	1.982	2.091	2.101	2.108
Ru2-N5	2.029(7)	2.081	2.086	2.081	2.061	2.055	2.066
Ru2-N6	2.049(8)	2.095	2.100	2.098	2.091	2.094	2.101
Ru2-N7	2.023(15)	2.093	2.112	2.133	2.097	2.097	2.101
Ru2-N8	2.007(12)	2.093	2.110	2.130	2.089	2.071	2.075
C7-O2	1.265(9)	1.265	1.260	1.259	1.261	1.258	1.257
C8-O3	1.283(9)	1.267	1.261	1.258	1.264	1.261	1.259
C7-C8	1.515(11)	1.539	1.543	1.552	1.535	1.537	1.538

¥Out of four bipyridine molecules, three were disordered and modeled through PART command. Hence, geometrical parameters with respect to major occupancy have been described here.

Table S5 Selected experimental and DFT calculated bond angles [deg] for $\mathbf{2}^{n}$ ¥

Bond	X-ray	DFT					
	$\mathbf{2}^{2+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$	$\mathbf{2}^{4+}$	$\mathbf{2}^{+}$	**2**	$\mathbf{2}^{-}$
O1-Ru1-O2	91.5(2)	89.17	88.08	87.00	88.70	87.88	88.12
N1A-Ru1-N2A	76.9(4)	78.08	77.63	77.22	78.47	78.79	78.88
N3-Ru1-N4	78.1(2)	78.51	78.44	78.49	78.64	78.97	79.06
O1-Ru1-N1A	172.5(4)	172.97	173.77	174.63	172.48	173.21	173.00
O2-Ru1-N4	167.8(3)	172.25	172.68	172.98	172.56	172.74	172.49
N2A-Ru1-N3	178.4(6)	176.82	174.40	172.23	176.11	174.28	174.42
O3-Ru2-O4	91.2(2)	88.77	87.92	86.90	88.63	87.55	87.59
N5-Ru2-N6	79.6(3)	78.34	78.35	78.48	78.58	78.89	79.07
N7-Ru2-N8	80.1(5)	78.15	77.68	77.14	78.58	78.80	78.83
O3-Ru2-N5	175.2(3)	171.96	172.15	171.19	173.79	173.51	173.65
O4-Ru2-N8	169.5(4)	172.35	172.85	172.95	172.74	173.26	173.53
N6-Ru2-N7	179.5(7)	175.29	172.72	170.74	176.03	174.24	178.83

¥Out of four bipyridine molecules, three were disordered and modeled through PART command. Hence, geometrical parameters with respect to major occupancy have been described here.

Table S6 Selected experimental and DFT calculated bond lengths [Å] for $\mathbf{3}^{n}$

Bond	X-ray	DFT			
	$\mathbf{3}^{2+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$	$\mathbf{3}^{+}$	**3**
Ru1-O1	2.032(4)	2.063	2.037	2.079	2.098
Ru1-O2	2.056(5)	2.108	2.131	2.114	2.133
Ru1-N1	1.989(5)	2.056	2.101	2.086	2.047
Ru1-N3	2.044(6)	2.082	2.104	2.090	2.100
Ru1-N4	2.022(6)	2.089	2.090	2.084	2.081
Ru1-N6	1.979(6)	2.079	2.078	2.020	2.002
C7-O2	1.262(8)	1.268	1.260	1.263	1.260
N1-N2	1.288(7)	1.281	1.276	1.305	1.325
N5-N6	1.286(7)	1.283	1.278	1.293	1.315

Table S7 Selected experimental and DFT calculated bond angles [deg] for $\mathbf{3}^{n}$

Bond	X-ray	DFT			
	$\mathbf{3}^{2+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$	$\mathbf{3}^{+}$	**3**
O1-Ru1-O2	89.03(18)	88.05	87.25	87.29	85.76
N1-Ru1-N3	77.6(2)	76.21	75.80	76.32	76.62
N4-Ru1-N6	77.0(2)	76.52	76.49	76.65	76.89
O1-Ru1-N1	168.1(2)	168.96	169.72	167.95	168.18
O2-Ru1-N6	173.1(2)	169.58	169.93	170.56	171.25
N4-Ru1-N3	177.2(2)	177.96	179.59	178.63	178.18

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

MO	Energy(eV)	Composition		
		Ru	L	acac$^-$
		α-spin		
HOMO−5	-5.905	0.63	0.13	0.24
HOMO−4	-5.853	0.55	0.14	0.31
HOMO−3	-5.564	0.47	0.08	0.45
HOMO−2	-5.511	0.49	0.12	0.39
SOMO2	-5.454	0.27	0.53	0.20
SOMO1	-5.385	0.29	0.56	0.15
LUMO	-2.014	0.05	0.94	0.01
LUMO+1	-1.595	0.06	0.92	0.02
LUMO+2	-1.036	0.05	0.03	0.92
LUMO+3	-0.996	0.09	0.02	0.89
LUMO+4	-0.943	0.03	0.01	0.95
LUMO+5	-0.942	0.05	0.01	0.95
		β-spin		
HOMO−5	-5.852	0.21	0.53	0.26
HOMO−4	-5.780	0.23	0.63	0.15
HOMO−3	-5.604	0.67	0.14	0.19
HOMO−2	-5.541	0.67	0.16	0.18
HOMO−1	-5.276	0.53	0.22	0.25
HOMO	-5.255	0.57	0.11	0.32
LUMO	-2.887	0.67	0.13	0.20
LUMO+1	-2.823	0.65	0.17	0.18
LUMO+2	-1.940	0.09	0.89	0.02
LUMO+3	-1.536	0.07	0.91	0.03
LUMO+4	-0.990	0.04	0.03	0.93
LUMO+5	-0.948	0.08	0.02	0.90

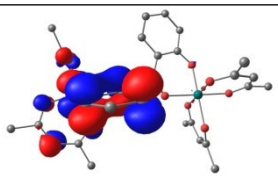
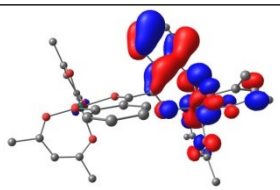
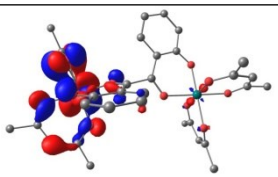
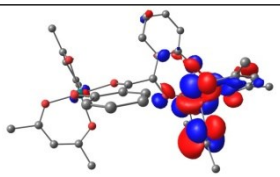
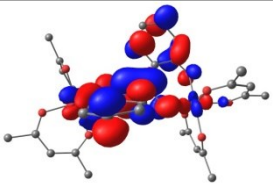
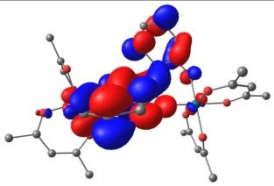
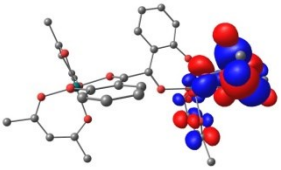
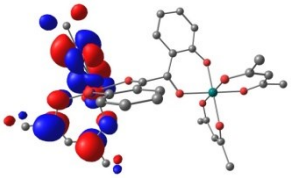
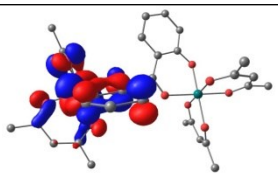
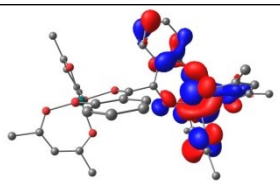
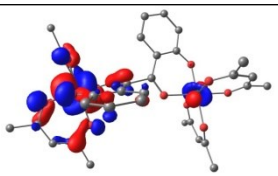
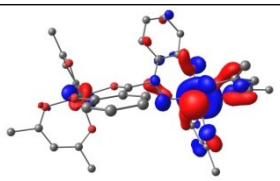
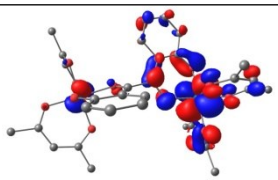
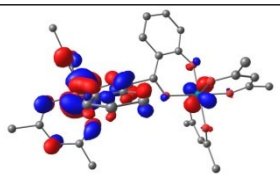
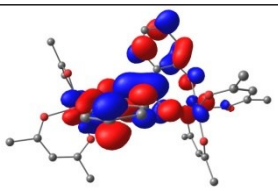
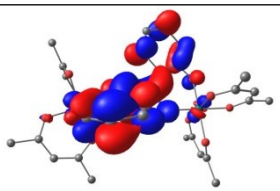
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 Composition and energies of selected molecular orbitals of **1a**$^{+}$(*rac*) (*S*=3/2)

MO	Energy(eV)	Composition		
		Ru	L	acac^{-}
		α-spin		
HOMO−5	-8.931	0.14	0.06	0.80
HOMO−4	-8.825	0.14	0.10	0.76
HOMO−3	-8.723	0.17	0.22	0.60
SOMO3	-8.617	0.22	0.19	0.58
SOMO2	-8.421	0.22	0.56	0.22
SOMO1	-8.320	0.23	0.54	0.23
LUMO	-4.911	0.06	0.92	0.02
LUMO+1	-4.510	0.08	0.88	0.03
LUMO+2	-3.836	0.22	0.04	0.73
LUMO+3	-3.706	0.46	0.18	0.46
LUMO+4	-3.687	0.21	0.06	0.74
LUMO+5	-3.666	0.05	0.02	0.94
		β-spin		
HOMO−5	-8.887	0.26	0.15	0.59
HOMO−4	-8.761	0.67	0.16	0.18
HOMO−3	-8.616	0.66	0.18	0.16
HOMO−2	-8.566	0.15	0.46	0.39
HOMO−1	-8.513	0.18	0.42	0.39
HOMO	-7.685	0.56	0.18	0.26
LUMO	-7.264	0.57	0.18	0.25
LUMO+1	-6.060	0.62	0.17	0.20
LUMO+2	-5.896	0.63	0.18	0.19
LUMO+3	-4.787	0.10	0.88	0.02
LUMO+4	-4.411	0.08	0.90	0.02
LUMO+5	-3.715	0.08	0.03	0.89

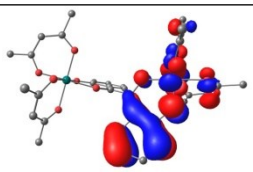
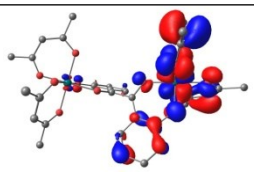
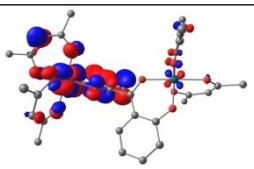
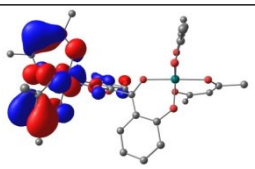
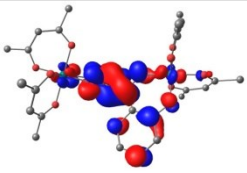
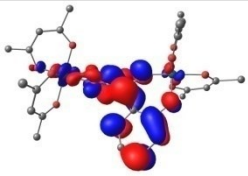
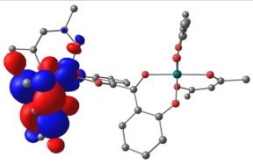
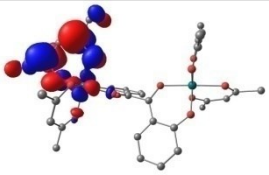
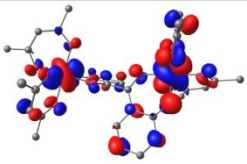
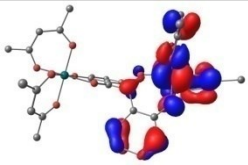
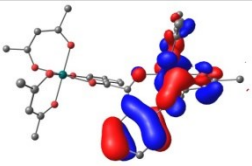
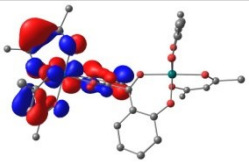
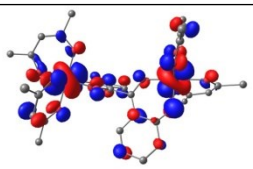
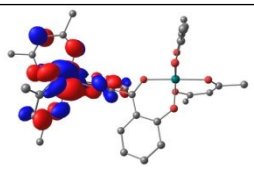
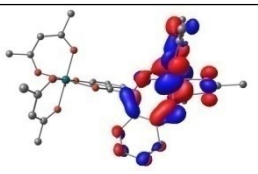
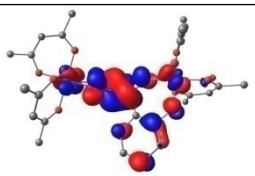
α-spin			
			
SOMO1	SOMO2	SOMO3	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy(eV)	Composition		
		Ru	L	acac$^-$
		α-spin		
HOMO−5	-11.753	0.08	0.03	0.90
HOMO−4	-11.693	0.07	0.03	0.90
SOMO4	-11.505	0.09	0.28	0.62
SOMO3	-11.415	0.11	0.28	0.61
SOMO2	-11.271	0.18	0.57	0.25
SOMO1	-11.217	0.18	0.56	0.26
LUMO	-7.725	0.08	0.89	0.03
LUMO+1	-7.310	0.12	0.83	0.06
LUMO+2	-6.789	0.51	0.24	0.25
LUMO+3	-6.720	0.48	0.09	0.44
LUMO+4	-6.630	0.43	0.08	0.49
LUMO+5	-6.554	0.48	0.22	0.30
		β-spin		
HOMO−5	-11.781	0.62	0.16	0.22
HOMO−4	-11.692	0.63	0.15	0.22
HOMO−3	-11.534	0.26	0.18	0.57
HOMO−2	-11.486	0.25	0.22	0.54
HOMO−1	-11.238	0.11	0.45	0.44
HOMO	-11.188	0.11	0.41	0.48
LUMO	-9.480	0.60	0.19	0.21
LUMO+1	-9.353	0.60	0.21	0.20
LUMO+2	-9.158	0.55	0.18	0.26
LUMO+3	-9.072	0.56	0.16	0.28
LUMO+4	-7.561	0.09	0.89	0.02
LUMO+5	-7.167	0.07	0.90	0.02

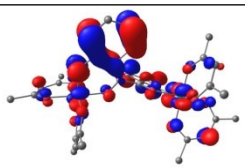
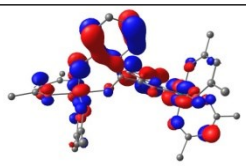
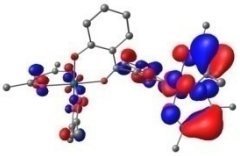
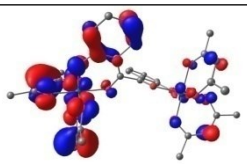
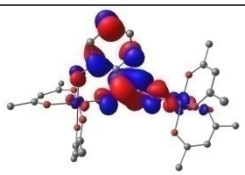
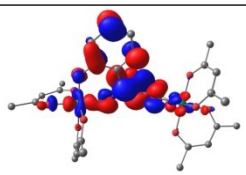
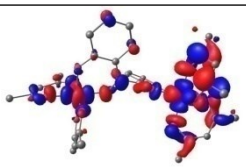
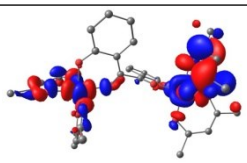
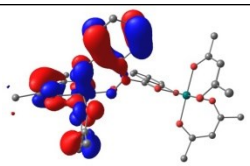
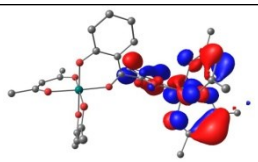
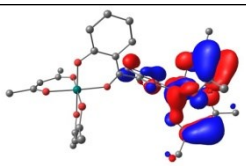
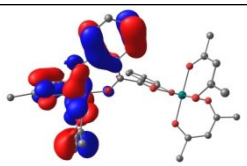
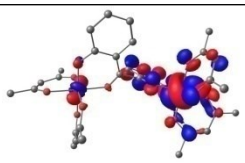
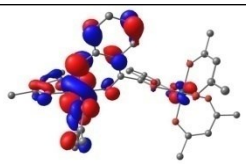
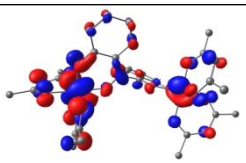
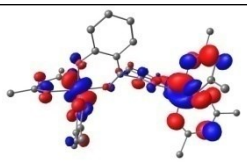
α-spin			
			
SOMO1	SOMO2	SOMO3	SOMO4
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Composition and energies of selected molecular orbitals of **1a**$^{-}$(*rac*) (*S*=1/2)

MO	Energy(eV)	Composition		
		Ru	L	acac^{-}
		α-spin		
HOMO−5	-2.941	0.28	0.42	0.30
HOMO−4	-2.938	0.18	0.21	0.61
HOMO−3	-2.672	0.09	0.67	0.24
HOMO−2	-1.545	0.73	0.10	0.17
HOMO−1	-1.497	0.72	0.11	0.18
SOMO	-0.957	0.64	0.17	0.19
LUMO	0.790	0.05	0.94	0.01
LUMO+1	1.139	0.02	0.02	0.96
LUMO+2	1.224	0.06	0.01	0.93
LUMO+3	1.481	0.10	0.86	0.86
LUMO+4	2.245	0.09	0.04	0.87
LUMO+5	2.251	0.47	0.11	0.47
		β-spin		
HOMO−5	-2.905	0.07	0.04	0.89
HOMO−4	-2.851	0.58	0.22	0.20
HOMO−3	-2.648	0.07	0.72	0.21
HOMO−2	-1.472	0.73	0.11	0.16
HOMO−1	-1.057	0.72	0.10	0.18
HOMO	-0.891	0.65	0.17	0.18
LUMO	-0.593	0.68	0.15	0.17
LUMO+1	0.828	0.07	0.90	0.03
LUMO+2	1.169	0.03	0.02	0.94
LUMO+3	1.255	0.06	0.01	0.92
LUMO+4	1.497	0.09	0.88	0.03
LUMO+5	2.255	0.04	0.02	0.94

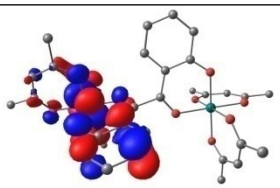
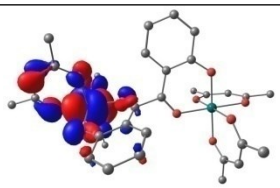
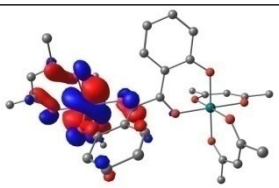
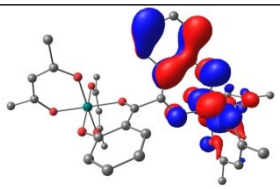
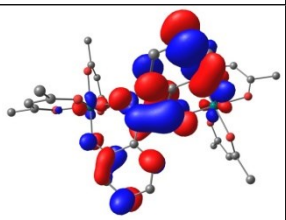
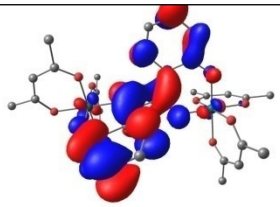
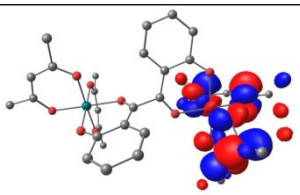
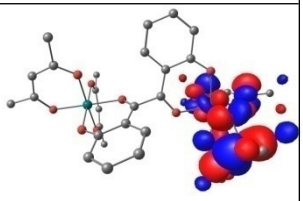
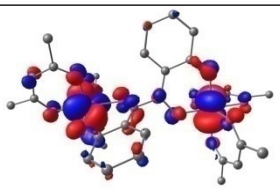
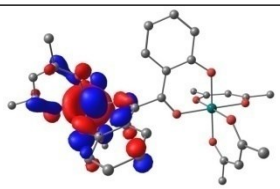
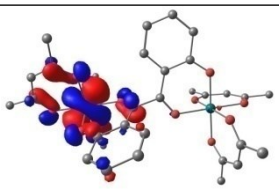
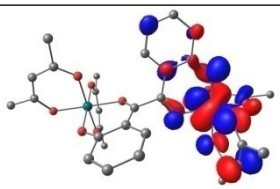
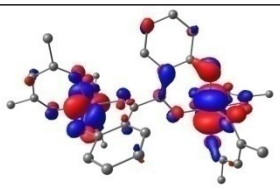
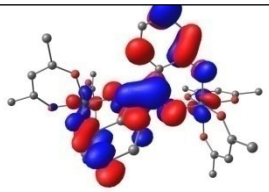
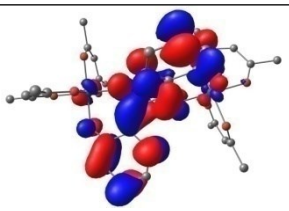
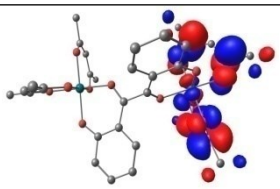
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Composition and energies of selected molecular orbitals of **1a**$^{2-}$(*rac*) (*S*=0)

MO	Energy(eV)	Composition		
		Ru	L	acac^{-}
HOMO–5	0.791	0.74	0.10	0.16
HOMO–4	0.896	0.75	0.09	0.16
HOMO–3	1.016	0.73	0.10	0.17
HOMO–2	1.083	0.73	0.10	0.17
HOMO–1	1.229	0.69	0.16	0.15
HOMO	1.361	0.68	0.17	0.16
LUMO	3.803	0.08	0.89	0.03
LUMO+1	4.128	0.04	0.92	0.03
LUMO+2	4.372	0.04	0.01	0.95
LUMO+3	4.462	0.03	0.02	0.95
LUMO+4	4.584	0.07	0.01	0.92
LUMO+5	4.606	0.08	0.03	0.89

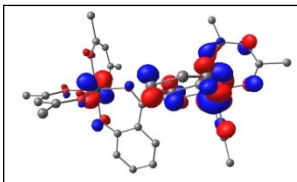
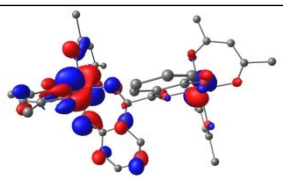
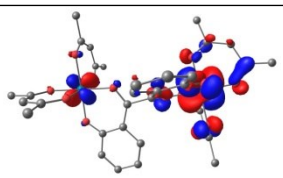
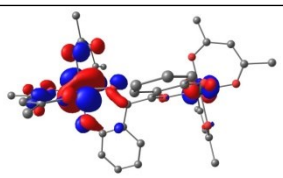
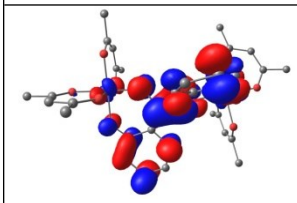
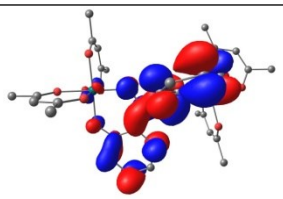
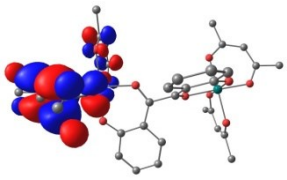
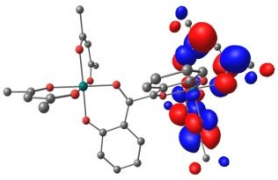
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Composition and energies of selected molecular orbitals of $\mathbf{2}^{2+}$ (*S*=0)

MO	Energy(eV)	Composition		
		Ru	L	bpy
HOMO–5	-9.975	0.72	0.13	0.15
HOMO–4	-9.881	0.60	0.14	0.26
HOMO–3	-9.628	0.68	0.12	0.20
HOMO–2	-9.574	0.65	0.15	0.20
HOMO–1	-9.327	0.39	0.47	0.15
HOMO	-8.965	0.19	0.71	0.09
LUMO	-7.354	0.11	0.02	0.86
LUMO+1	-6.833	0.11	0.02	0.86
LUMO+2	-6.636	0.07	0.04	0.89
LUMO+3	-6.318	0.05	0.83	0.11
LUMO+4	-6.244	0.07	0.04	0.90
LUMO+5	-5.718	0.03	0.07	0.91

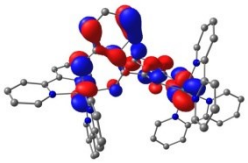
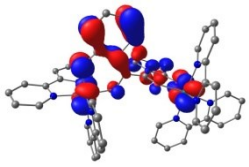
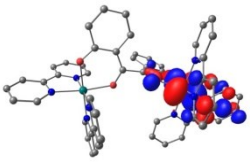
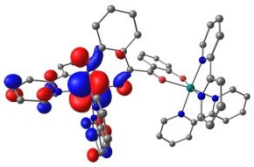
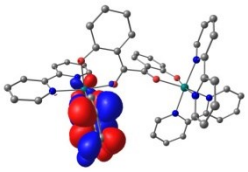
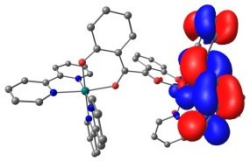
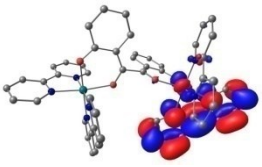
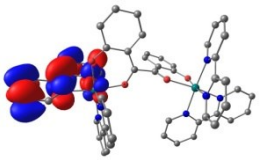
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Composition and energies of selected molecular orbitals of $\mathbf{2}^{3+}$ (S=1/2)

MO	Energy(eV)	Composition		
		Ru	L	bpy
		α-spin		
HOMO–5	-12.918	0.57	0.11	0.33
HOMO–4	-12.665	0.68	0.14	0.19
HOMO–3	-12.635	0.69	0.10	0.21
HOMO–2	-12.535	0.30	0.59	0.10
HOMO–1	-12.230	0.67	0.12	0.22
SOMO	-12.086	0.34	0.56	0.10
LUMO	-10.003	0.07	0.01	0.92
LUMO+1	-9.274	0.09	0.06	0.86
LUMO+2	-9.013	0.05	0.80	0.15
LUMO+3	-8.817	0.06	0.13	0.81
LUMO+4	-8.748	0.06	0.62	0.32
LUMO+5	-8.640	0.06	0.23	0.71
		β-spin		
HOMO–5	-12.790	0.51	0.34	0.15
HOMO–4	-12.597	0.49	0.25	0.26
HOMO–3	-12.547	0.68	0.13	0.18
HOMO–2	-12.513	0.67	0.17	0.16
HOMO–1	-12.091	0.60	0.22	0.18
HOMO	-11.582	0.43	0.38	0.19
LUMO	-11.063	0.37	0.47	0.16
LUMO+1	-9.962	0.12	0.03	0.85
LUMO+2	-9.222	0.14	0.05	0.82
LUMO+3	-8.994	0.05	0.80	0.15
LUMO+4	-8.807	0.06	0.11	0.83
LUMO+5	8.705	0.06	0.40	0.54

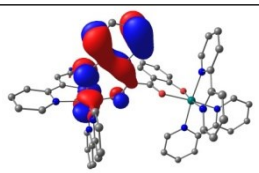
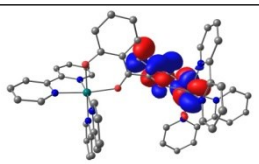
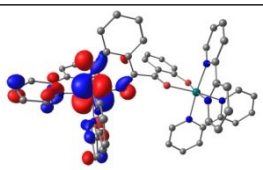
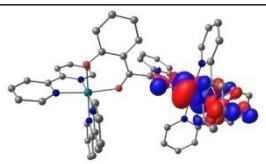
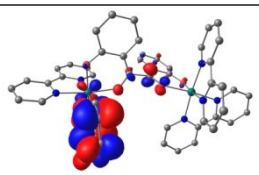
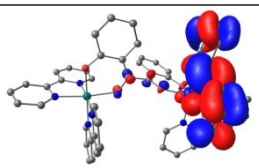
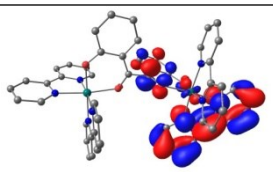
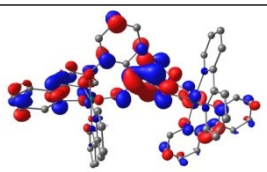
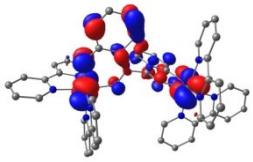
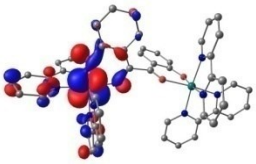
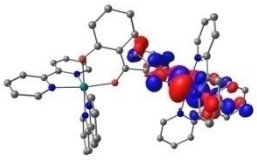
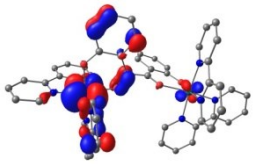
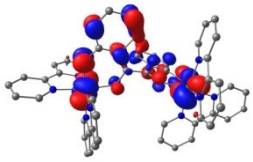
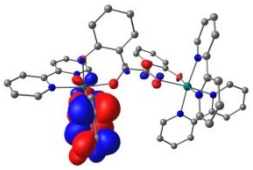
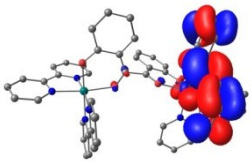
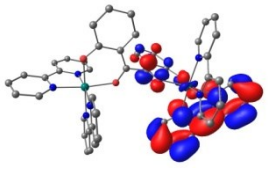
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 Composition and energies of selected molecular orbitals of $\mathbf{2}^{4+}$ (*S*=1)

MO	Energy(eV)	Composition		
		Ru	L	bpy
		α-spin		
HOMO–5	-15.573	0.09	0.02	0.89
HOMO–4	-15.497	0.11	0.03	0.85
HOMO–3	-15.472	0.60	0.12	0.28
HOMO–2	-15.361	0.63	0.12	0.26
SOMO2	-14.937	0.15	0.80	0.05
SOMO1	-14.908	0.14	0.81	0.05
LUMO	-11.202	0.05	0.84	0.10
LUMO+1	-11.178	0.05	0.86	0.09
LUMO+2	-11.006	0.04	0.07	0.89
LUMO+3	-10.957	0.04	0.05	0.91
LUMO+4	-10.830	0.04	0.01	0.95
LUMO+5	-10.747	0.04	0.01	0.95
		β-spin		
HOMO–5	-15.500	0.05	0.02	0.93
HOMO–4	-15.469	0.67	0.18	0.16
HOMO–3	-15.393	0.61	0.20	0.18
HOMO–2	-15.253	0.60	0.25	0.15
HOMO–1	-14.893	0.46	0.44	0.11
HOMO	-14.544	0.39	0.51	0.10
LUMO	-12.985	0.58	0.31	0.11
LUMO+1	-12.955	0.60	0.29	0.11
LUMO+2	-11.112	0.06	0.78	0.16
LUMO+3	-11.078	0.05	0.84	0.11
LUMO+4	-10.980	0.05	0.11	0.84
LUMO+5	-10.917	0.05	0.07	0.88

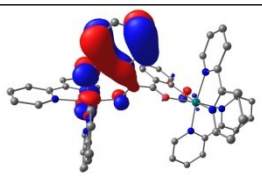
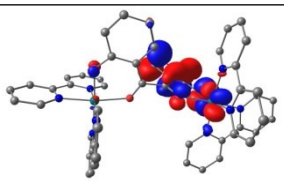
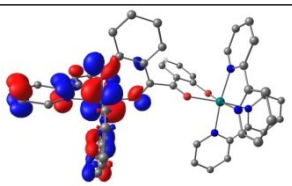
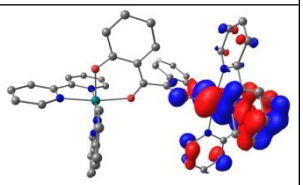
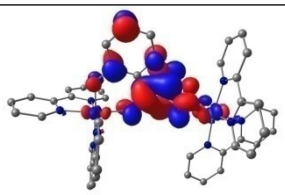
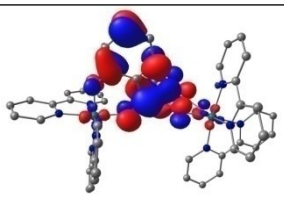
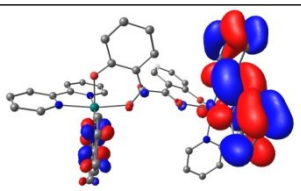
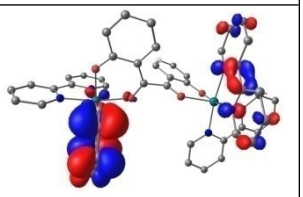
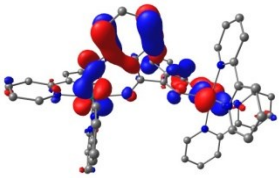
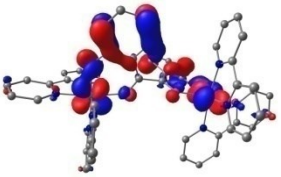
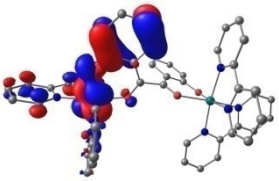
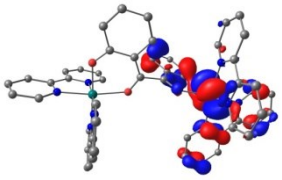
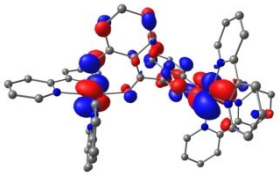
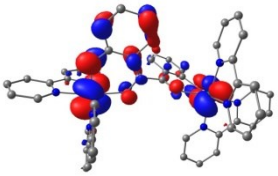
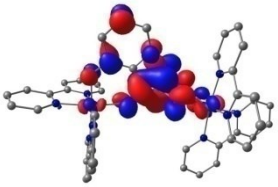
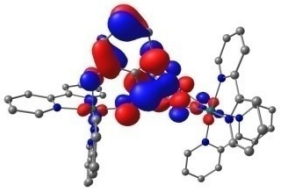
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy(eV)	Composition		
		Ru	L	bpy
		α-spin		
HOMO–5	-7.255	0.65	0.16	0. 20
HOMO–4	-7.074	0.50	0.33	0.17
HOMO–3	-7.047	0.56	0.19	0.25
HOMO–2	-6.740	0.68	0.08	0.24
HOMO–1	-6.395	0.34	0.55	0.11
SOMO	-5.147	0.10	0.02	0.88
LUMO	-4.587	0.08	0.01	0.91
LUMO+1	-4.481	0.10	0.04	0.86
LUMO+2	-4.068	0.05	0.86	0.09
LUMO+3	-3.800	0.08	0.02	0.90
LUMO+4	-3.265	0.05	0.05	0.90
LUMO+5	-3.076	0.08	0.79	0.13
		β-spin		
HOMO–5	-7.294	0.64	0.20	0.17
HOMO–4	-7.238	0.63	0.17	0.20
HOMO–3	-7.021	0.48	0.36	0.16
HOMO–2	-6.906	0.56	0.19	0.26
HOMO–1	-6.584	0.53	0.08	0.40
HOMO	-6.339	0.39	0.48	0.13
LUMO	-4.504	0.07	0.02	0.91
LUMO+1	-4.290	0.11	0.09	0.81
LUMO+2	-4.055	0.06	0.81	0.13
LUMO+3	-3.825	0.07	0.01	0.92
LUMO+4	-3.724	0.08	0.04	0.88
LUMO+5	-3.262	0.05	0.05	0.90

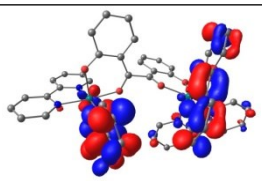
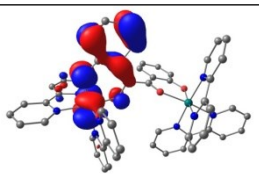
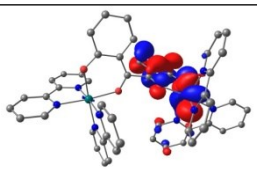
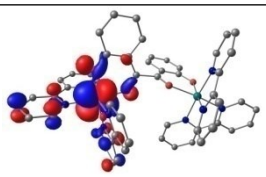
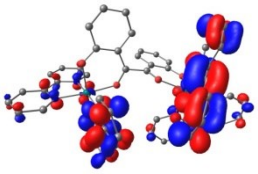
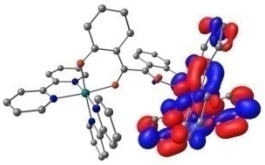
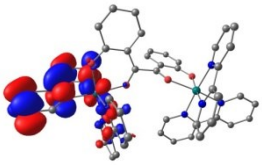
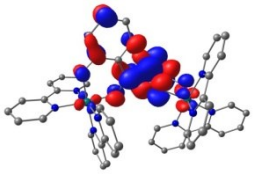
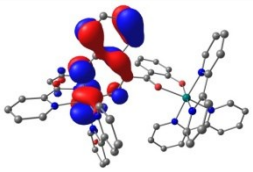
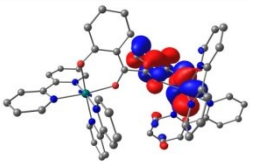
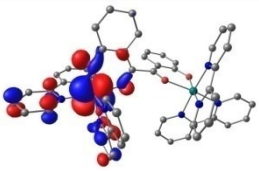
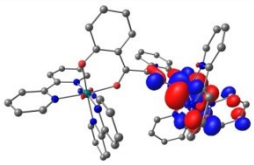
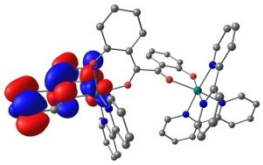
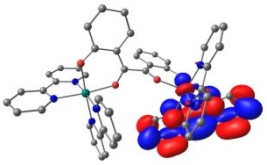
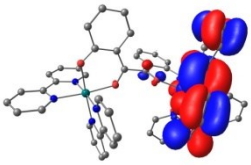
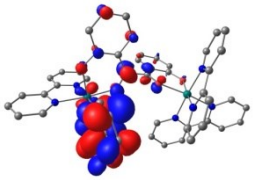
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 Composition and energies of selected molecular orbitals of **2** (*S*=1)

MO	Energy(eV)	Composition		
		Ru	L	bpy
		α-spin		
HOMO–5	-4.626	0.70	0.14	0.17
HOMO–4	-4.506	0.63	0.26	0.11
HOMO–3	-4.498	0.69	0.17	0.13
HOMO–2	-4.450	0.57	0.31	0.12
SOMO2	-2.454	0.05	0.01	0.94
SOMO1	-2.282	0.05	0.01	0.94
LUMO	-1.792	0.09	0.02	0.89
LUMO+1	-1.648	0.09	0.03	0.88
LUMO+2	-1.262	0.06	0.85	0.09
LUMO+3	-1.156	0.05	0.89	0.07
LUMO+4	-0.758	0.04	0.04	0.92
LUMO+5	-0.586	0.03	0.02	0.96
		β-spin		
HOMO–5	-4.966	0.78	0.08	0.14
HOMO–4	-4.880	0.78	0.08	0.14
HOMO–3	-4.637	0.73	0.11	0.16
HOMO–2	-4.514	0.76	0.10	0.14
HOMO–1	-4.454	0.59	0.31	0.10
HOMO	-4.399	0.58	0.31	0.11
LUMO	-1.458	0.06	0.02	0.91
LUMO+1	-1.297	0.05	0.25	0.70
LUMO+2	-1.278	0.06	0.60	0.34
LUMO+3	-1.203	0.04	0.53	0.43
LUMO+4	-1.087	0.06	0.39	0.54
LUMO+5	-1.013	0.06	0.07	0.87

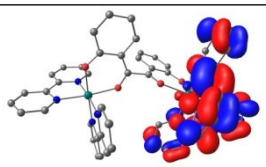
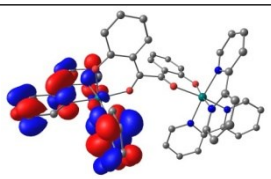
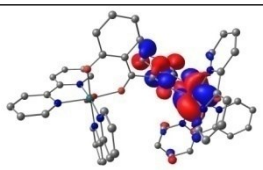
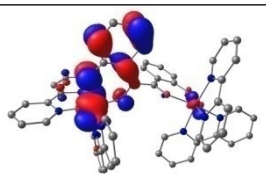
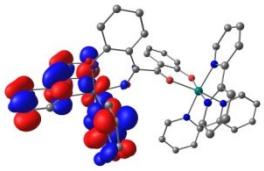
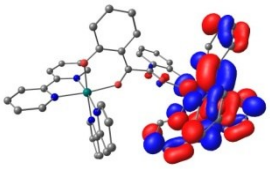
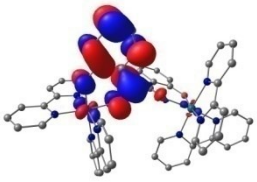
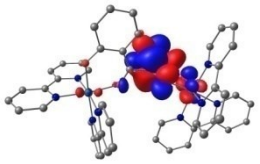
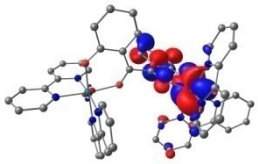
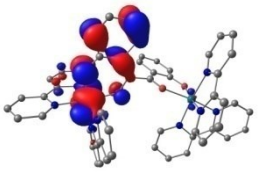
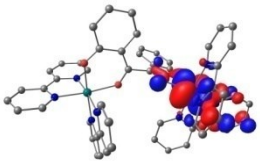
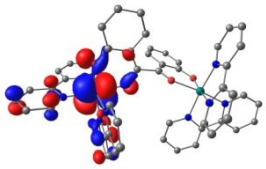
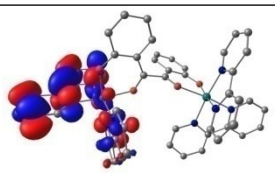
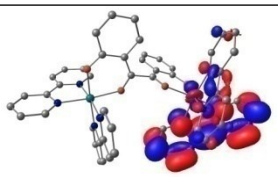
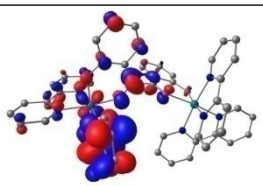
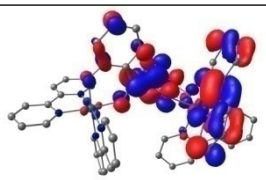
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy(eV)	Composition		
		Ru	L	bpy
		α-spin		
HOMO−5	-2.181	0.71	0.14	0.15
HOMO−4	-2.131	0.65	0.24	0.11
HOMO−3	-2.048	0.66	0.23	0.11
SOMO3	-0.296	0.04	0.01	0.95
SOMO2	-0.257	0.04	0.01	0.95
SOMO1	-0.019	0.10	0.03	0.86
LUMO	0.353	0.10	0.03	0.87
LUMO+1	1.030	0.06	0.86	0.08
LUMO+2	1.060	0.05	0.89	0.06
LUMO+3	1.725	0.04	0.01	0.95
LUMO+4	1.811	0.04	0.03	0.93
LUMO+5	1.936	0.05	0.01	0.94
		β-spin		
HOMO−5	-2.509	0.78	0.06	0.16
HOMO−4	-2.412	0.78	0.07	0.15
HOMO−3	-2.148	0.71	0.12	0.16
HOMO−2	-2.087	0.67	0.20	0.13
HOMO−1	-2.064	0.70	0.15	0.15
HOMO	-1.985	0.66	0.21	0.12
LUMO	1.023	0.05	0.13	0.82
LUMO+1	1.026	0.05	0.77	0.19
LUMO+2	1.041	0.03	0.71	0.26
LUMO+3	1.146	0.05	0.08	0.87
LUMO+4	1.254	0.09	0.12	0.80
LUMO+5	1.323	0.07	0.07	0.84

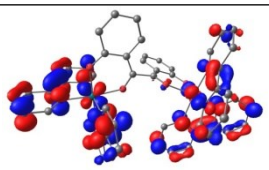
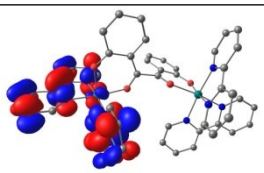
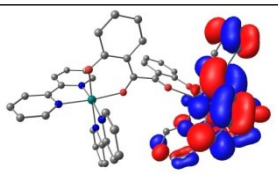
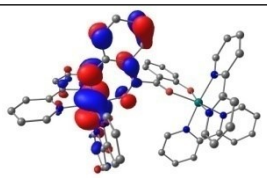
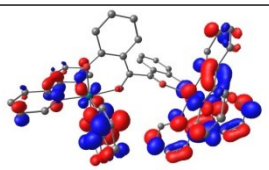
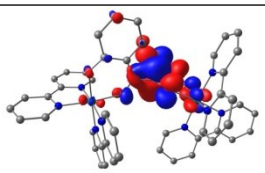
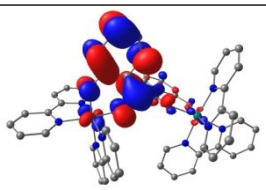
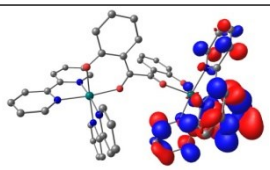
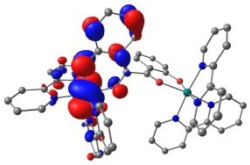
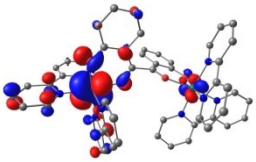
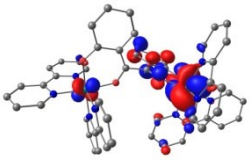
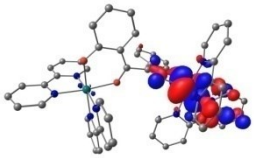
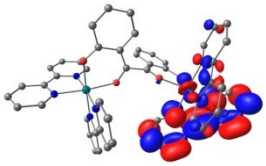
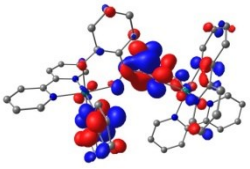
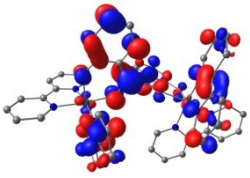
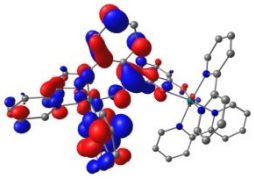
α-spin			
			
SOMO1	SOMO2	SOMO3	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19 Composition and energies of selected molecular orbitals of $\mathbf{3}^{2+}$ (*S*=0)

MO	Energy(eV)	Composition		
		Ru	L	pap
HOMO–5	-10.757	0.41	0.11	0.48
HOMO–4	-10.744	0.43	0.10	0.48
HOMO–3	-10.550	0.54	0.12	0.34
HOMO–2	-10.542	0.54	0.13	0.33
HOMO–1	-9.983	0.23	0.68	0.09
HOMO	-9.956	0.24	0.67	0.09
LUMO	-7.526	0.12	0.03	0.85
LUMO+1	-7.513	0.12	0.02	0.86
LUMO+2	-7.178	0.20	0.03	0.77
LUMO+3	-7.177	0.19	0.03	077
LUMO+4	-6.461	0.05	0.88	0.07
LUMO+5	-6.458	0.05	0.88	0.07

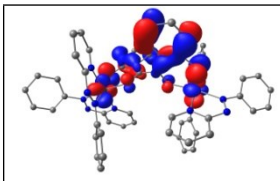
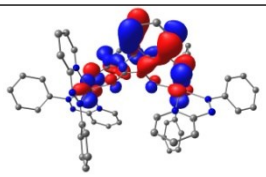
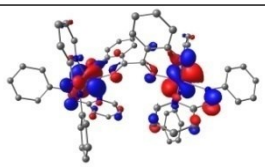
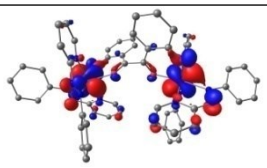
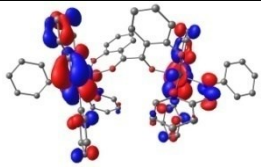
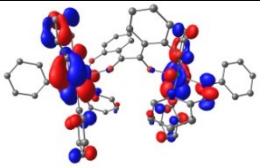
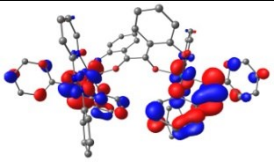
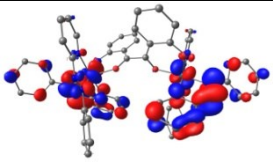
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 Composition and energies of selected molecular orbitals of $\mathbf{3}^{3+}$ (S=1/2)

MO	Energy(eV)	Composition		
		Ru	L	pap
		α-spin		
HOMO–5	-12.877	0.01	0.01	0.98
HOMO–4	-12.876	0.01	0.01	0.99
HOMO–3	-12.763	0.25	0.52	0.23
HOMO–2	-12.754	0.09	0.07	0.83
HOMO–1	-12.750	0.31	0.57	0.12
SOMO	-12.738	0.16	0.15	0.69
LUMO	-9.733	0.08	0.03	0.89
LUMO+1	-9.713	0.08	0.01	0.91
LUMO+2	-9.503	0.12	0.02	0.86
LUMO+3	-9501	0.12	0.02	0.86
LUMO+4	-9.110	0.05	0.89	0.06
LUMO+5	-8.975	0.05	0.89	0.06
		β-spin		
HOMO–5	-12.932	0.58	0.11	0.32
HOMO–4	-12.875	0.01	0.00	0.98
HOMO–3	-12.873	0.03	0.01	0.96
HOMO–2	-12744	0.14	0.02	0.84
HOMO–1	-12735	0.13	0.02	0.84
HOMO	-12.034	0.40	0.51	0.09
LUMO	-11.548	0.39	0.52	0.09
LUMO+1	-9.711	0.11	0.02	0.87
LUMO+2	-9.695	0.10	0.02	0.88
LUMO+3	-9.488	0.13	0.02	0.85
LUMO+4	-9.487	0.13	0.02	0.85
LUMO+5	-9.052	0.05	0.88	0.06

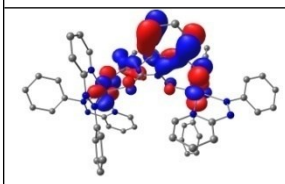
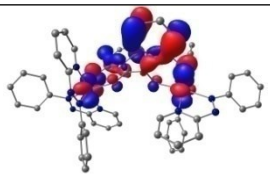
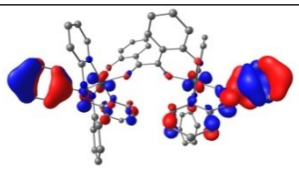
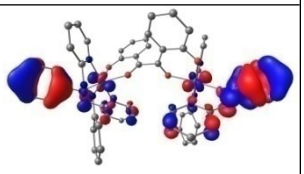
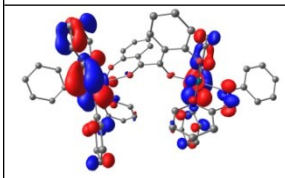
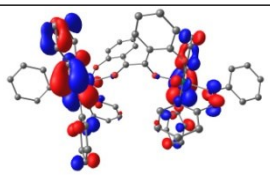
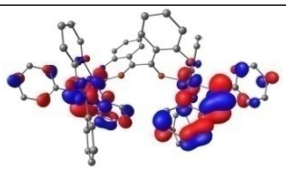
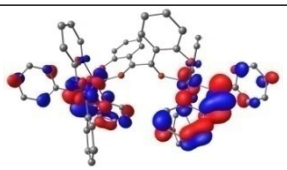
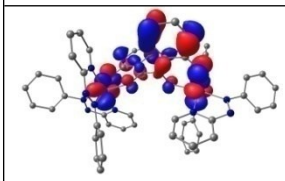
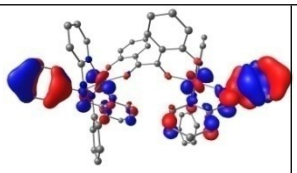
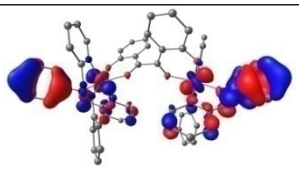
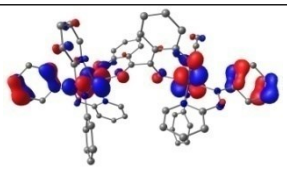
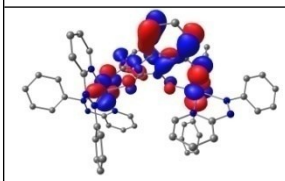
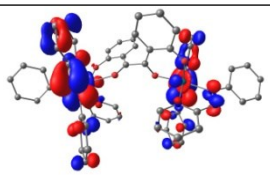
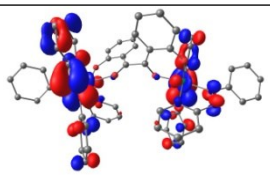
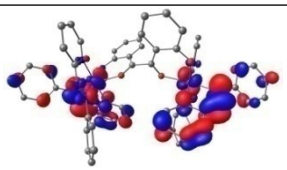
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 Composition and energies of selected molecular orbitals of $\mathbf{3}^{+}$ (S=1/2)

MO	Energy(eV)	Composition		
		Ru	L	pap
		α-spin		
HOMO–5	-8.118	0.68	0.09	0.23
HOMO–4	-7.835	0.64	0.11	0.25
HOMO–3	-7.819	0.64	0.12	0.25
HOMO–2	-7.428	0.35	0.57	0.08
HOMO–1	-7.411	0.35	057	0.08
SOMO	-5.610	0.09	0.02	0.89
LUMO	-5.265	0.09	0.01	0.90
LUMO+1	-4.857	0.20	0.02	0.77
LUMO+2	-4.846	0.20	0.03	0.77
LUMO+3	-3.992	0.05	0.88	0.07
LUMO+4	-3.866	0.05	0.89	0.06
LUMO+5	-3.182	0.05	0.01	0.94
		β-spin		
HOMO–5	-8.126	0.67	0.13	0.20
HOMO–4	-8113	0.68	0.10	0.22
HOMO–3	-7868	0.65	0.11	0.25
HOMO–2	-7.853	0.65	0.11	0.24
HOMO–1	-7.407	0.36	0.55	0.08
HOMO	-7.389	0.37	0.55	0.08
LUMO	-4.745	0.11	0.02	0.87
LUMO+1	-4.738	0.11	0.01	0.88
LUMO+2	-4.561	0.13	0.03	0.84
LUMO+3	-4.550	0.12	0.02	0.86
LUMO+4	-3.990	0.05	0.88	0.07
LUMO+5	-3.859	0.05	0.88	0.07

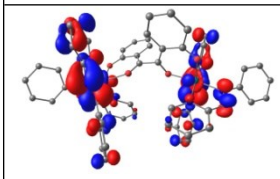
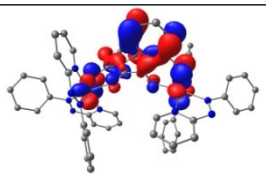
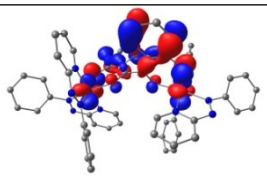
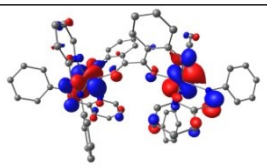
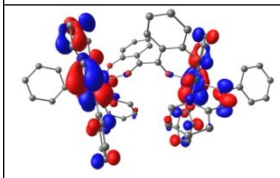
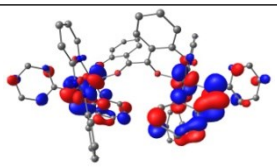
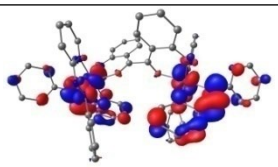
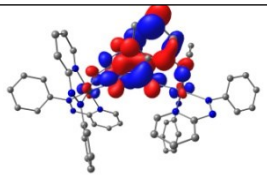
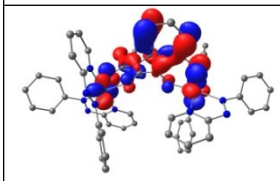
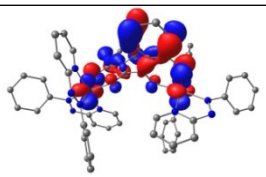
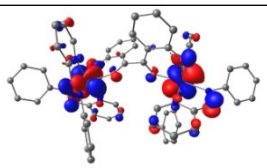
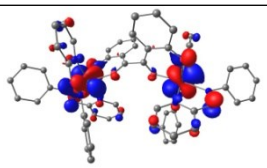
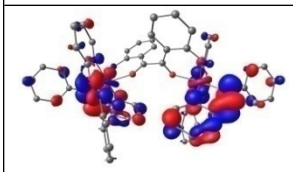
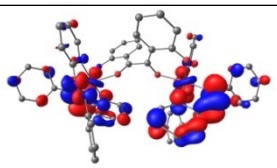
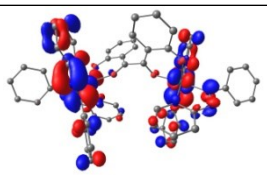
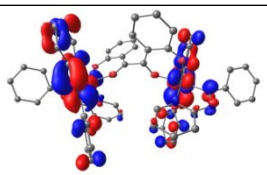
α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22 Composition and energies of selected molecular orbitals of **3** (*S*=1)

MO	Energy(eV)	Composition		
		Ru	L	pap
		α-spin		
HOMO–5	-5.386	0.59	0.09	0.32
HOMO–4	-5.373	0.59	0.10	0.31
HOMO–3	-5.167	0.42	0.49	0.09
HOMO–2	-5.145	0.43	0.48	0.09
SOMO2	-3.674	0.09	0.02	0.90
SOMO1	-3.653	0.08	0.01	0.90
LUMO	-2.518	0.27	0.03	0.70
LUMO+1	-2.513	0.27	0.03	0.70
LUMO+2	-1.760	0.05	0.89	0.06
LUMO+3	-1.627	0.05	0.89	0.06
LUMO+4	-0.878	0.05	0.01	0.93
LUMO+5	-0.862	004	0.01	0.95
		β-spin		
HOMO–5	-5.736	0.66	0.09	0.25
HOMO–4	-5726	0.68	0.08	0.24
HOMO–3	-5.434	0.58	0.09	0.33
HOMO–2	-5.422	0.59	0.09	0.32
HOMO–1	-5.136	0.45	0.46	0.09
HOMO	-5.113	0.45	0.46	0.09
LUMO	-2.309	0.12	0.02	0.86
LUMO+1	-2.303	0.12	0.02	0.86
LUMO+2	-1.966	0.10	0.08	0.82
LUMO+3	-1.942	0.10	0.02	0.88
LUMO+4	-1.758	0.05	0.89	0.06
LUMO+5	-1.607	0.05	0.84	0.11

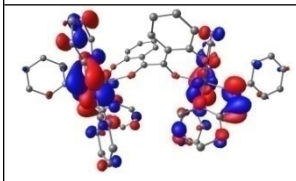
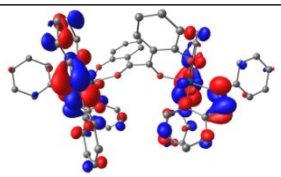
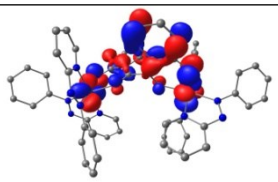
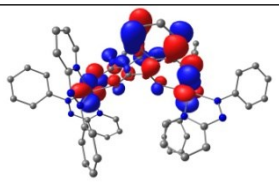
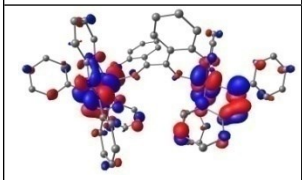
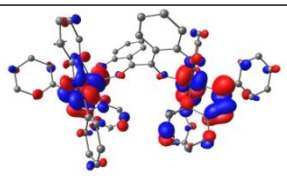
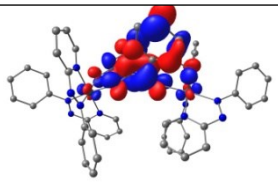
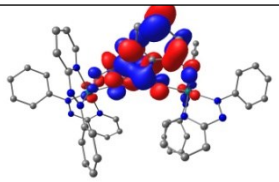
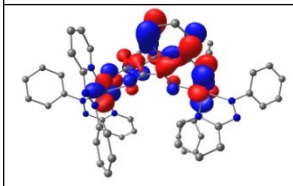
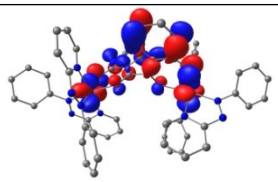
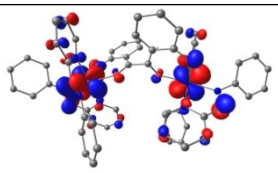
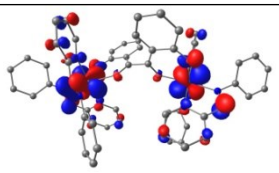
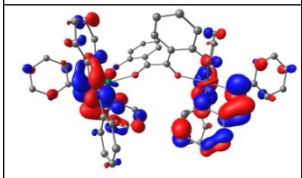
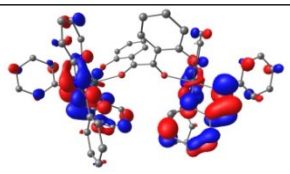
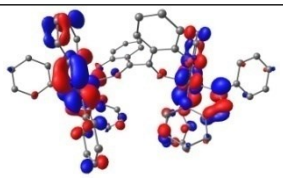
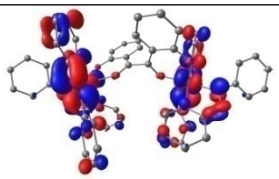
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) optimised structures of **1**^{n}, **2**^{n}, **3**^{n} and **4**^{n}

Compd	$E_{(S=0)}$ (Hartrees)	$E_{(S=1/2)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$E_{(S=3/2)}$ (Hartrees)	$E_{(S=2)}$ (Hartrees)	$\Delta E_{(HE-LE)}$[a]
1a	-2407.8879		**-2407.9351**			0.0472 Hartrees 123.92 kJ mol^{-1} 10359 cm^{-1}
1a$^+$		-2407.7068		**-2407.7081**		0.0013 Hartrees 3.41 kJ mol^{-1} 285 cm^{-1}
1a^{2+}			-2407.3963		**-2407.4011**	0.0048 Hartrees 12.60 kJ mol^{-1} 1053 cm^{-1}
1a$^-$		**-2408.0066**		-2407.9905		0.0161 Hartrees 42.27 kJ mol^{-1} 3533 cm^{-1}
1a^{2-}	**-2407.9969**		-2407.9575			0.0394 Hartrees 103.44 kJ mol^{-1} 8647 cm^{-1}
2^{4+}	-3007.5050		**-3007.5405**			0.0355 Hartrees 93.20 kJ mol^{-1} 7791 cm^{-1}
2	-3008.6531		**-3008.6660**			0.0129 Hartrees 33.86 kJ mol^{-1} 2831 cm^{-1}
2$^-$		-3008.6989		**-3008.7006**		0.0017 Hartrees 4.46 kJ mol^{-1} 373 cm^{-1}
3	-3382.3770		**-3382.3987**			0.0217 Hartrees 56.97 kJ mol^{-1} 4762 cm^{-1}

Table S24 Experimental and TD-DFT ((U)B3LYP/CPCM/CH_3CN or CH_2Cl_2) calculated electronic transitions

λ_{max}[a][nm] expt.(λ_{DFT})	ε/dm^3 mol^{-1} cm^{-1} [b](f)[c]	Transitions	Character
1a (S=1)			
507(537)	6690(0.033)	HOMO-6(β)→LUMO+1(β)(0.42) HOMO-6(β)→LUMO(β)(0.39)	acac(π)→Ru(dπ)/acac(π*)
421(422)	19100(0.044)	HOMO-3(β)→LUMO+2(β)(0.37) HOMO-2(β)→LUMO+2(β)(0.33)	Ru(dπ)/acac(π)→L(π*)
343(394)	14800(0.044)	SOMO2→LUMO+1(α)(0.37) HOMO-4(β)→LUMO+2(β)(0.26)	L(π)→L(π*) L(π)/Ru(dπ)→L(π*)
1a$^+$ (S=3/2)			
754(799)	5500(0.061)	HOMO-6(β)→LUMO+1(β)(0.77)	acac(π)/Ru(dπ)→Ru(dπ)/acac(π*)
525(589)	8900(0.038)	HOMO-2(β)→LUMO+2(β)(0.76)	L(π)/acac(π)→Ru(dπ)/acac(π*)
424(469)	16258(0.019)	SOMO3→LUMO(α)(0.70)	acac(π)/Ru(dπ)→L(π*)
344(384)	16650(0.017)	HOMO-3(β)→LUMO+3(β)(0.35) SOMO3→LUMO+1(α)(0.26)	Ru(dπ)→L(π*) acac(π)/Ru(dπ)→L(π*)
(347)	(0.011)	HOMO-7(β)→LUMO+2(β)(0.67)	acac(π)/Ru(dπ)→Ru(dπ)/acac(π*)
1a$^+$ (S=1/2)			
798(799)	5500(0.066)	HOMO-6(β)→LUMO(β)(0.81)	acac(π)/L(π)/Ru(dπ)→Ru(dπ)/L(π*)
525(589)	8900(0.043)	HOMO-2(α)→LUMO(α)(0.82)	acac(π)→Ru(dπ)/acac(π*)
424(438)	16258(0.016)	HOMO-2(α)→LUMO+1(α)(0.56)	acac(π)→L(π*)
344(384)	16650(0.03)	HOMO-16(β)→LUMO+1(β)(0.41) HOMO-4(β)→LUMO+1(β)(0.30)	acac(π)→Ru(dπ) acac(π)/Ru(dπ)→ Ru(dπ)
1a^{2+} (S=2)			
750(805)	13480(0.024)	HOMO-2(β)→LUMO+3(β)(0.55)	acac(π)/Ru(dπ)/L(π)→Ru(dπ)/acac(π*)
525(476)	7580(0.010)	HOMO-8(β)→LUMO+2(β)(0.72)	L(π)→Ru(dπ)/acac(π*)
390(390)	14470(0.019)	SOMO1→LUMO+1(α)(0.48) HOMO-14(β)→LUMO+3(β)(0.23)	L(π)/acac(π)→L(π*) Ru(dπ)/acac(π)→Ru(dπ)/acac(π*)
1a$^-$ (S=1/2)			
(1729)	(0.0003)	HOMO-2(β)→LUMO(β)(0.98)	Ru(dπ)/acac(π)→Ru(dπ)/acac(π*)
1045(1124)	950(0.0003)	SOMO1→LUMO(α)(0.64)	Ru(dπ)/acac(π)→L(π*)
660(659)	10060(0.074)	HOMO-8(β)→LUMO(β)(0.75)	L(π)/Ru(dπ)→Ru(dπ)/acac(π*)
410(397)	16080(0.101)	HOMO-2(β)→LUMO+5(β)(0.56)	Ru(dπ)/acac(π)→acac(π*)
351(344)	16080(0.033)	HOMO-3(α)→LUMO+1(α)(0.47) HOMO-3(β)→LUMO+2(β)(0.47)	L(π)/acac(π)→acac(π*)
1a^{2-} (S=0)			
660(689)	10080(0.012)	HOMO→LUMO(0.52)	Ru(dπ)→L(π*)
480(533)	11600(0.109)	HOMO-1→LUMO+1(0.42) HOMO-2→LUMO(0.22)	Ru(dπ)→L(π*)
380(400)	12700(0.122)	HOMO-4→LUMO+2(0.44) HOMO-5→LUMO+2(0.41)	Ru(dπ)→acac(π*)
2^{2+} (S=0)			

555(539)	sh(0.015)	HOMO-1→LUMO+2(0.49) HOMO→LUMO+2(0.23)	L(π)/Ru(dπ)→bpy(π*)
(508)	(0.019)	HOMO-3→LUMO(0.64)	Ru(dπ)→bpy(π*)
495(490)	14050(0.137)	HOMO→LUMO+5(0.39) HOMO-2→LUMO+3(0.26)	L(π)/Ru(dπ)→bpy(π*) Ru(dπ)→L(π*)
420(436)	8500(0.067)	HOMO-2→LUMO(0.36) HOMO-5→LUMO(0.19)	Ru(dπ)→bpy(π*)
355(393)	18850(0.068)	HOMO-4→LUMO+5(0.39) HOMO-4→LUMO(0.27)	Ru(dπ)→bpy(π*)
2^{3+} (S=1/2)			
(523)	(0.023)	HOMO(β)→LUMO+6(β)(0.55)	Ru(dπ)/L(π)→L(π*)/bpy(π*)
493(497)	16380(0.032)	HOMO-1(β)→LUMO+4(β)(0.62)	Ru(dπ)/L(π)→bpy(π*)
(472)	(0.011)	HOMO-2(β)→LUMO+3(β)(0.46) HOMO-2(β)→LUMO+1(β)(0.44)	Ru(dπ)/L(π)→L(π*) Ru(dπ)/L(π)→bpy(π*)
361(426)	14190(0.069)	HOMO-2(α)→LUMO+3(α)(0.46) HOMO-2(β)→LUMO+4(β)(0.46)	L(π)/Ru(dπ)→bpy(π*) Ru(dπ)/L(π)→bpy(π*)
(389)	(0.036)	HOMO-4(β)→LUMO+1(β)(0.56)	Ru(dπ)/ bpy(π)→bpy(π*)
2^{4+} (S=1)			
493(508)	25540(0.004)	SOMO2→LUMO(α)(0.61)	L(π)→L(π*)
(418)	(0.015)	SOMO2→LUMO(α)(0.32) HOMO(β)→LUMO+2(β)(0.25)	L(π)→L(π*) L(π)/Ru(dπ)→L(π*)
361(401)	26440(0.022)	SOMO1→LUMO+1(α)(0.58)	L(π)→L(π*)
(360)	(0.015)	HOMO-2(β)→LUMO+3(β)(0.37) SOMO1→LUMO+5(α)(0.31)	Ru(dπ)/L(π)→L(π*) L(π)→bpy(π*)
2^{+} (S=1/2)			
493(485)	20000(0.017)	HOMO-5(α)→LUMO+2(α)(0.52)	Ru(dπ)/bpy(π)→L(π*)
(436)	(0.075)	HOMO-5(β)→LUMO+2(β)(0.55)	Ru(dπ)/L(π)→L(π*)
361(393)	17823(0.021)	HOMO-10(α)→LUMO(α)(0.43) HOMO-9(β)→LUMO+2(β)(0.38)	L(π)→bpy(π*) L(π)→L(π*)
2 (S=3/2)			
591(564)	17440(0.005)	HOMO-7(α)→LUMO(α)(0.65)	Ru(dπ)/bpy(π)→bpy(π*)
(517)	(0.018)	HOMO-2(β)→LUMO+1(β)(0.54)	Ru(dπ)→bpy(π*)
389(405)	22585(0.018)	HOMO-1(β)→LUMO+5(β)(0.51)	Ru(dπ)/L(π)→bpy(π*)
2^{-} (S=3/2)			
1057(1038)	3000(0.005)	SOMO1→LUMO+7(α)(0.82)	bpy(π)→bpy(π*)
685(680)	12300(0.007)	HOMO-6(α)→LUMO(α)(0.68)	Ru(dπ)→bpy(π*)
434(459)	28200(0.102)	SOMO1→LUMO+21(α)(0.46) SOMO2→LUMO+18(α)(0.40)	bpy(π)→Ru(dπ)/bpy(π*) bpy(π)→bpy(π*)/Ru(dπ)
364(376)	38000(0.014)	HOMO-3(β)→LUMO+6(β)(0.43) HOMO-6(α)→LUMO+3(α)(0.41)	Ru(dπ)→bpy(π*)
2^{-} (S=1/2)			
1057(1066)	3000(0.005)	HOMO(β)→LUMO+9(β)(0.88)	bpy(π)→bpy(π*)
(906)	(0.016)	HOMO(β)→LUMO+9(β)(0.77)	bpy(π)→bpy(π*)
(856)	(0.013)	SOMO(α)→LUMO+9(α)(0.81)	bpy(π)→bpy(π*)
685(668)	12300(0.010)	HOMO-6(α)→LUMO(α)(0.84)	Ru(dπ)→bpy(π*)
434(459)	28200(0.117)	SOMO1→LUMO+20(α)(0.59)	bpy(π)→Ru(dπ)/bpy(π*)

364(383)	38000(0.012)	HOMO-12(α)→LUMO(α)(0.52)	L(π)→bpy(π*)
3^{2+} (S=0)			
552(599)	15385(0.016)	HOMO-3→LUMO(0.44) HOMO-2→LUMO+1(0.44)	Ru(dπ)/pap(π)→pap(π*)
516(517)	11630(0.120)	HOMO-4→LUMO(0.40) HOMO-3→LUMO+3(0.16)	pap(π)/Ru(dπ)→pap(π*) Ru(dπ)/pap(π)→pap(π*)
(476)	(0.053)	HOMO-6→LUMO(0.33) HOMO-5→LUMO+2(0.22)	Ru(dπ)/pap(π)→pap(π*) pap(π)/Ru(dπ)→pap(π*)
458(446)	8175(0.100)	HOMO→LUMO+4(0.40) HOMO-7→LUMO+1(0.11)	L(π)/Ru(dπ)→L(π*) pap(π)/Ru(dπ)→pap(π*)
355(380)	31670(0.323)	HOMO-9→LUMO+3(0.33) HOMO-8→LUMO+2(0.33)	pap(π)/Ru(dπ)→pap(π*)
3^{3+} (S=1/2)			
(1152)	(0.074)	HOMO-5(β)→LUMO(β)(0.69)	Ru(dπ)/pap(π)→L(π*)/Ru(dπ)
1033(1137)	5248(0.067)	HOMO-3(β)→LUMO(β)(0.90)	pap(π*)→L(π*)/Ru(dπ)
542(531)	9060(0.025)	HOMO-4(α)→LUMO(α)(0.34) HOMO-2(β)→LUMO+1(β)(0.31)	L(π)/Ru(dπ)→pap(π*) pap(π)→pap(π*)
361(376)	28240(0.349)	HOMO-2(α)→LUMO+5(α)(0.30) HOMO-1(β)→LUMO+6(β)(0.28)	pap(π*)→L(π*)
3^{+} (S=1/2)			
990(938)	1140(0.005)	SOMO→LUMO+4(α)(0.99)	pap(π*)→L(π*)
584(590)	11100(0.035)	HOMO-2(β)→LUMO+1(β)(0.37) HOMO-3(β)→LUMO(β)(0.36)	Ru(dπ)/pap(π)→pap(π*)
483(513)	9926(0.099)	HOMO-4(β)→LUMO(β)(0.48) HOMO-5(β)→LUMO+1(β)(0.43)	Ru(dπ)/pap(π)→pap(π*)
(459)	(0.084)	HOMO-4(β)→LUMO+2(β)(0.40) HOMO-10(α)→LUMO(α)(0.18)	Ru(dπ)/pap(π)→pap(π*) pap(π)→pap(π*)
347(370)	31400(0.327)	HOMO-8(β)→LUMO+1(β)(0.33) SOMO→LUMO+19(α)(0.31)	pap(π)→pap(π*)
3 (S=1)			
1009(887)	12430(0.008)	HOMO-2(α)→LUMO+1(α)(0.53)	L(π)/Ru(dπ)→pap(π*)
345(349)	46420(0.407)	HOMO-9(β)→LUMO+2(β)(0.37) HOMO-8(β)→LUMO+3(β)(0.27)	pap(π)/Ru(dπ)→pap(π*)

[a]Experimental absorption maxima (λ_{max} > 300 nm) from OTTLE spectroelectrochemistry in CH_2Cl_2/0.1 M Bu_4NPF_6. [b]Molar extinction coefficients in $dm^3mol^{-1}cm^{-1}$. [c]Calculated oscillator strengths.

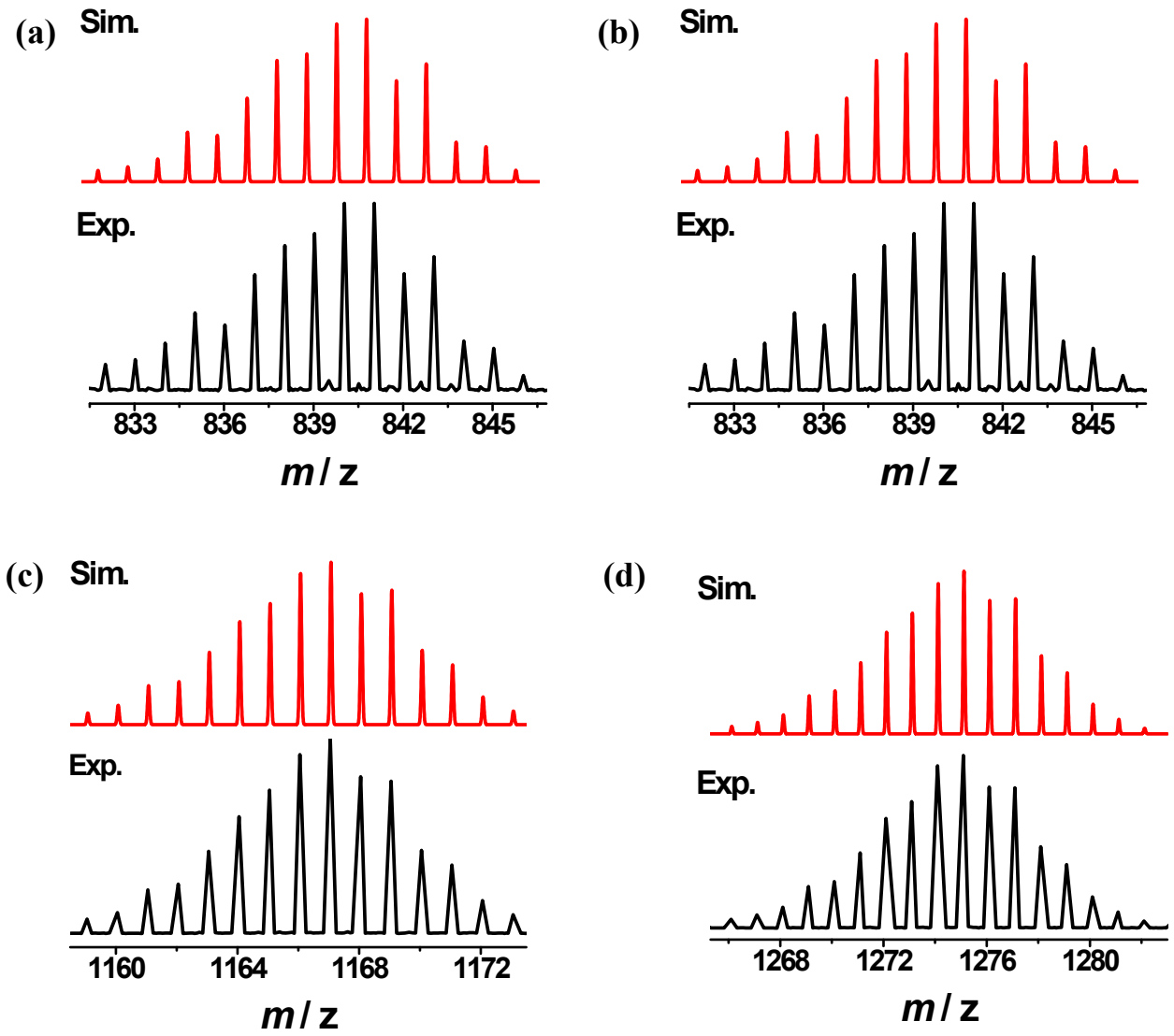


Fig. S1 ESI-MS(+) of (a) [**1a**]$^+$, (b) [**1b**]$^+$, (c) [**2**(ClO_4)]$^+$ and (d) [**3**(ClO_4)]$^+$ in CH_3CN.

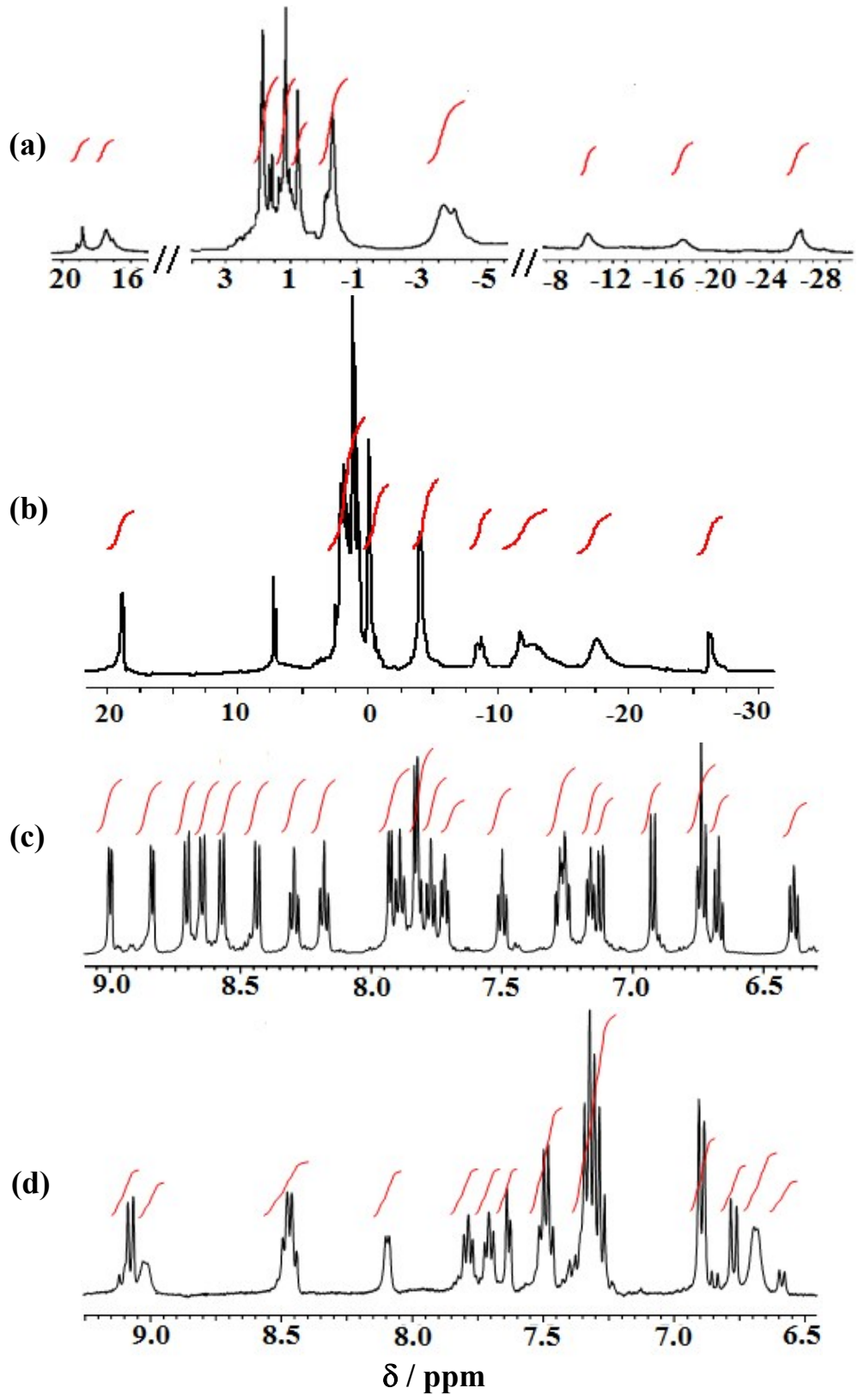


Fig. S2 ^{1}H-NMR spectra of (a) **1a** (in $CDCl_3$), (b) **1b** (in $CDCl_3$), (c) [**2**]$(ClO_4)_2$ (in (CD_3OD) and (d) [**3**]$(ClO_4)_2$ (in $(CD_3)_2SO$).

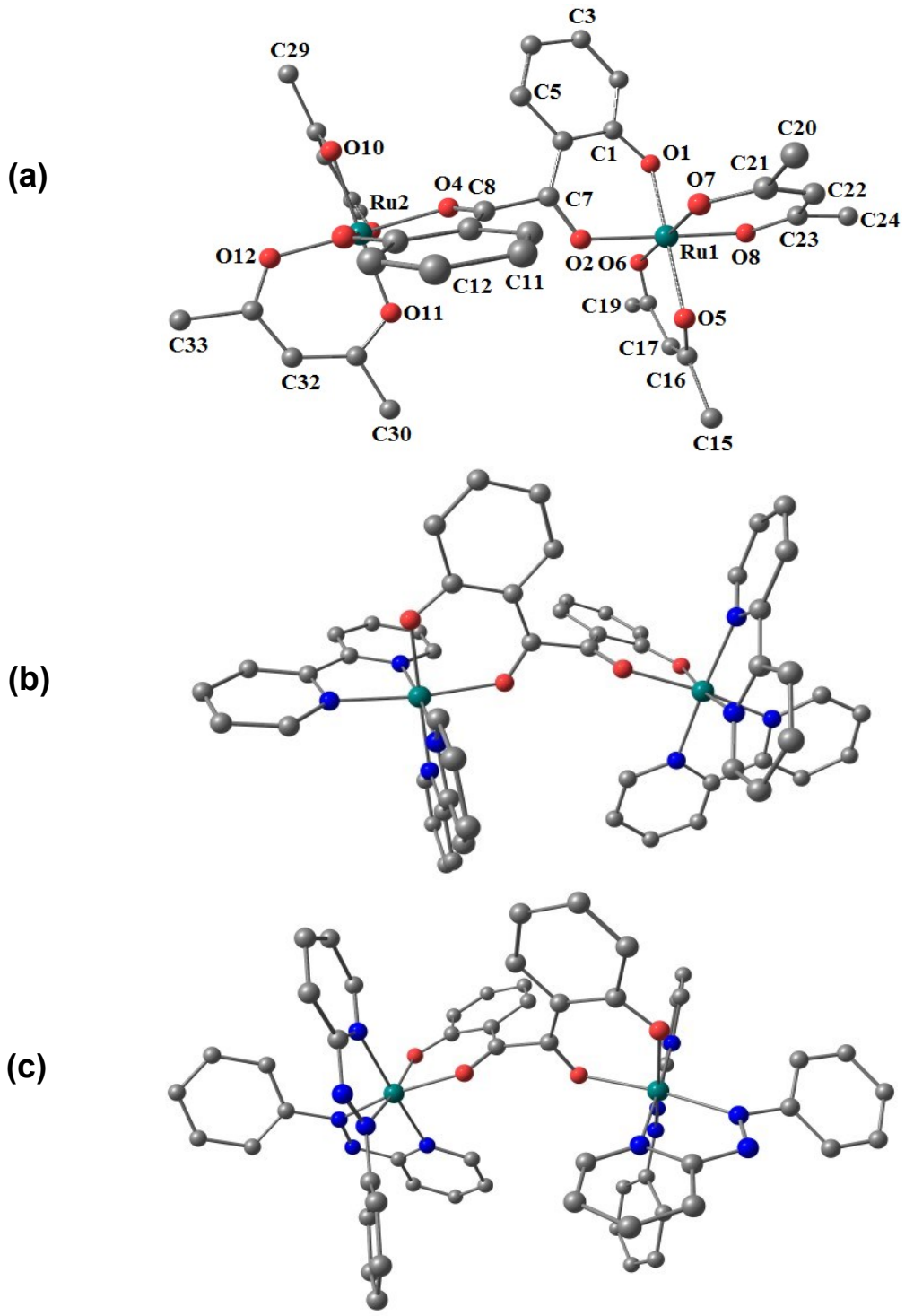


Fig. S3 DFT optimised structures of (a) **1**, (b) $[\mathbf{2}]^{2+}$ and (c) $[\mathbf{3}]^{2+}$.

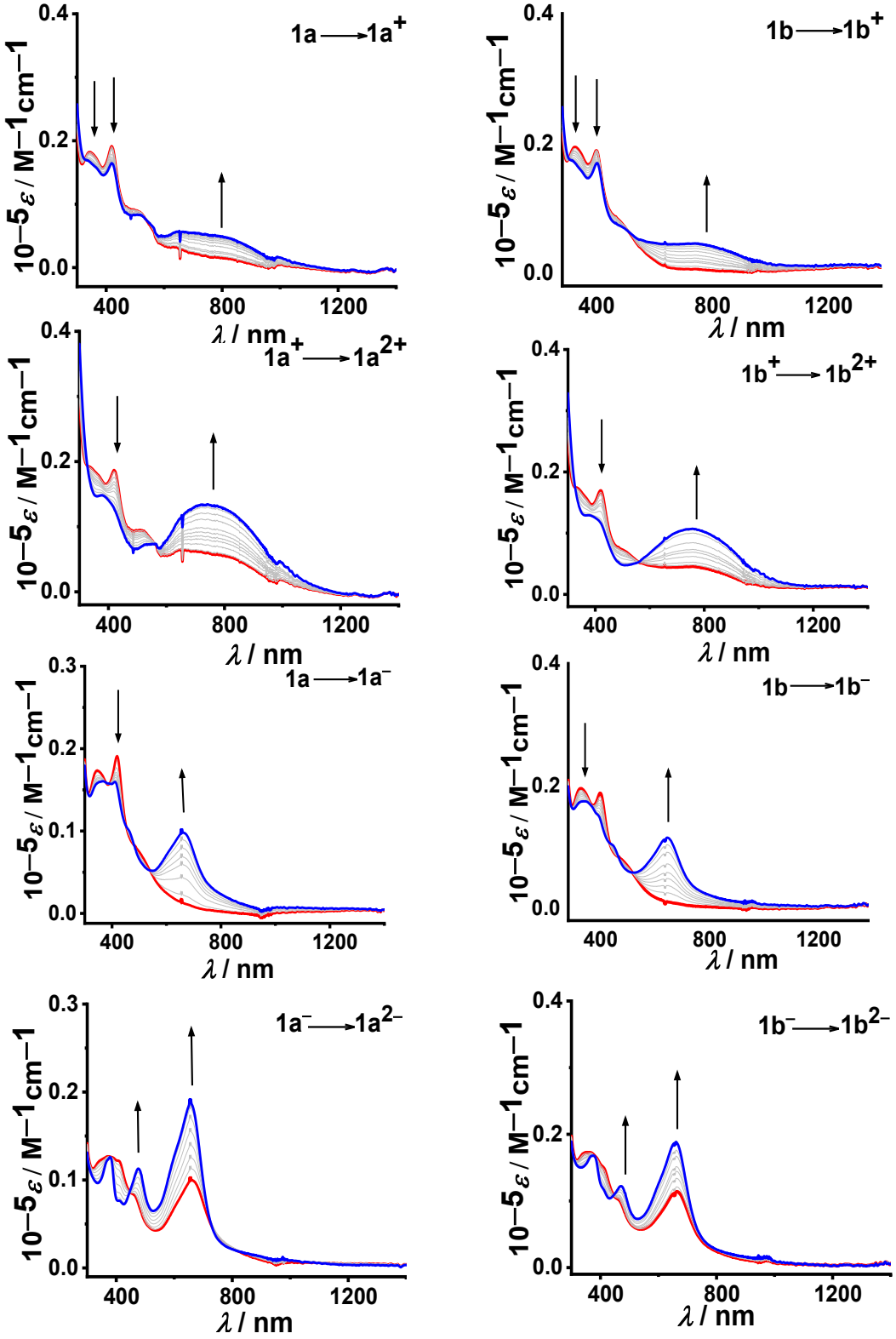


Fig. S4a UV-vis-NIR spectroelectrochemical response (on expanded scale) in CH_3CN/0.1 M nBu_4NPF_6 for $\mathbf{1}^n$.

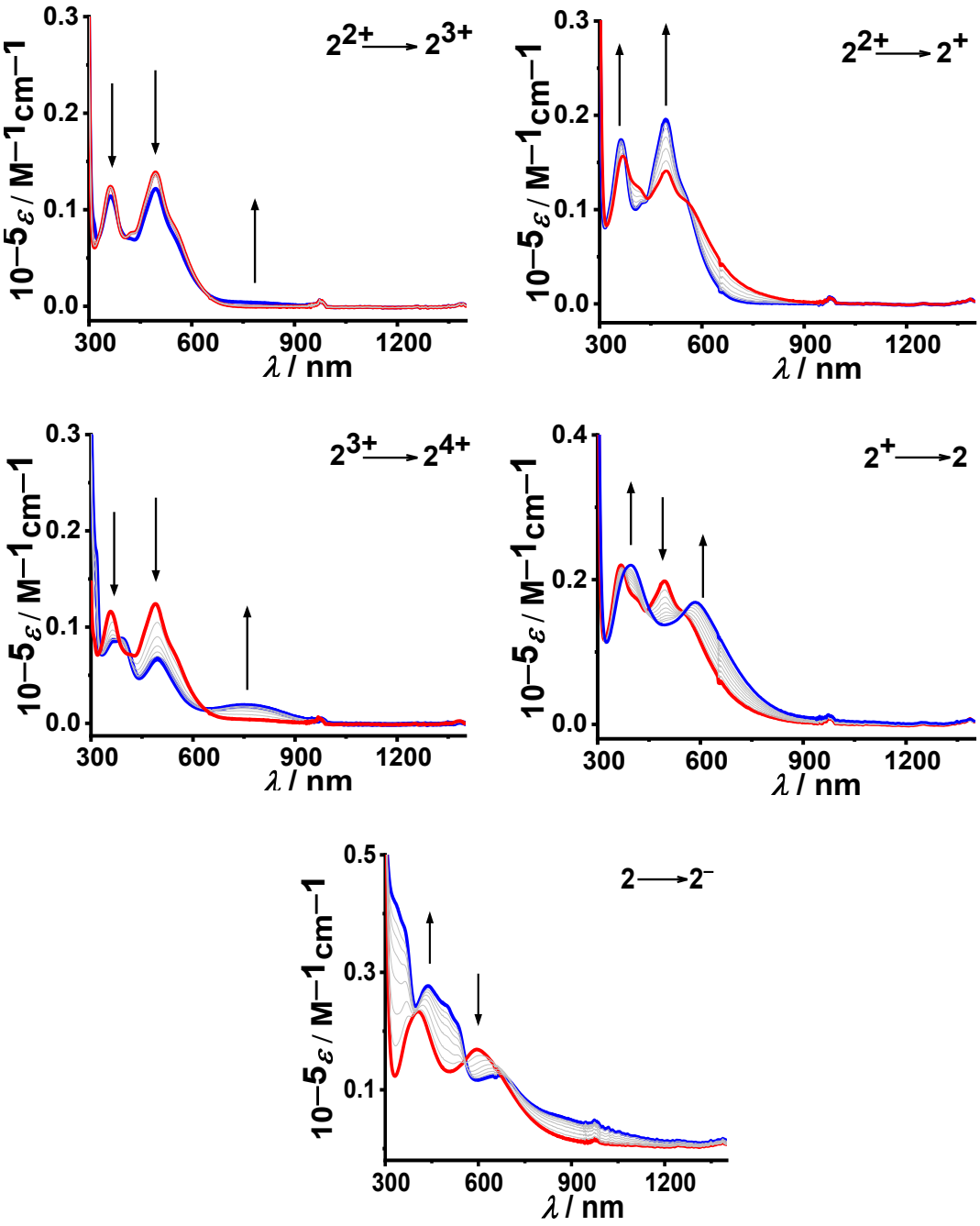


Fig. S4b UV-vis-NIR spectroelectrochemical response (on expanded scale) in CH_3CN/0.1 M nBu_4NPF_6 for $\mathbf{2}^n$.

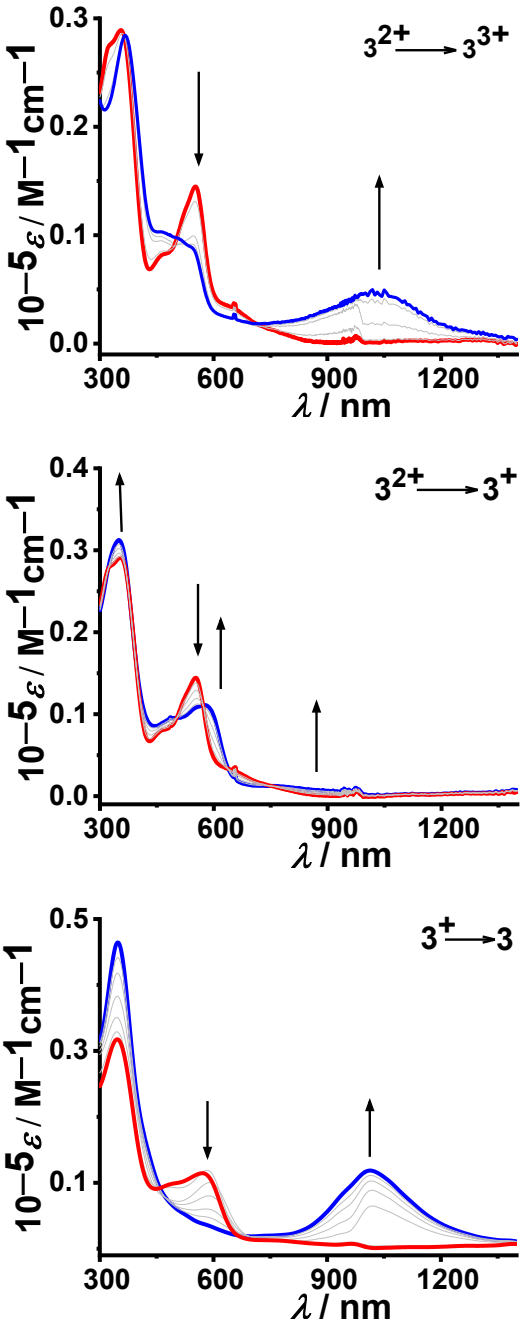


Fig. S4c UV-vis-NIR spectroelectrochemical response (on expanded scale) in CH_3CN/0.1 M nBu$_4$NPF$_6$ for **3**^{n}.