Supplementary Information

Different manifestations of enhanced π-acceptor ligation at every redox level of $[Os(9\text{-}OP)L_2]^n$, n=2+,+,0,– (9-OP^- = 9-oxidophenalenone and L = bpy or pap)†

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Table S1 Experimental and DFT ((R)B3LYP/(U)B3LYP) calculated selected bond lengths (Å) for $\mathbf{1}^{n}$

Bond lengths(Å)	X-ray	DFT					
	$\mathbf{1}^{+}$	$\mathbf{1}^{3+}$ (S=1)	$\mathbf{1}^{2+}$ (S=1/2)	$\mathbf{1}^{+}$ (S=0)	**1** (S=1/2)	$\mathbf{1}^{-}$ (S=1)	$\mathbf{1}^{2-}$ (S=3/2)
Os(1)-N(1)	2.037(3)	2.106	2.111	2.071	2.057	2.069	2.076
Os(1)-N(2)	2.014(4)	2.081	2.099	2.049	2.057	2.046	2.053
Os(1)-N(3)	2.012(3)	2.081	2.081	2.049	2.060	2.047	2.054
Os(1)-N(4)	2.048(3)	2.105	2.082	2.071	2.058	2.069	2.075
Os(1)-O(1)	2.037(3)	1.995	2.002	2.068	2.065	2.071	2.092
Os(1)-O(2)	2.042(3)	1.998	2.038	2.069	2.066	2.070	2.093
C(1)-O(1)	1.297(5)	1.306	1.315	1.294	1.295	1.308	1.307
C(11)-O(2)	1.292(5)	1.306	1.302	1.294	1.295	1.308	1.308
C(1)-C(2)	1.431(6)	1.423	1.425	1.439	1.438	1.425	1.421
C(1)-C(12)	1.458(6)	1.442	1.434	1.441	1.444	1.445	1.451
C(2)-C(3)	1.348(6)	1.371	1.369	1.360	1.361	1.372	1.381
C(3)-C(4)	1.421(6)	1.427	1.424	1.431	1.430	1.422	1.415
C(4)-C(5)	1.399(6)	1.405	1.411	1.405	1.406	1.415	1.424
C(4)-C(13)	1.412(6)	1.435	1.426	1.426	1.430	1.436	1.441
C(5)-C(6)	1.382(7)	1.398	1.390	1.392	1.392	1.392	1.392
C(6)-C(7)	1.362(7)	1.399	1.395	1.392	1.392	1.392	1.392
C(7)-C(8)	1.391(7)	1.405	1.406	1.405	1.406	1.415	1.424
C(8)-C(9)	1.420(6)	1.427	1.429	1.430	1.430	1.422	1.415
C(8)-C(13)	1.426(6)	1.434	1.425	1.426	1.430	1.436	1.441
C(9)-C(10)	1.347(6)	1.371	1.366	1.360	1.361	1.373	1.381
C(10)-C(11)	1.436(6)	1.423	1.429	1.439	1.438	1.425	1.421
C(11)-C(12)	1.435(6)	1.443	1.442	1.441	1.444	1.445	1.451
C(12)-C(13)	1.425(6)	1.416	1.435	1.440	1.442	1.442	1.444

Table S2 Experimental and DFT ((R)B3LYP/(U)B3LYP) calculated selected bond angles (deg) for $\mathbf{1}^n$

Bond angles (deg)	X-ray	DFT					
	$\mathbf{1}^+$	$\mathbf{1}^{3+}$ (S=1)	$\mathbf{1}^{2+}$ (S=1/2)	$\mathbf{1}^+$ (S=0)	**1** (S=1/2)	$\mathbf{1}^-$ (S=1)	$\mathbf{1}^{2-}$ (S=3/2)
O(1)-Os(1)-O(2)	90.34(12)	85.49	88.00	88.18	89.36	87.79	86.84
N(1)-Os(1)-N(2)	79.02(14)	78.12	77.63	78.29	78.59	78.91	79.13
N(1)-Os(1)-N(3)	98.83(13)	97.84	100.90	100.70	100.50	96.80	98.21
N(1)-Os(1)-N(4)	177.72(12)	173.93	176.26	178.18	178.30	173.84	175.83
N(1)-Os(1)-O(1)	94.54(13)	96.79	96.59	94.86	93.05	92.56	93.65
N(1)-Os(1)-O(2)	86.37(12)	87.60	86.90	86.34	87.95	91.86	89.32
N(2)-Os(1)-N(3)	96.46(14)	94.18	93.83	96.84	95.69	92.96	93.34
N(2)-Os(1)-N(4)	101.42(13)	97.51	98.82	100.29	100.04	96.81	97.77
N(2)-Os(1)-O(1)	172.85(11)	173.65	174.12	172.35	171.36	171.15	172.34
N(2)-Os(1)-O(2)	86.18(13)	90.44	90.54	87.98	88.15	90.08	90.49
N(3)-Os(1)-N(4)	78.91(13)	78.13	78.03	78.27	78.56	78.88	79.09
N(3)-Os(1)-O(1)	87.54(13)	90.26	88.31	87.71	87.92	90.40	90.19
N(3)-Os(1)-O(2)	174.52(11)	173.46	171.70	172.11	171.24	171.21	172.06
N(4)-Os(1)-O(1)	85.13(12)	87.82	86.96	86.61	88.33	91.85	89.55
N(4)-Os(1)-O(2)	95.88(12)	96.70	94.34	94.77	93.03	92.58	93.51

Table S3 Experimental and DFT ((R)B3LYP/(U)B3LYP) calculated selected bond lengths (Å) for $\mathbf{2}^n$

Bond lengths (Å)	X-ray	DFT					
	$\mathbf{2}^+$	$\mathbf{2}^{3+}$ (S=1)	$\mathbf{2}^{2+}$ (S=1/2)	$\mathbf{2}^+$ (S=0)	**2** (S=1/2)	$\mathbf{2}^-$ (S=0)	$\mathbf{2}^{2-}$ (S=1/2)
Os(1)-N(1)	2.022(5)	2.088	2.090	2.057	2.076	2.093	2.084
Os(1)-N(3)	1.956(6)	2.096	2.061	2.001	1.982	1.958	1.982
Os(1)-N(4)	1.974(5)	2.095	2.046	2.001	1.982	1.968	1.983
Os(1)-N(6)	2.035(5)	2.087	2.067	2.057	2.076	2.079	2.082
Os(1)-O(1)	2.030(4)	1.995	2.005	2.062	2.092	2.105	2.110
Os(1)-O(2)	2.026(4)	1.995	2.051	2.062	2.093	2.134	2.096
C(1)-O(1)	1.305(7)	1.317	1.311	1.296	1.284	1.279	1.305
C(11)-O(2)	1.308(7)	1.317	1.296	1.296	1.284	1.281	1.312
C(1)-C(2)	1.425(9)	1.419	1.426	1.436	1.444	1.446	1.420
C(1)-C(12)	1.435(8)	1.438	1.433	1.436	1.439	1.443	1.446
C(2)-C(3)	1.357(8)	1.379	1.365	1.362	1.359	1.361	1.383
C(3)-C(4)	1.434(9)	1.418	1.430	1.430	1.433	1.432	1.416
C(4)-C(5)	1.406(8)	1.417	1.403	1.406	1.404	1.406	1.423
C(4)-C(13)	1.408(8)	1.430	1.428	1.425	1.427	1.430	1.439
C(5)-C(6)	1.384(9)	1.394	1.398	1.392	1.393	1.392	1.393
C(6)-C(7)	1.378(9)	1.394	1.390	1.392	1.393	1.395	1.393
C(7)-C(8)	1.429(8)	1.417	1.410	1.406	1.404	1.403	1.422
C(8)-C(9)	1.420(9)	1.418	1.425	1.430	1.433	1.435	1.417
C(8)-C(13)	1.408(8)	1.430	1.429	1.425	1.427	1.431	1.439
C(9)-C(10)	1.362(8)	1.380	1.369	1.362	1.359	1.360	1.382
C(10)-C(11)	1.422(9)	1.419	1.431	1.437	1.444	1.446	1.417
C(11)-C(12)	1.421(8)	1.439	1.444	1.436	1.439	1.439	1.442
C(12)-C(13)	1.446(8)	1.423	1.428	1.437	1.435	1.433	1.437
N(2)-N(3)	1.335(7)	1.281	1.284	1.303	1.342	1.377	1.389
N(4)-N(5)	1.312(6)	1.281	1.288	1.303	1.342	1.386	1.401

Table S4 Experimental and DFT ((R)B3LYP/(U)B3LYP) calculated selected bond angles (deg) for $\mathbf{2}^{n}$

Bond angles (deg)	X-ray	DFT					
	$\mathbf{2}^{+}$	$\mathbf{2}^{3+}$ (S=1)	$\mathbf{2}^{2+}$ (S=1/2)	$\mathbf{2}^{+}$ (S=0)	**2** (S=1/2)	$\mathbf{2}^{-}$ (S=0)	$\mathbf{2}^{2-}$ (S=1/2)
O(1)-Os(1)-O(2)	87.32(16)	88.84	86.71	86.52	84.50	82.32	81.84
N(1)-Os(1)-N(3)	77.3(2)	75.42	75.42	76.63	76.93	77.04	77.23
N(1)-Os(1)-N(4)	101.1(2)	102.98	102.30	103.57	102.38	104.41	104.00
N(1)-Os(1)-N(6)	177.36(19)	177.61	176.63	179.75	178.89	177.10	178.07
N(1)-Os(1)-O(1)	93.30(19)	94.47	94.81	94.62	95.35	95.44	95.42
N(1)-Os(1)-O(2)	90.58(18)	87.22	86.56	85.10	85.31	84.02	87.14
N(3)-Os(1)-N(4)	105.5(2)	99.01	102.17	102.96	102.37	103.11	102.44
N(3)-Os(1)-N(6)	105.2(2)	103.02	101.83	103.51	102.35	100.40	101.33
N(3)-Os(1)-O(1)	166.60(19)	169.18	168.44	168.74	168.83	167.96	168.62
N(3)-Os(1)-O(2)	83.31(18)	86.82	86.54	85.68	86.80	87.49	89.04
N(4)-Os(1)-N(6)	77.3(2)	75.40	76.23	76.58	76.90	77.41	77.50
N(4)-Os(1)-O(1)	85.47(19)	86.90	85.76	85.83	87.05	87.77	87.66
N(4)-Os(1)-O(2)	166.50(18)	169.20	168.81	168.86	169.08	167.59	165.40
N(6)-Os(1)-O(1)	84.45(18)	94.48	95.26	85.20	85.47	94.53	85.79
N(6)-Os(1)-O(2)	90.70(18)	87.21	88.11	94.71	95.49	86.83	91.56

Table S5 DFT ((R)B3LYP) calculated selected MO compositions for $\mathbf{1}^{+}$ in $S = 0$ state

MO	Energy (eV)	Composition		
		Os	bpy	9-OP
LUMO+5	-3.311	0.09	0.89	0.02
LUMO+4	-3.594	0.03	0.96	0.01
LUMO+3	-3.713	0.03	0.95	0.02
LUMO+2	-4.332	0.06	0.13	0.81
LUMO+1	-4.521	0.11	0.83	0.06
LUMO	-4.561	0.11	0.84	0.06
HOMO	-7.338	0.50	0.19	0.31
HOMO-1	-7.351	0.61	0.23	0.17
HOMO-2	-7.687	0.57	0.17	0.26
HOMO-3	-8.415	0.28	0.12	0.60
HOMO-4	-8.639	0.23	0.07	0.70
HOMO-5	-9.219.	0.00	0.01	0.99

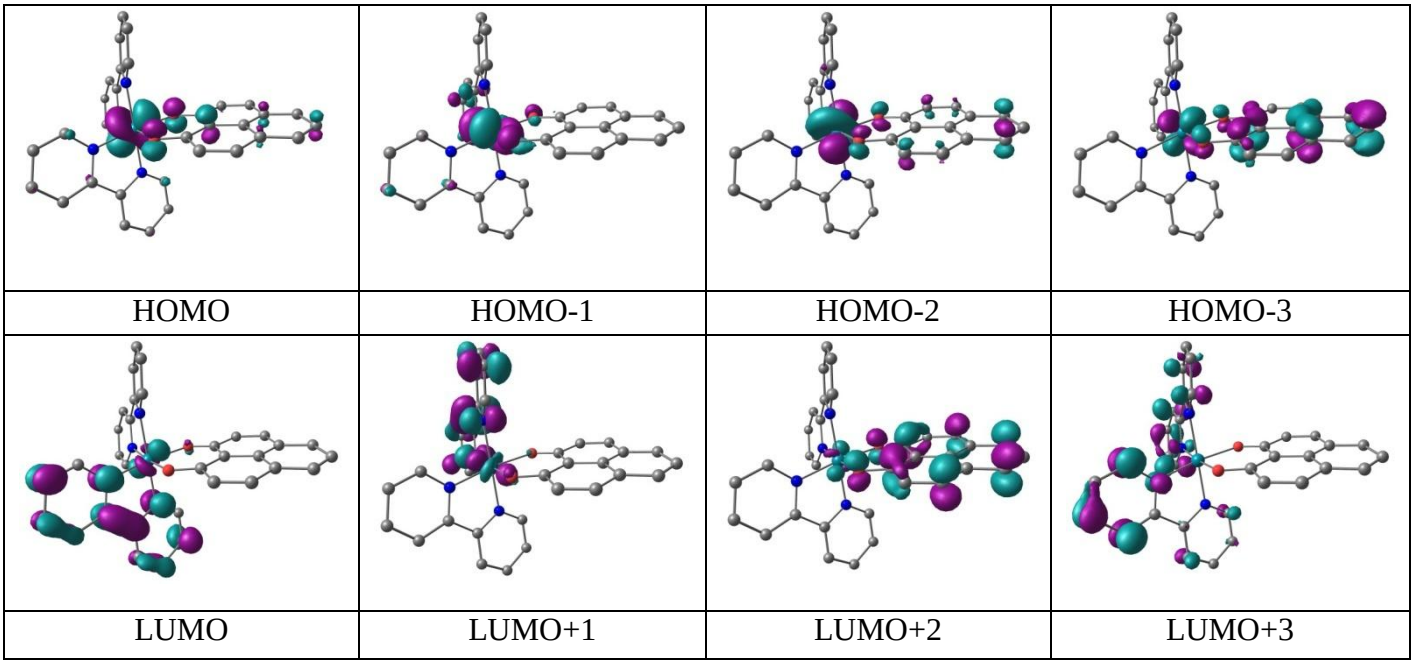


Table S6 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{1}^{2+}$ in S = 1/2 state

MO	Energy (eV)	Composition		
		Os	bpy	9-OP
		α-MO		
LUMO+5	-6.642	0.04	0.96	0.00
LUMO+4	-6.676	0.03	0.96	0.01
LUMO+3	-6.926	0.02	0.97	0.01
LUMO+2	-7.225	0.02	0.05	0.93
LUMO+1	-7.787	0.07	0.92	0.02
LUMO	-7.856	0.06	0.92	0.02
SOMO	-10.700	0.16	0.06	0.78
HOMO-1	-10.957	0.12	0.04	0.85
HOMO-2	-11.766	0.58	0.19	0.23
HOMO-3	-11.874	0.33	0.11	0.56
HOMO-4	-11.929	0.40	0.13	0.47
HOMO-5	-12.276	0.62	0.26	0.12
		β-MO		
LUMO+5	-6.633	0.03	0.96	0.00
LUMO+4	-6.883	0.02	0.97	0.01
LUMO+3	-7.187	0.03	0.06	0.91
LUMO+2	-7.681	0.12	0.85	0.03
LUMO+1	-7.778	0.07	0.91	0.01
LUMO	-9.271	0.61	0.25	0.14
HOMO	-10.630	0.23	0.08	0.69
HOMO-1	-10.898	0.20	0.07	0.73
HOMO-2	-11.618	0.56	0.17	0.27
HOMO-3	-11.813	0.63	0.16	0.21
HOMO-4	-11.882	0.02	0.01	0.97
HOMO-5	-12.516	0.00	0.99	0.01

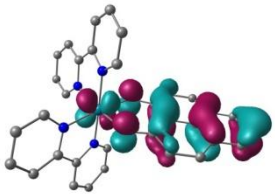
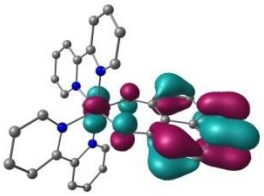
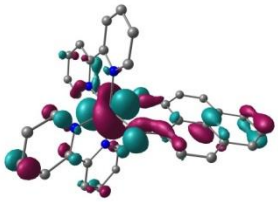
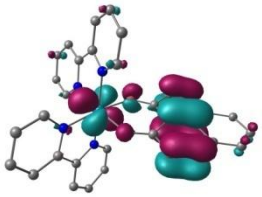
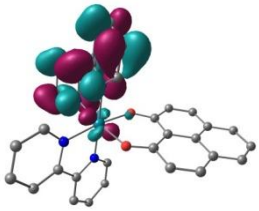
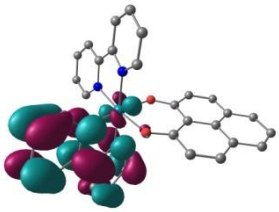
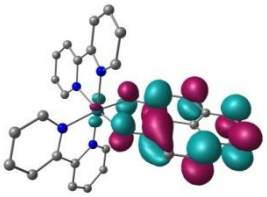
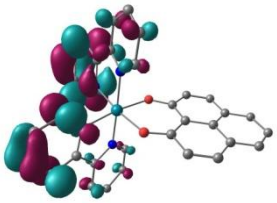
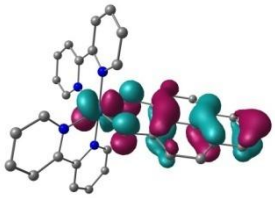
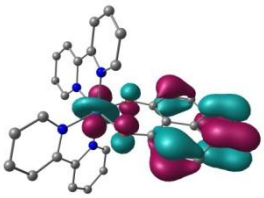
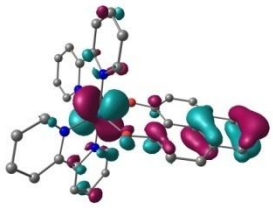
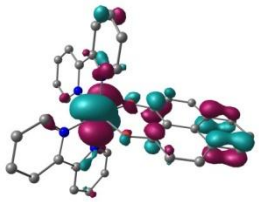
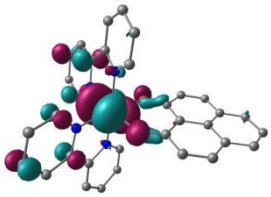
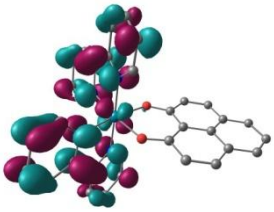
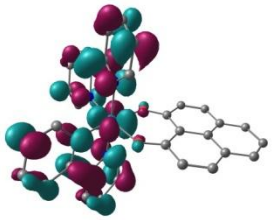
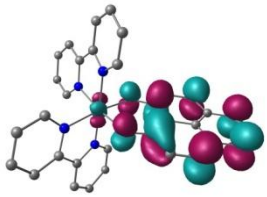
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{1}^{3+}$ in $S = 1$ state

MO	Energy (eV)	Composition		
		Os	bpy	9-OP
		α-MO		
LUMO+5	-9.404	0.03	0.96	0.01
LUMO+4	-9.477	0.02	0.97	0.01
LUMO+3	-9.611	0.01	0.97	0.01
LUMO+2	-10.586	0.05	0.91	0.03
LUMO+1	-10.616	0.04	0.95	0.01
LUMO	-10.849	0.03	0.05	0.92
SOMO1	-14.504	0.13	0.04	0.83
SOMO2	-14.513	0.11	0.03	0.85
HOMO-2	-15.235	0.06	0.91	0.03
HOMO-3	-15.291	0.05	0.85	0.10
HOMO-4	-15.393	0.01	0.12	0.87
HOMO-5	-15.506	0.53	0.27	0.20
		β-MO		
LUMO+5	-9.572	0.02	0.97	0.01
LUMO+4	-10.476	0.09	0.88	0.03
LUMO+3	-10.538	0.06	0.92	0.02
LUMO+2	-10.725	0.04	0.06	0.89
LUMO+1	-12.579	0.62	0.16	0.22
LUMO	-13.023	0.47	0.12	0.42
HOMO	-14.250	0.20	0.06	0.74
HOMO-1	-14.666	0.39	0.11	0.49
HOMO-2	-15.245	0.10	0.83	0.07
HOMO-3	-15.277	0.23	0.54	0.23
HOMO-4	-15.306	0.23	0.21	0.56
HOMO-5	-15.352	0.20	0.53	0.27

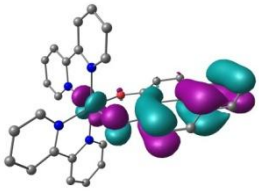
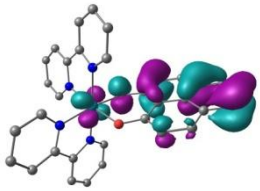
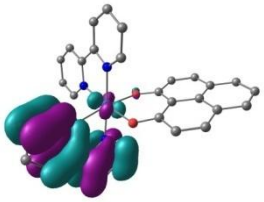
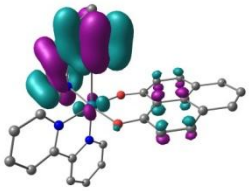
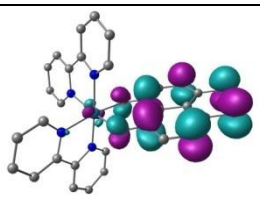
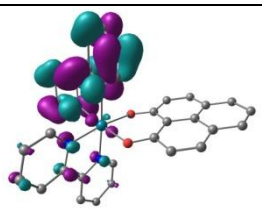
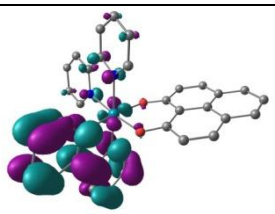
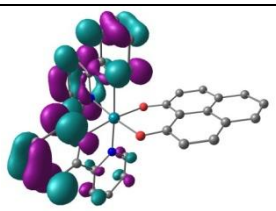
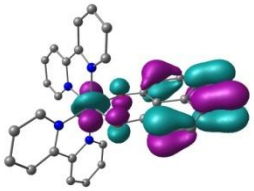
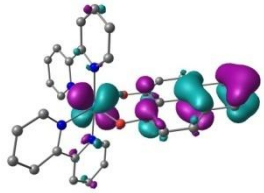
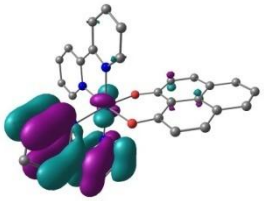
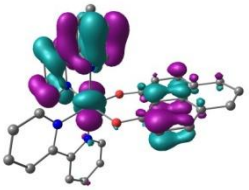
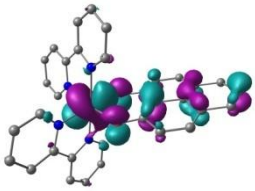
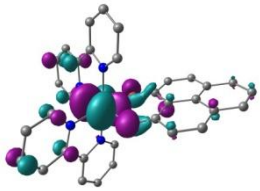
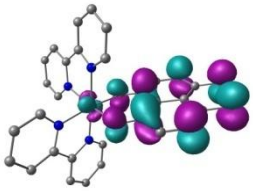
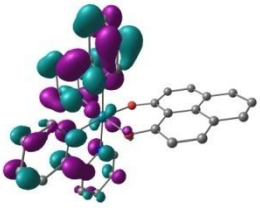
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 DFT ((U)B3LYP) calculated selected MO compositions for **1** in *S* = 1/2 state

MO	Energy (eV)	Composition		
		Os	bpy	9-OP
		α-MO		
LUMO+5	-0.459	0.08	0.90	0.02
LUMO+4	-0.537	0.04	0.94	0.02
LUMO+3	-0.598	0.05	0.95	0.01
LUMO+2	-0.819	0.03	0.96	0.01
LUMO+1	-1.675	0.09	0.26	0.65
LUMO	-1.751	0.12	0.86	0.02
SOMO	-2.377	0.08	0.69	0.23
HOMO-1	-4.293	0.52	0.23	0.25
HOMO-2	-4.391	0.68	0.18	0.14
HOMO-3	-4.657	0.62	0.19	0.19
HOMO-4	-5.544	0.20	0.10	0.70
HOMO-5	-5.842	0.12	0.05	0.83
		β-MO		
LUMO+5	-0.428	0.04	0.94	0.02
LUMO+4	-0.529	0.05	0.94	0.01
LUMO+3	-0.790	0.02	0.96	0.02
LUMO+2	-1.330	0.11	0.74	0.15
LUMO+1	-1.442	0.09	0.89	0.02
LUMO	-1.470	0.05	0.20	0.76
HOMO	-4.213	0.64	0.23	0.13
HOMO-1	-4.309	0.54	0.18	0.28
HOMO-2	-4.637	0.64	0.17	0.20
HOMO-3	-5.510	0.22	0.11	0.67
HOMO-4	-5.749	0.14	0.06	0.80
HOMO-5	-6.359	0.00	0.55	0.45

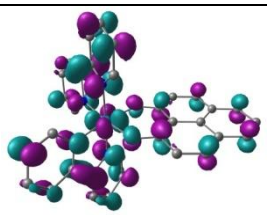
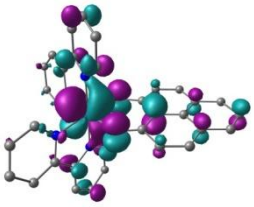
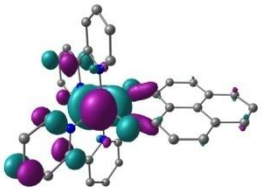
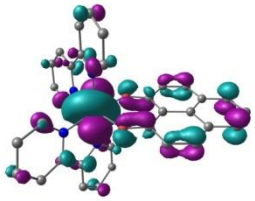
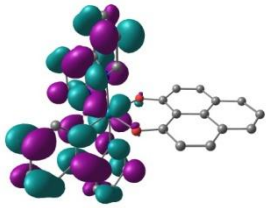
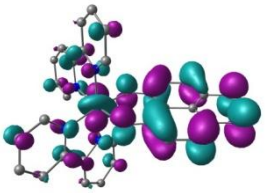
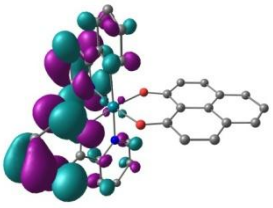
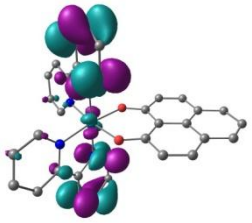
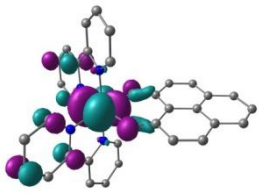
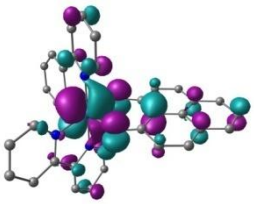
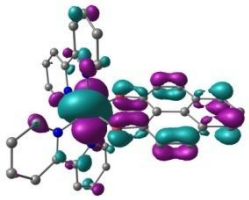
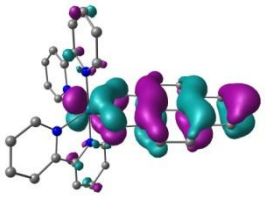
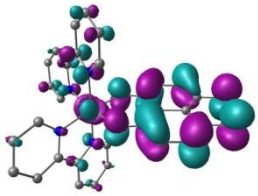
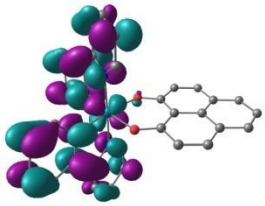
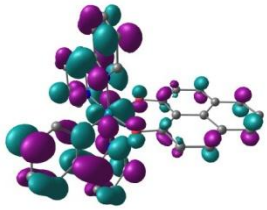
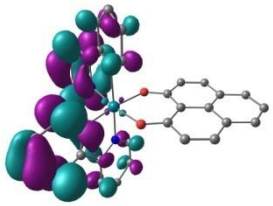
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{1}^{-}$ in $S = 1$ state

MO	Energy (eV)	Composition		
		Os	bpy	9-OP
		α-MO		
LUMO+5	3.001	0.02	0.04	0.94
LUMO+4	2.560	0.10	0.88	0.02
LUMO+3	2.438	0.04	0.94	0.02
LUMO+2	2.370	0.05	0.94	0.01
LUMO+1	2.189	0.04	0.94	0.02
LUMO	1.033	0.15	0.45	0.40
SOMO1	0.348	0.13	0.85	0.02
SOMO2	0.266	0.08	0.45	0.47
HOMO-2	-1.364	0.64	0.23	0.12
HOMO-3	-1.468	0.53	0.23	0.23
HOMO-4	-1.594	0.62	0.20	0.17
HOMO-5	-2.759	0.18	0.10	0.71
		β-MO		
LUMO+5	2.605	0.05	0.93	0.02
LUMO+4	2.462	0.06	0.93	0.01
LUMO+3	2.271	0.04	0.94	0.02
LUMO+2	1.697	0.11	0.87	0.02
LUMO+1	1.622	0.10	0.79	0.11
LUMO	1.404	0.05	0.14	0.81
HOMO	-1.136	0.65	0.22	0.13
HOMO-1	-1.160	0.57	0.24	0.19
HOMO-2	-1.593	0.65	0.18	0.17
HOMO-3	-2.585	0.13	0.11	0.76
HOMO-4	-2.921	0.08	0.08	0.84
HOMO-5	-3.242	0.02	0.96	0.02

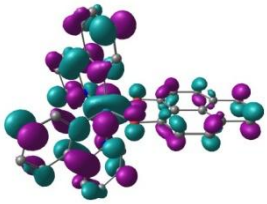
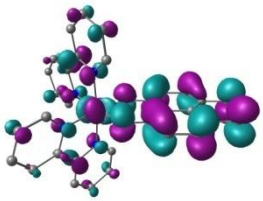
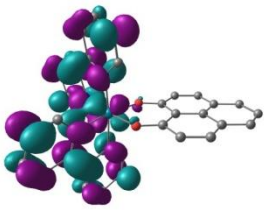
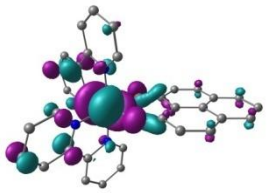
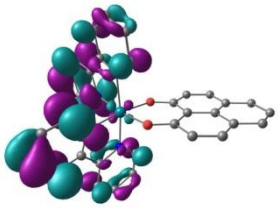
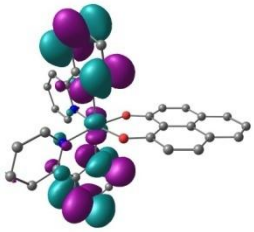
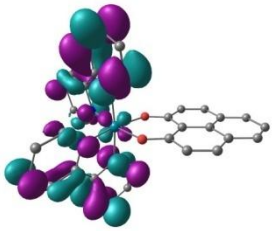
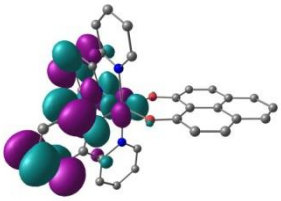
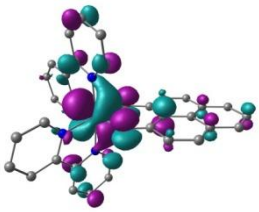
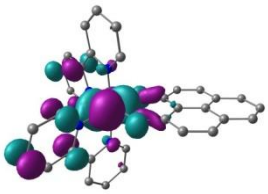
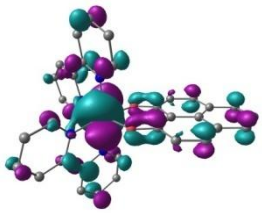
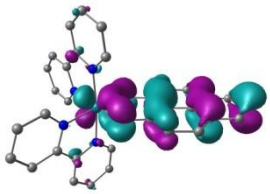
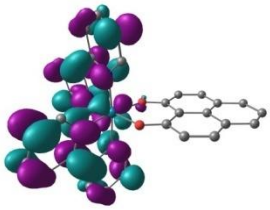
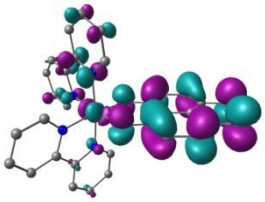
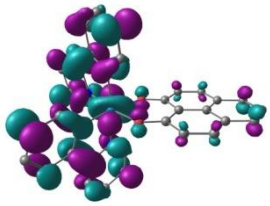
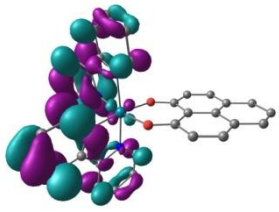
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{1}^{2-}$ in S = 3/2 state

MO	Energy (eV)	Composition		
		Os	bpy	9-OP
		α-MO		
LUMO+5	6.179	0.02	0.02	0.96
LUMO+4	5.843	0.04	0.04	0.92
LUMO+3	5.391	0.10	0.88	0.02
LUMO+2	5.258	0.03	0.96	0.01
LUMO+1	5.238	0.06	0.93	0.01
LUMO	5.012	0.04	0.95	0.01
SOMO1	3.196	0.18	0.61	0.21
SOMO2	2.894	0.07	0.26	0.67
SOMO3	2.807	0.10	0.89	0.02
HOMO-3	1.685	0.64	0.20	0.15
HOMO-4	1.671	0.57	0.22	0.21
HOMO-5	1.097	0.57	0.27	0.16
		β-MO		
LUMO+5	5.415	0.04	0.94	0.01
LUMO+4	5.368	0.07	0.91	0.02
LUMO+3	5.100	0.04	0.95	0.01
LUMO+2	4.772	0.13	0.75	0.12
LUMO+1	4.357	0.04	0.19	0.77
LUMO	4.337	0.08	0.89	0.03
HOMO	2.045	0.57	0.22	0.21
HOMO-1	2.018	0.62	0.25	0.13
HOMO-2	1.684	0.58	0.27	0.15
HOMO-3	0.374.	0.16	0.10	0.75
HOMO-4	0.156	0.07	0.05	0.88
HOMO-5	-0.326	0.02	0.97	0.02

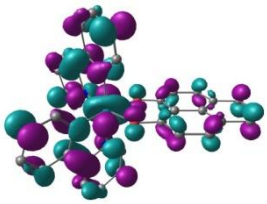
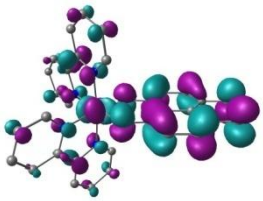
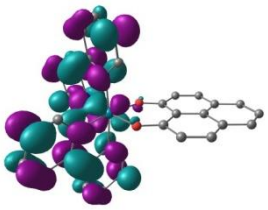
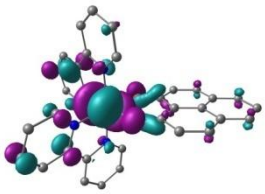
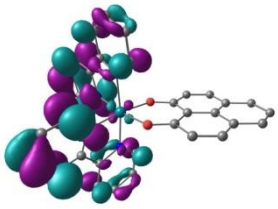
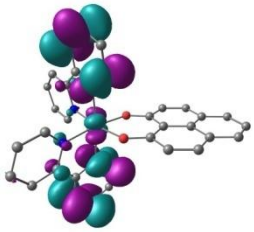
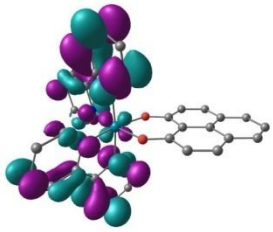
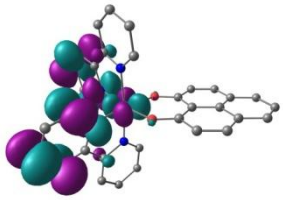
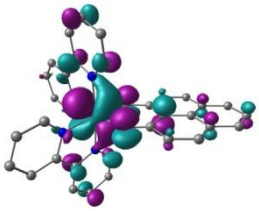
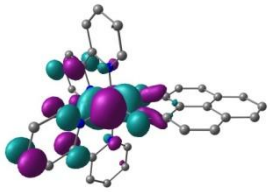
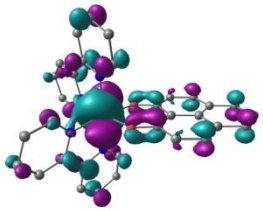
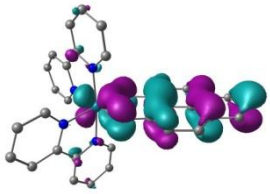
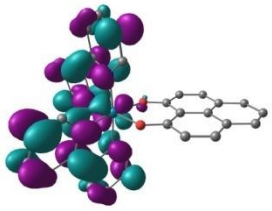
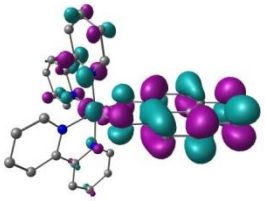
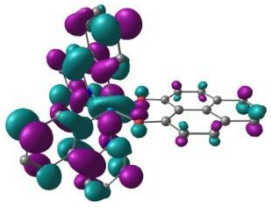
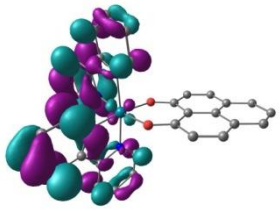
α-MO			
			
SOMO1	SOMO2	SOMO3	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 DFT ((R)B3LYP) calculated selected MO compositions for $\mathbf{2}^{+}$ in $S = 0$ state

MO	Energy (eV)	Composition		
		Os	pap	9-OP
LUMO+5	-3.008	0.02	0.07	0.91
LUMO+4	-3.554	0.05	0.92	0.03
LUMO+3	-3.705	0.05	0.94	0.01
LUMO+2	-5.021	0.09	0.18	0.73
LUMO+1	-5.160	0.24	0.57	0.19
LUMO	-5.607	0.16	0.77	0.07
HOMO	-8.102	0.33	0.30	0.37
HOMO-1	-8.334	0.55	0.21	0.25
HOMO-2	-8.611	0.38	0.39	0.23
HOMO-3	-9.028	0.11	0.47	0.42
HOMO-4	-9.104	0.12	0.81	0.07
HOMO-5	-9.211	0.28	0.20	0.52

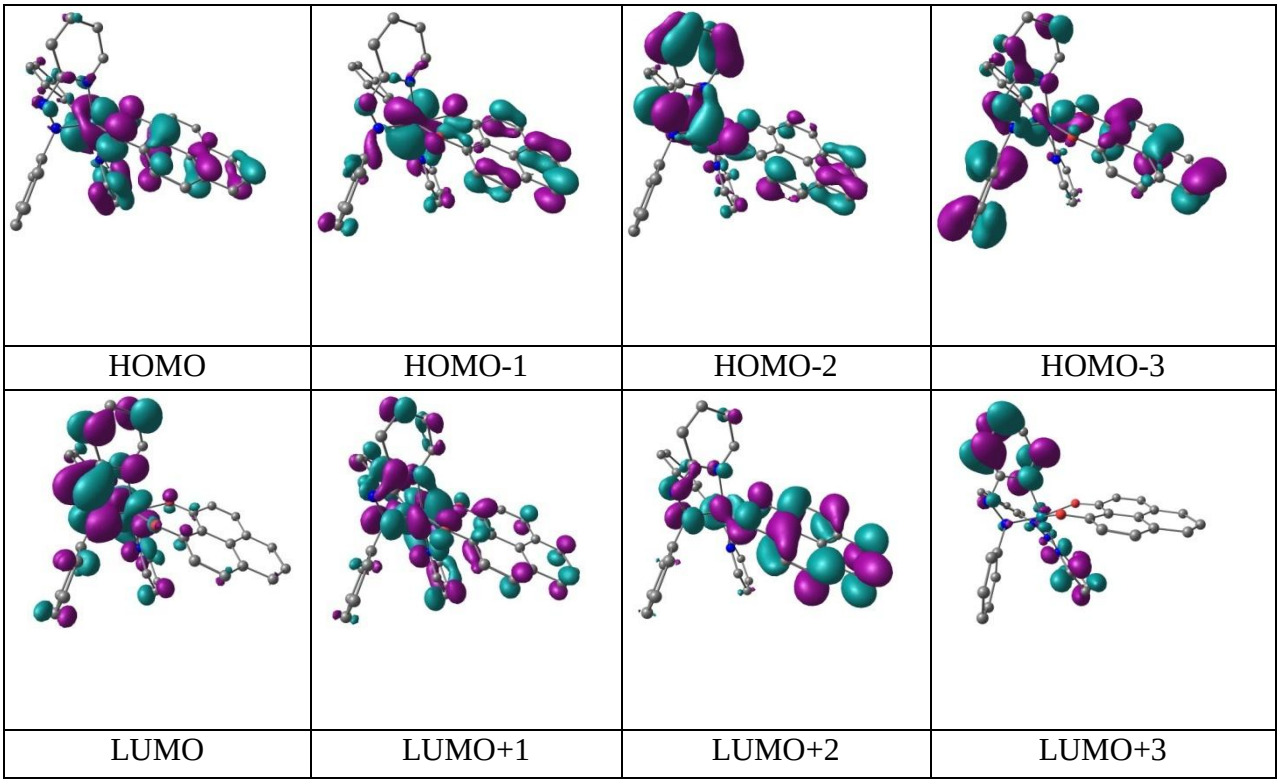


Table S12 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{2}^{2+}$ in S = 1/2 state

MO	Energy (eV)	Composition		
		Os	pap	9-OP
		α-MO		
LUMO+5	-5.819	0.02	0.05	0.93
LUMO+4	-6.638	0.03	0.95	0.02
LUMO+3	-6.708	0.04	0.96	0.00
LUMO+2	-7.867	0.02	0.03	0.95
LUMO+1	-8.390	0.20	0.76	0.05
LUMO	-8.732	0.08	0.90	0.02
SOMO	-11.501	0.17	0.10	0.73
HOMO-1	-11.541	0.27	0.07	0.66
HOMO-2	-11.765	0.22	0.72	0.06
HOMO-3	-11.870	0.03	0.89	0.08
HOMO-4	-12.021	0.01	0.98	0.01
HOMO-5	-12.034	0.04	0.95	0.01
		β-MO		
LUMO+5	-6.568	0.05	0.93	0.02
LUMO+4	-6.685	0.04	0.95	0.00
LUMO+3	-7.798	0.03	0.04	0.93
LUMO+2	-8.304	0.23	0.72	0.05
LUMO+1	-8.546	0.20	0.75	0.05
LUMO	-10.045	0.36	0.29	0.34
HOMO	-11.364	0.31	0.07	0.62
HOMO-1	-11.625	0.19	0.29	0.52
HOMO-2	-11.686	0.33	0.57	0.10
HOMO-3	-11.942	0.24	0.62	0.14
HOMO-4	-11.958	0.10	0.81	0.09
HOMO-5	-12.021	0.02	0.96	0.02

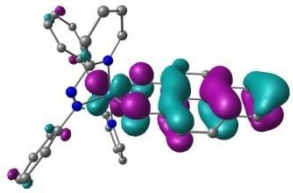
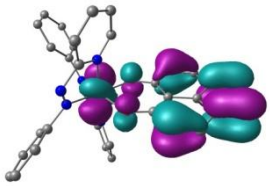
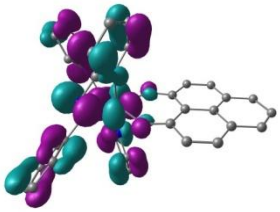
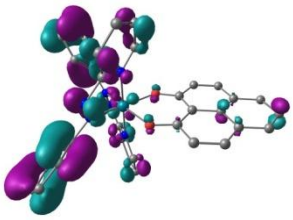
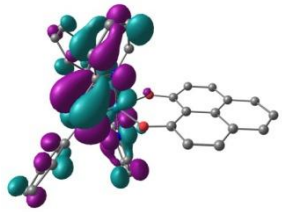
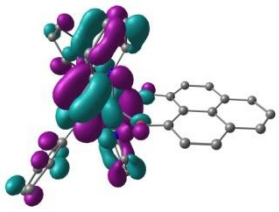
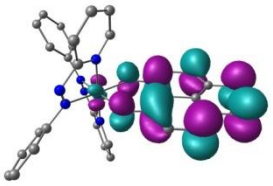
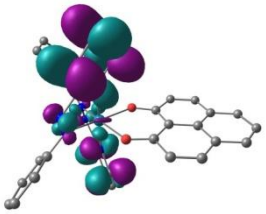
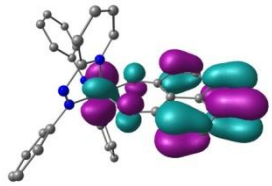
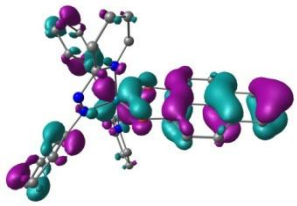
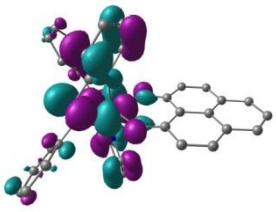
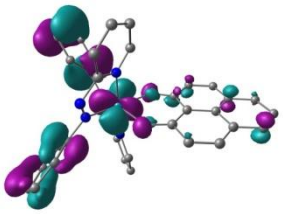
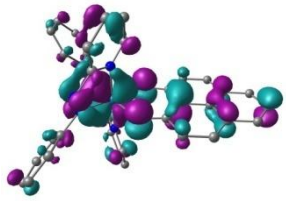
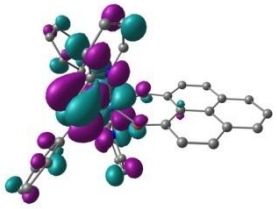
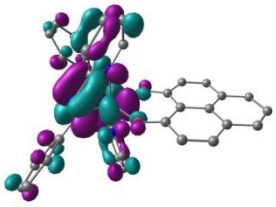
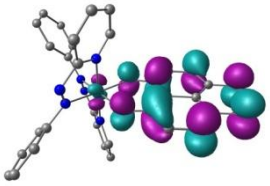
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{2}^{3+}$ in $S = 1$ state

MO	Energy (eV)	Composition		
		Os	pap	9-OP
		α-MO		
LUMO+5	-9.016	0.43	0.35	0.22
LUMO+4	-9.454	0.06	0.91	0.04
LUMO+3	-9.532	0.05	0.94	0.01
LUMO+2	-11.141	0.03	0.06	0.91
LUMO+1	-11.320	0.13	0.81	0.06
LUMO	-11.551	0.05	0.93	0.02
SOMO1	-14.509	0.06	0.87	0.07
SOMO2	-14.526	0.02	0.98	0.01
HOMO-2	-14.584	0.01	0.98	0.01
HOMO-3	-14.601	0.01	0.99	0.01
HOMO-4	-14.752	0.10	0.13	0.77
HOMO-5	-14.998	0.10	0.03	0.87
		β-MO		
LUMO+5	-9.499	0.05	0.94	0.01
LUMO+4	-10.870	0.06	0.04	0.90
LUMO+3	-11.215	0.18	0.78	0.04
LUMO+2	-11.494	0.10	0.87	0.03
LUMO+1	-13.055	0.45	0.19	0.36
LUMO	-13.393	0.50	0.12	0.37
HOMO	-14.444	0.01	0.90	0.09
HOMO-1	-14.454	0.02	0.90	0.08
HOMO-2	-14.570	0.00	0.99	0.01
HOMO-3	-14.582	0.00	0.99	0.01
HOMO-4	-14.733	0.36	0.18	0.46
HOMO-5	-14.985	0.32	0.21	0.47

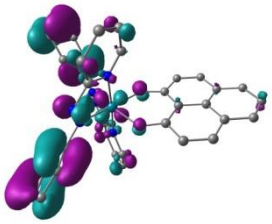
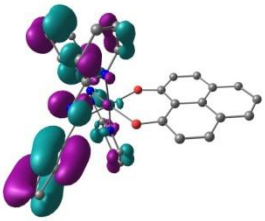
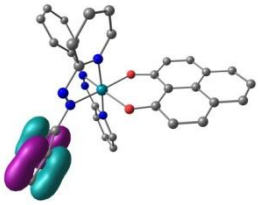
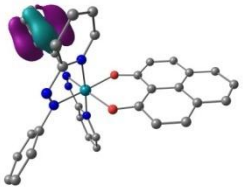
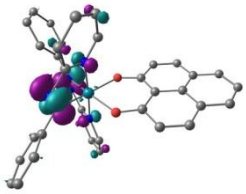
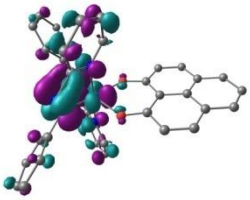
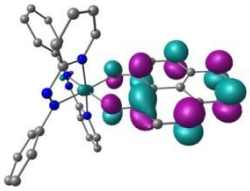
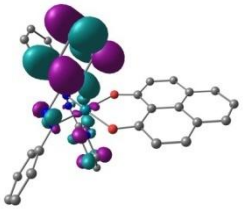
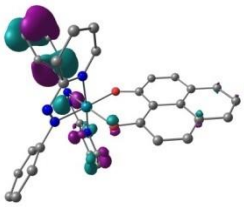
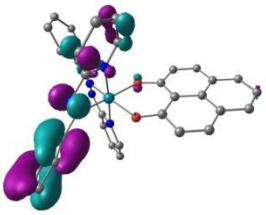
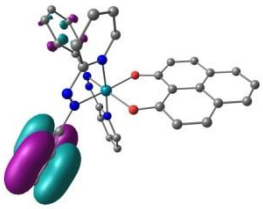
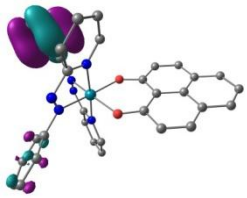
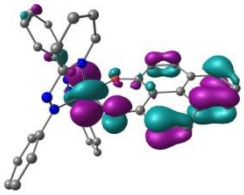
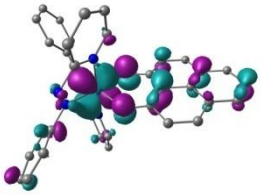
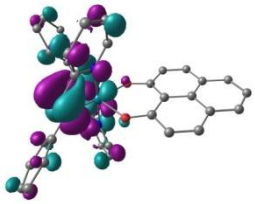
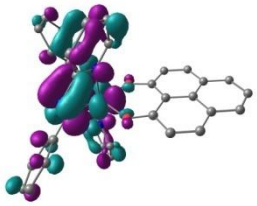
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 DFT ((U)B3LYP) calculated selected MO compositions for **2** in *S* = 1/2 state

MO	Energy (eV)	Composition		
		Os	pap	9-OP
		α-MO		
LUMO+5	0.093.	0.02	0.04	0.95
LUMO+4	-0.368	0.01	0.05	0.94
LUMO+3	-0.577	0.04	0.91	0.05
LUMO+2	-0.674	0.06	0.93	0.01
LUMO+1	-2.033	0.34	0.59	0.07
LUMO	-2.272	0.05	0.03	0.91
SOMO	-3.428	0.15	0.82	0.03
HOMO-1	-5.066	0.57	0.30	0.13
HOMO-2	-5.110	0.49	0.24	0.28
HOMO-3	-5.369	0.50	0.35	0.15
HOMO-4	-6.134.	0.07	0.56	0.37
HOMO-5	-6.290.	0.06	0.91	0.03
		β-MO		
LUMO+5	-0.361	0.02	0.09	0.89
LUMO+4	-0.493	0.05	0.85	0.10
LUMO+3	-0.585	0.06	0.94	0.01
LUMO+2	-1.780	0.19	0.76	0.05
LUMO+1	-1.911	0.14	0.82	0.03
LUMO	-2.272	0.05	0.03	0.91
HOMO	-4.869	0.54	0.24	0.22
HOMO-1	-5.050	0.58	0.30	0.12
HOMO-2	-5.302	0.59	0.25	0.17
HOMO-3	-6.009	0.01	0.81	0.17
HOMO-4	-6.193	0.14	0.29	0.57
HOMO-5	-6.226	0.15	0.76	0.09

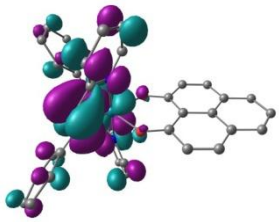
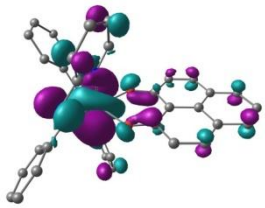
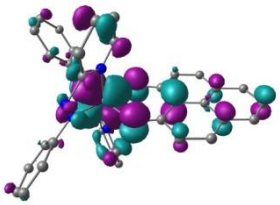
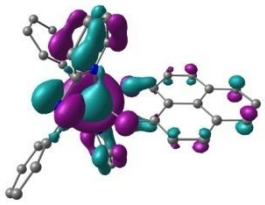
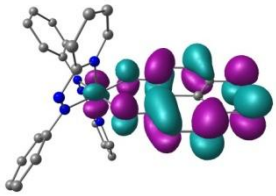
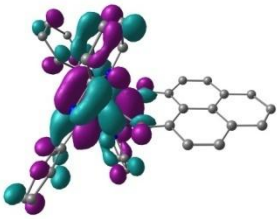
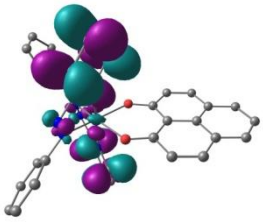
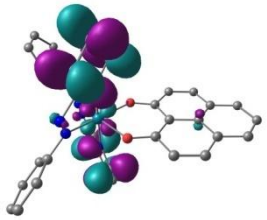
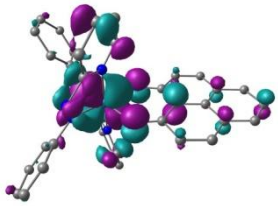
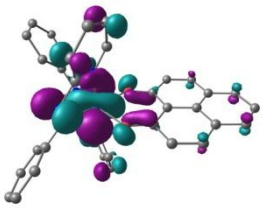
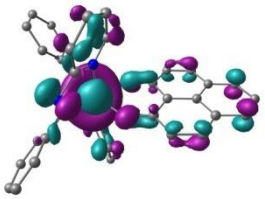
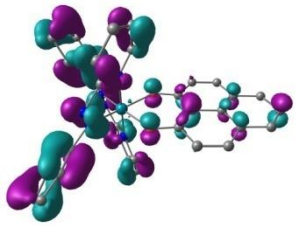
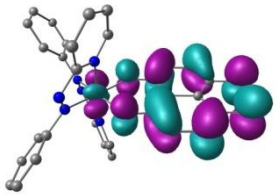
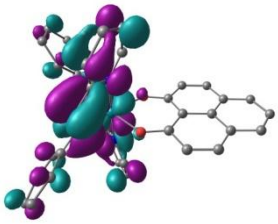
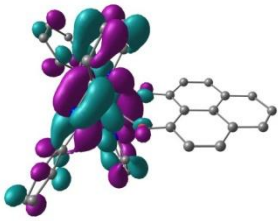
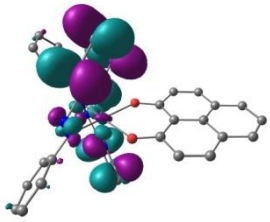
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 DFT ((R)B3LYP) calculated selected MO compositions for $\mathbf{2}^{-}$ in $S = 0$ state

MO	Energy (eV)	Composition		
		Os	pap	9-OP
LUMO+5	2.660	0.02	0.02	0.95
LUMO+4	2.543	0.04	0.92	0.05
LUMO+3	2.462	0.06	0.92	0.02
LUMO+2	2.208	0.01	0.03	0.96
LUMO+1	1.188	0.29	0.65	0.06
LUMO	0.414	0.07	0.08	0.85
HOMO	-0.168	0.12	0.07	0.81
HOMO-1	-1.865	0.53	0.37	0.10
HOMO-2	-1.937	0.59	0.22	0.19
HOMO-3	-2.285	0.58	0.31	0.12
HOMO-4	-3.148	0.01	0.89	0.11
HOMO-5	-3.382	0.11	0.81	0.08

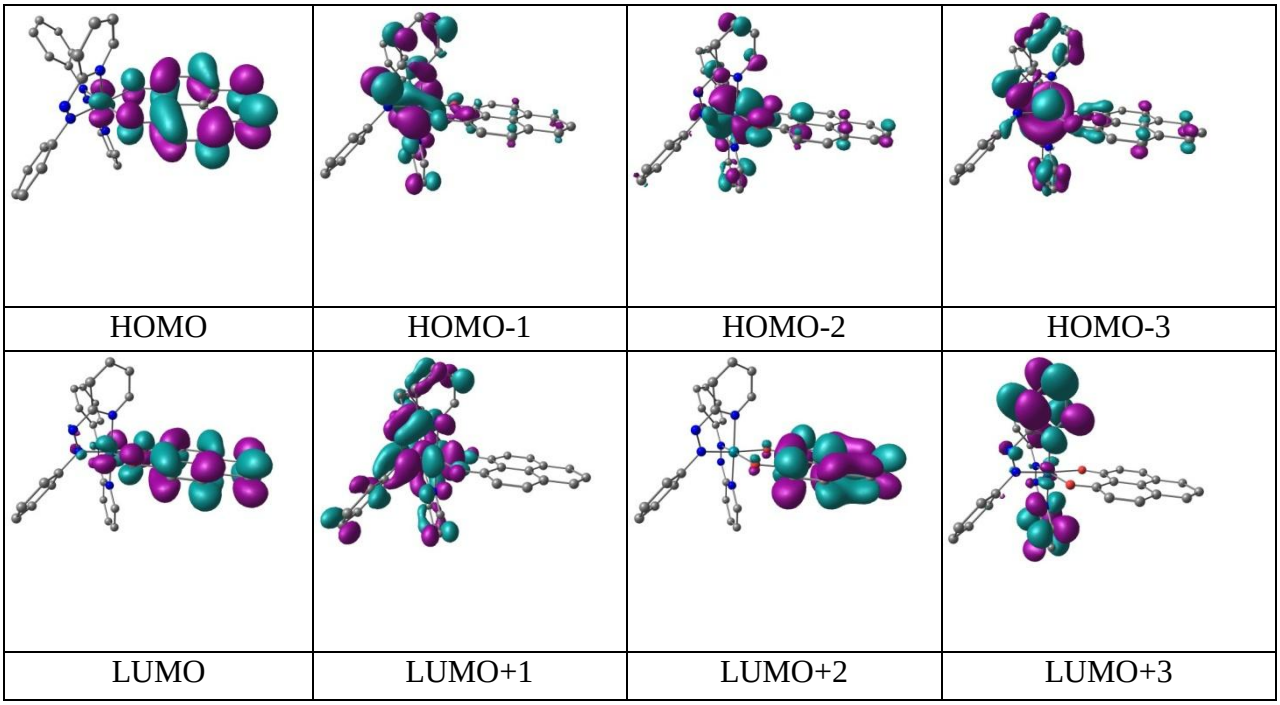


Table S16 DFT ((U)B3LYP) calculated selected MO compositions for $\mathbf{2}^{2-}$ in S = 1/2 state

MO	Energy (eV)	Composition		
		Os	pap	9-OP
		α-MO		
LUMO+5	5.442	0.05	0.91	0.03
LUMO+4	5.268	0.03	0.95	0.02
LUMO+3	5.166	0.02	0.97	0.01
LUMO+2	5.054	0.06	0.92	0.02
LUMO+1	4.984	0.04	0.94	0.01
LUMO	3.768	0.32	0.61	0.07
SOMO	2.801	0.04	0.04	0.91
HOMO-1	2.038	0.13	0.83	0.04
HOMO-2	0.925	0.43	0.22	0.34
HOMO-3	0.855	0.55	0.36	0.10
HOMO-4	0.334	0.48	0.38	0.14
HOMO-5	-0.135	0.26	0.20	0.54
		β-MO		
LUMO+5	5.266	0.03	0.95	0.02
LUMO+4	5.167	0.02	0.97	0.01
LUMO+3	5.056	0.06	0.92	0.02
LUMO+2	4.987	0.05	0.94	0.01
LUMO+1	4.288	0.03	0.04	0.94
LUMO	3.786	0.33	0.60	0.07
HOMO	2.043	0.14	0.83	0.04
HOMO-1	1.057	0.36	0.23	0.41
HOMO-2	0.948	0.58	0.28	0.14
HOMO-3	0.435	0.35	0.41	0.23
HOMO-4	0.010	0.34	0.20	0.46
HOMO-5	-0.165	0.22	0.10	0.68

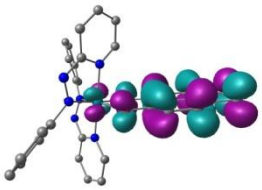
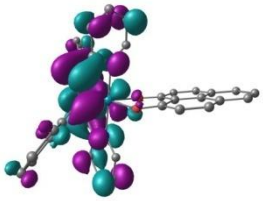
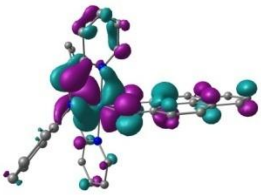
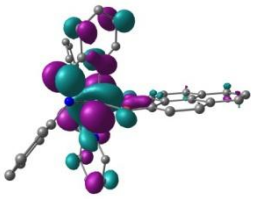
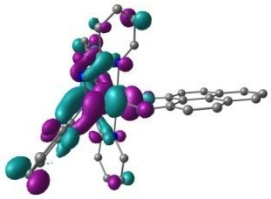
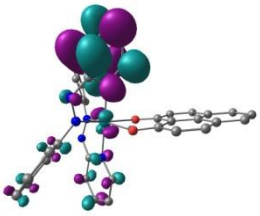
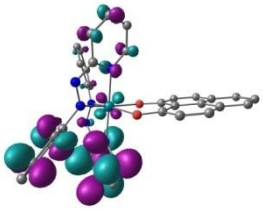
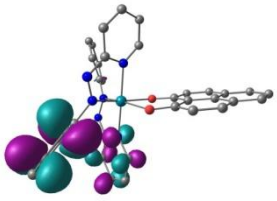
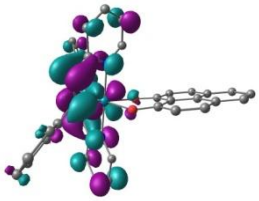
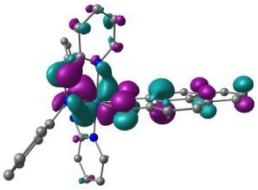
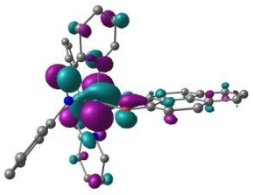
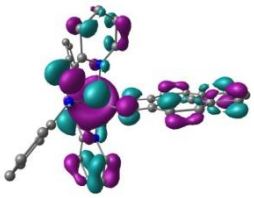
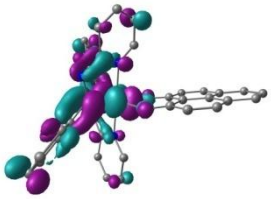
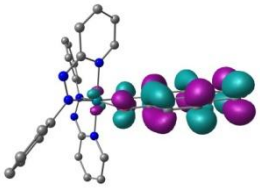
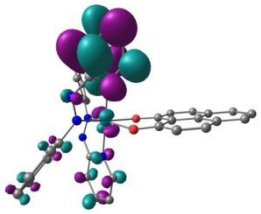
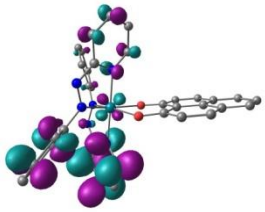
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 Energies of DFT ((U)/(R)B3LYP/LANL2DZ/6-31G*) optimized $\mathbf{1}^n$ (n = 3+, 1–, 2–) and $\mathbf{2}^n$ (n = 3+, 1–, 2–)

Complex	E (Hartrees)				$\Delta E_{(HE-LE)}$ [a]
	S = 0	S = 1/2	S = 1	S = 3/2	
$\mathbf{1}^{3+}$	-1731.0986374	-	-1731.1118086	-	0.013171 Hartrees 2890.70035 cm^{-1} 34.5804631 kJ/mol
$\mathbf{1}^{-}$	-1731.9931938	-	-1732.0062657	-	0.013072 Hartrees 2868.97236 cm^{-1} 34.3205386 kJ/mol
$\mathbf{1}^{2-}$	-	-1731.9311114	-	-1731.9213308	0.009781 Hartrees 2146.6814 cm^{-1} 25.680017 kJ/mol
$\mathbf{2}^{3+}$	-1917.8988617	-	-1917.9053953	-	0.006534 Hartrees 1434.04723 cm^{-1} 17.1550183 kJ/mol
$\mathbf{2}^{-}$	-1918.9061215	-	-1918.9048069	-	0.001315 Hartrees 288.609138 cm^{-1} 3.45253276 kJ/mol
$\mathbf{2}^{2-}$	-	-1918.8530218	-	-1918.8440737	0.008948 Hartrees 1963.858989 cm^{-1} 23.49297579 kJ/mol

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

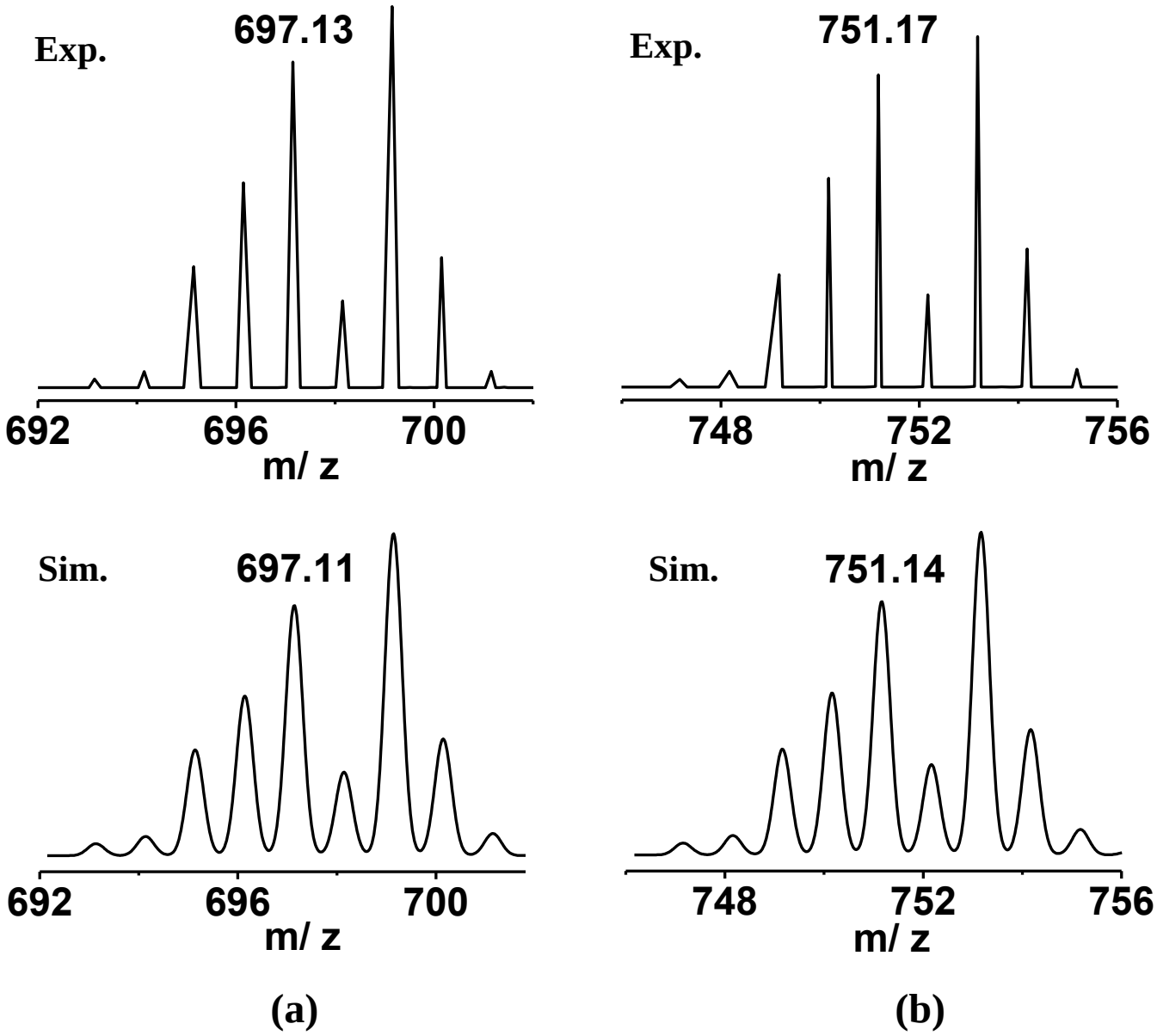


Fig. S1 Experimental and simulated ESI-MS(+) spectra of (a) [**1**]ClO_4 and (b) [**2**]ClO_4 in CH_3CN.

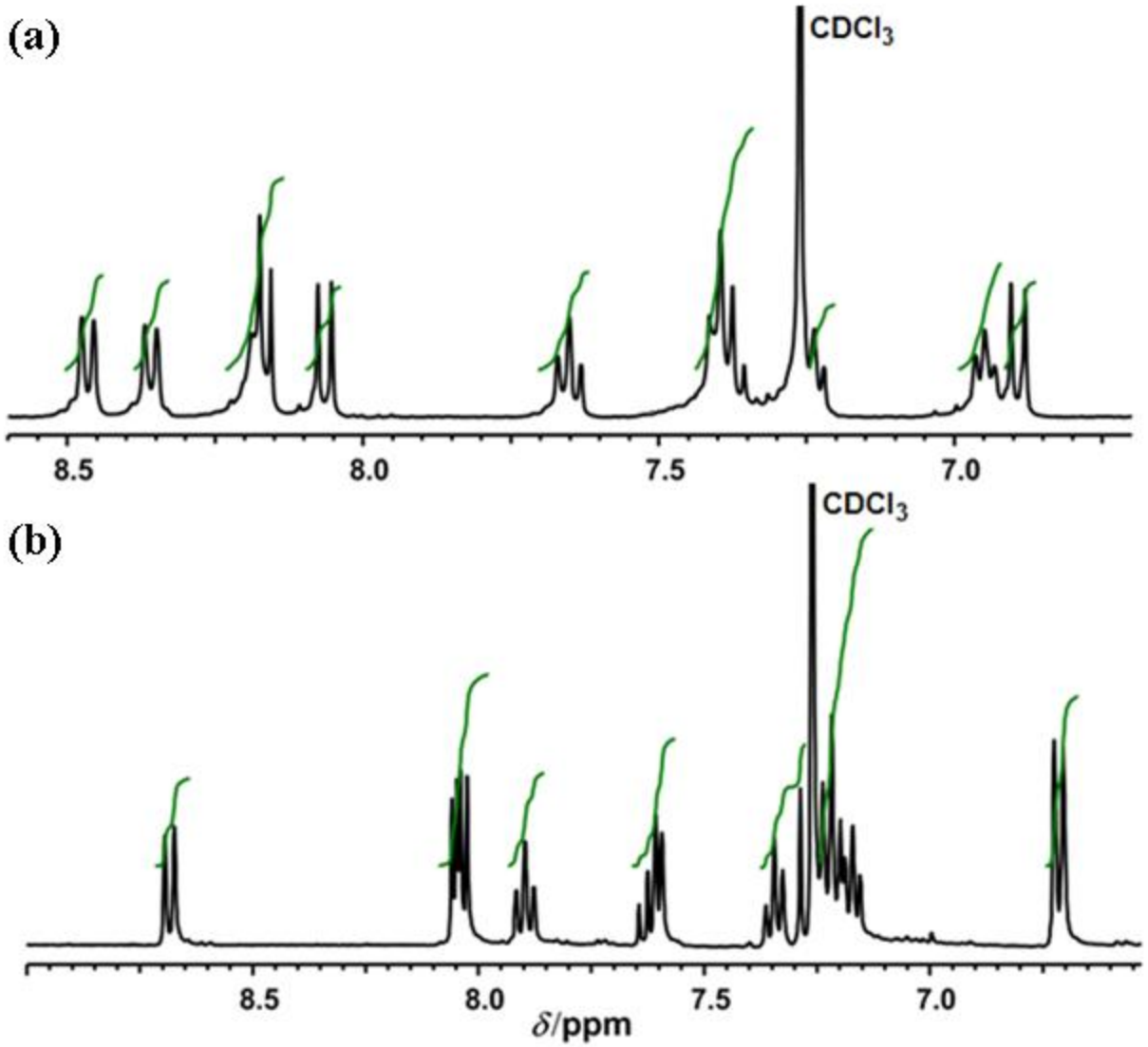


Fig. S2 ^{1}H NMR spectra of (a) [**1**]ClO_4 and (b) [**2**]ClO_4 in $CDCl_3$.

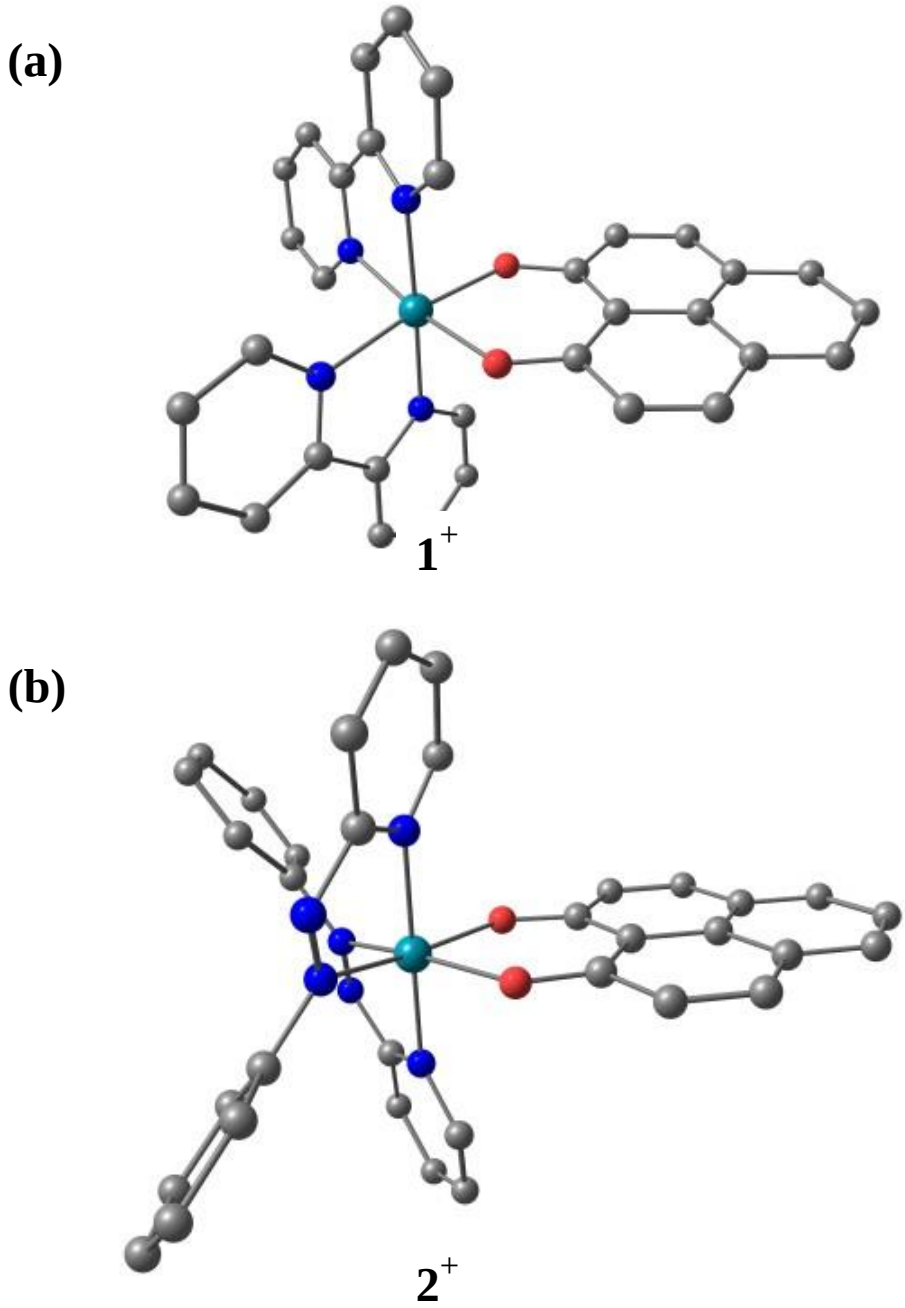


Fig. S3 DFT (B3LYP/LANL2DZ/6-31G*) optimized geometries of (a) $\mathbf{1}^{+}$ and (b) $\mathbf{2}^{+}$.

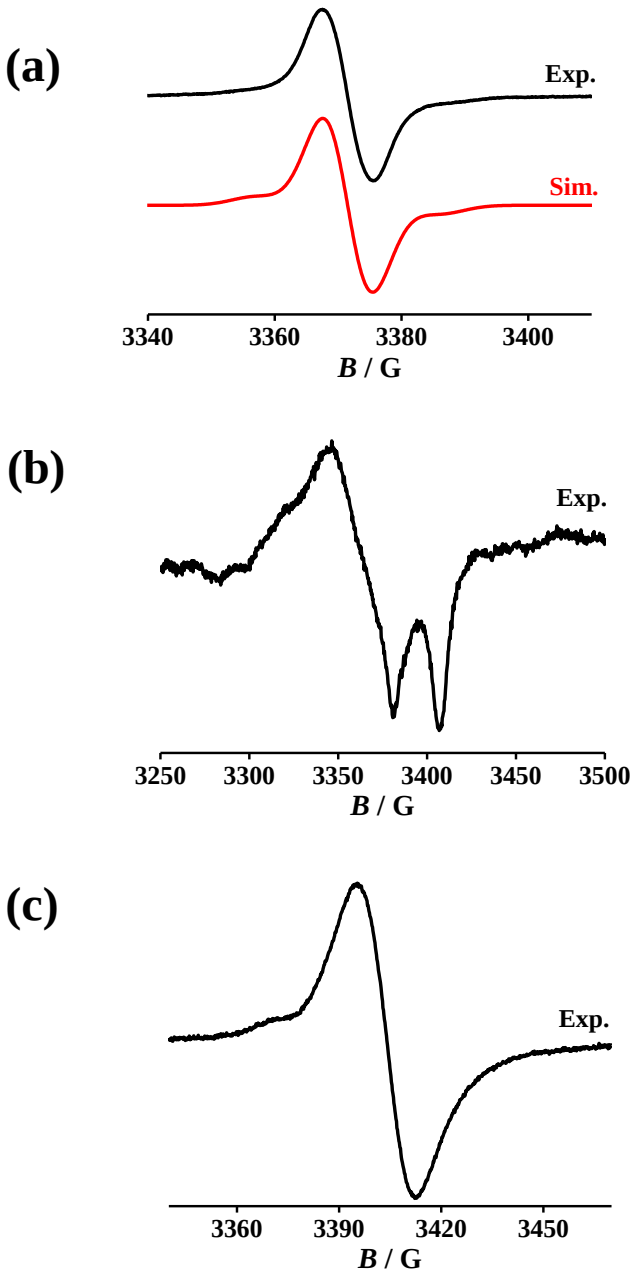


Fig. S4 EPR spectra after *in situ* reduction of [**1**]ClO_4 at (a) 298 K, (b) 120 K and after *in situ* oxidation of (c) [**2**]ClO_4 at 298 K in CH_2Cl_2/0.1 M Bu_4NPF_6.