Supporting Information

Variable electronic structure and spin distribution in bis(2,2′-bipyridine)-metal complexes (M = Ru or Os) of 4,5-dioxido- and 4,5-diimido-pyrene

Madhumita Chatterjee,[§] Sudipta Mondal,[†] Arijit Singha Hazari[§], Stanislav Zalis,[‡] Wolfgang Kaim,[*,†] and Goutam Kumar Lahiri[*,§]

[§]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in (G.K.L)*

[†]*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550, E-mail: wolfgang.kaim@iac.uni-stuttgart.de (W.K)*

[‡]*J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejskova 3, CZ-18223 Prague, Czech Republic*

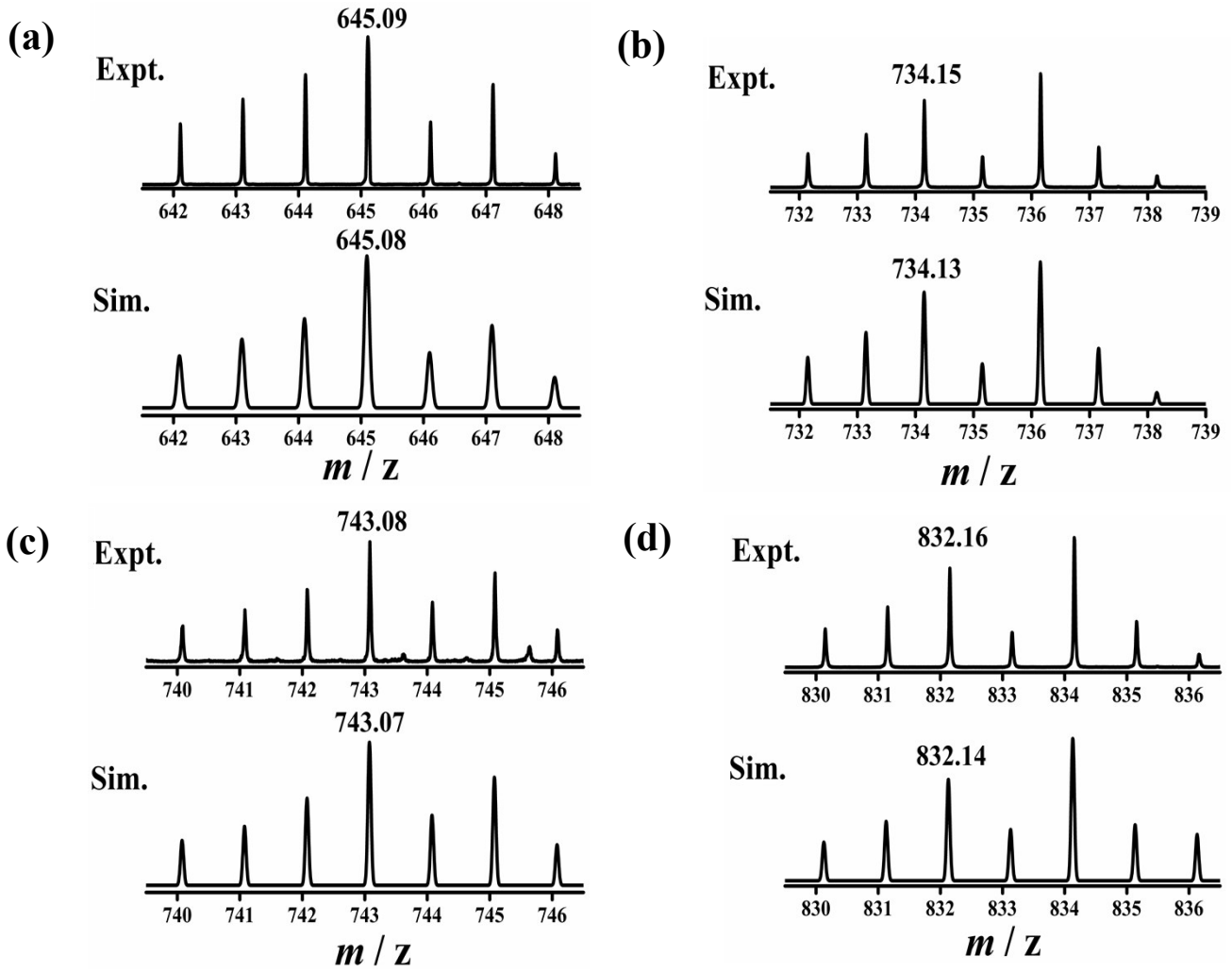


Fig. S1 Experimental and simulated ESI(+) mass spectra of (a) [**1**]ClO_4, (b) [**2**]ClO_4 (c) [**3**]$(ClO_4)_2$ and (d) [**4**]$(ClO_4)_2$ in CH_3CN.

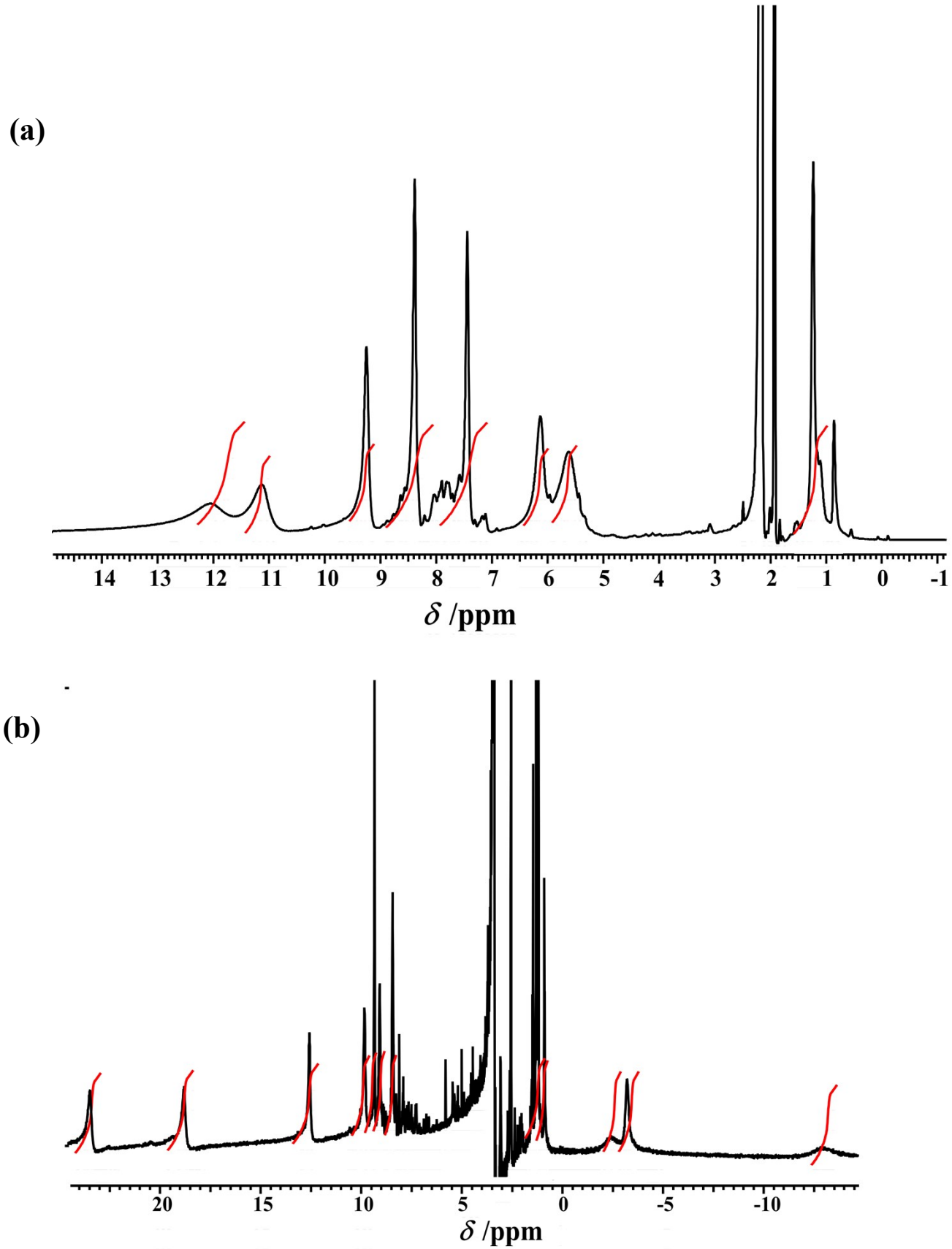


Fig. S2 ^{1}H NMR spectra of (a) [**1**]ClO_4 in CD_3CN and (b) [**2**]ClO_4 in $(CD_3)SO$.

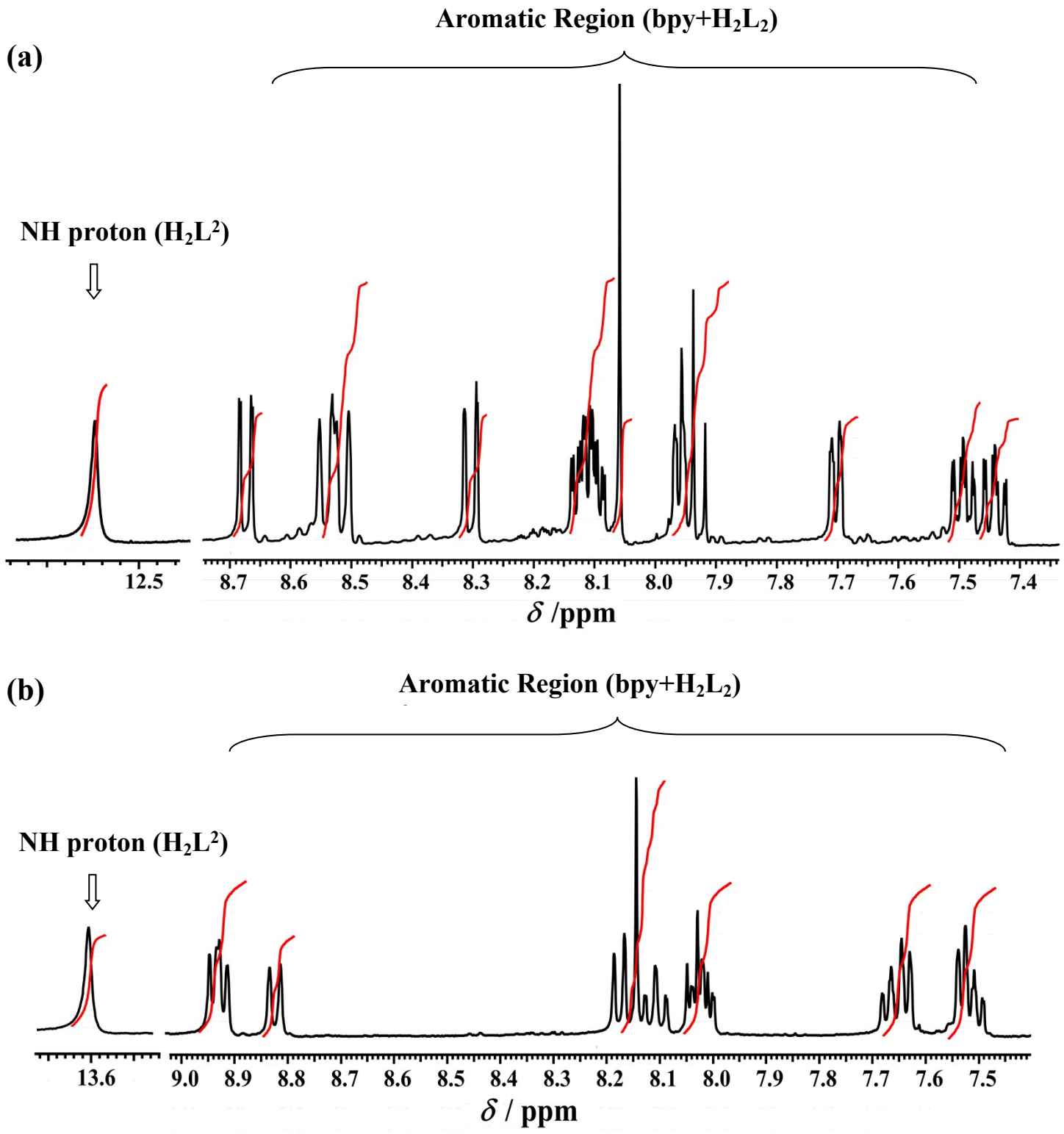


Fig. S3 ^{1}H NMR spectra of (a) [**3**]$(ClO_4)_2$ in CD_3CN and (b) [**4**]$(ClO_4)_2$ in $(CD_3)_2SO$.

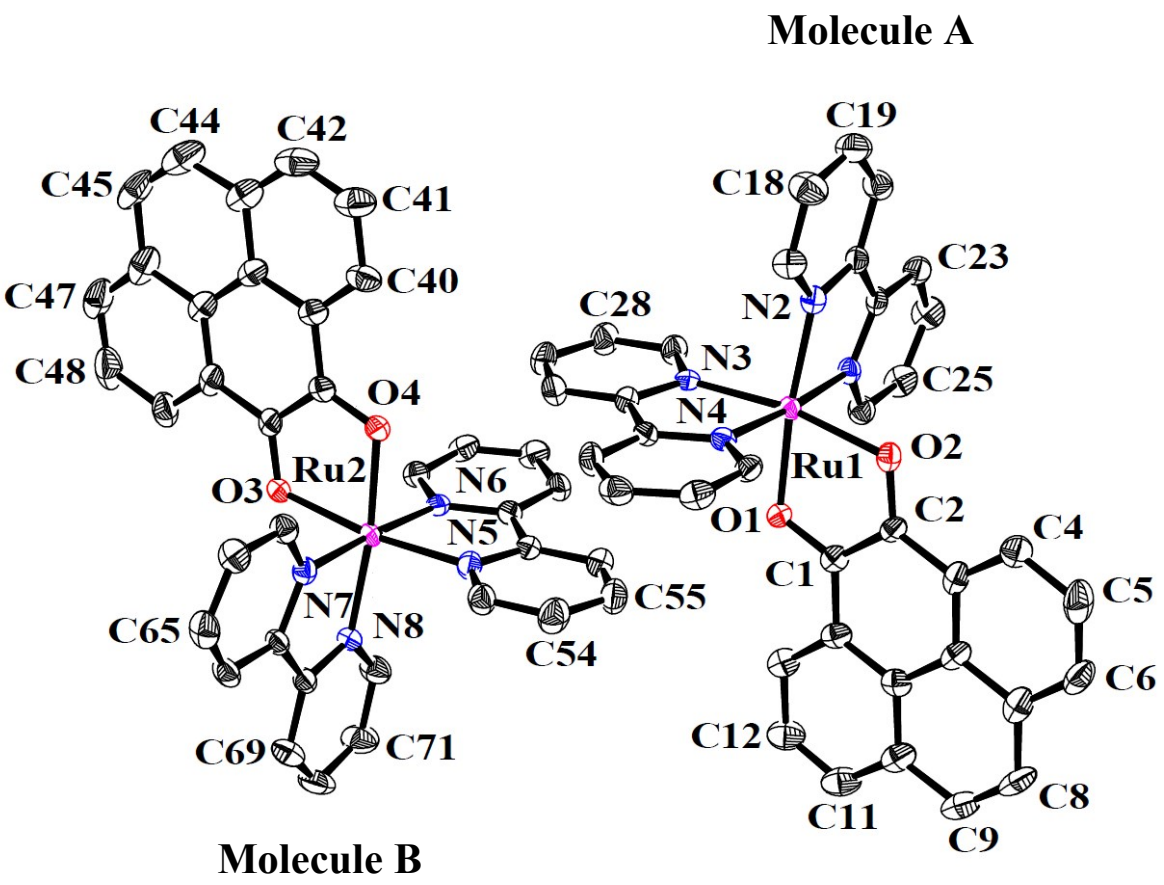


Fig. S4 Molecular structure of [**1**]ClO_4 showing two molecules (**molecule A** and **molecule B**) in the asymmetric unit. Ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

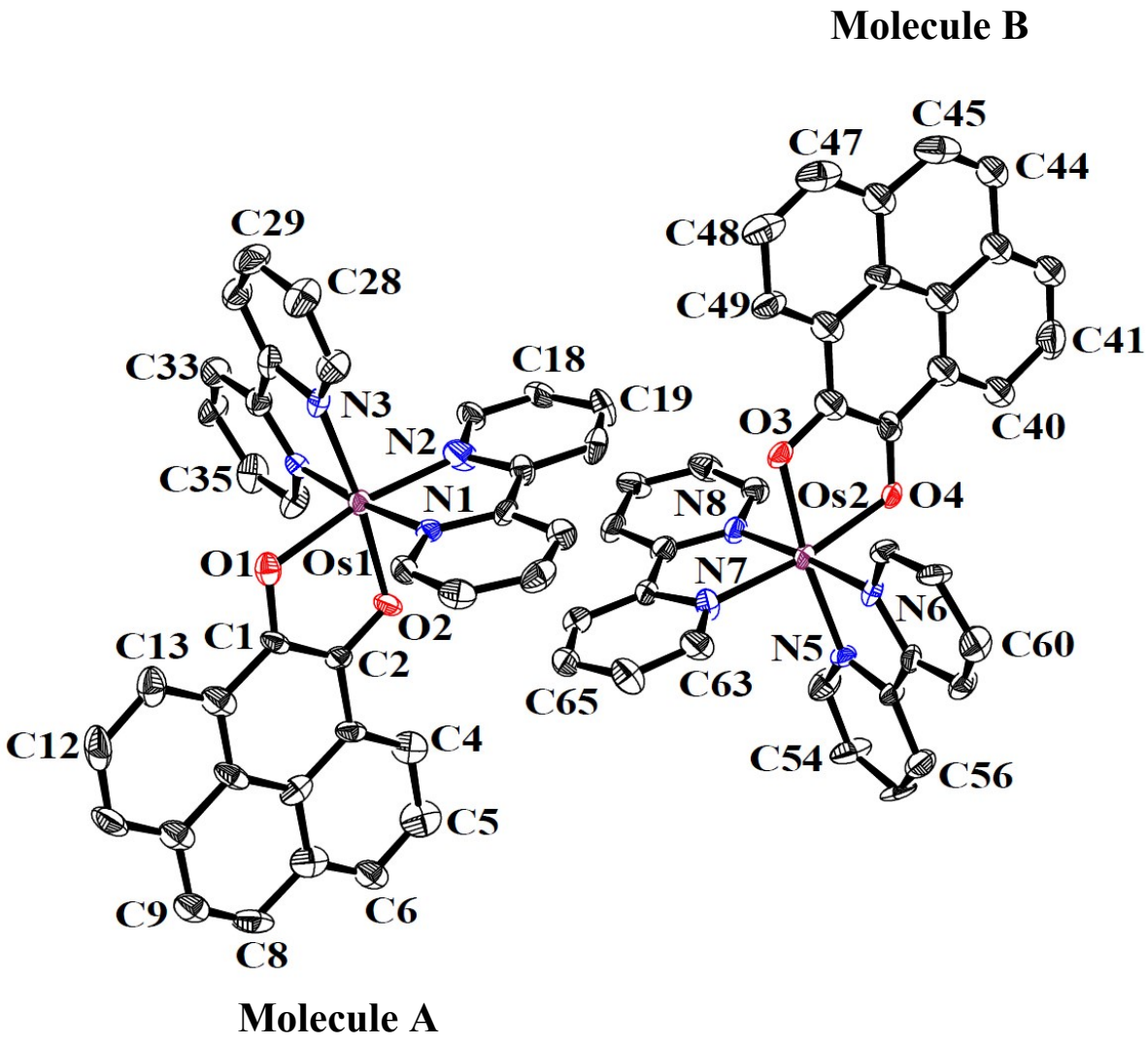


Fig. S5 Molecular structure of [**2**]ClO_4 showing two molecules (**molecule A** and **molecule B**) in the asymmetric unit. Ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

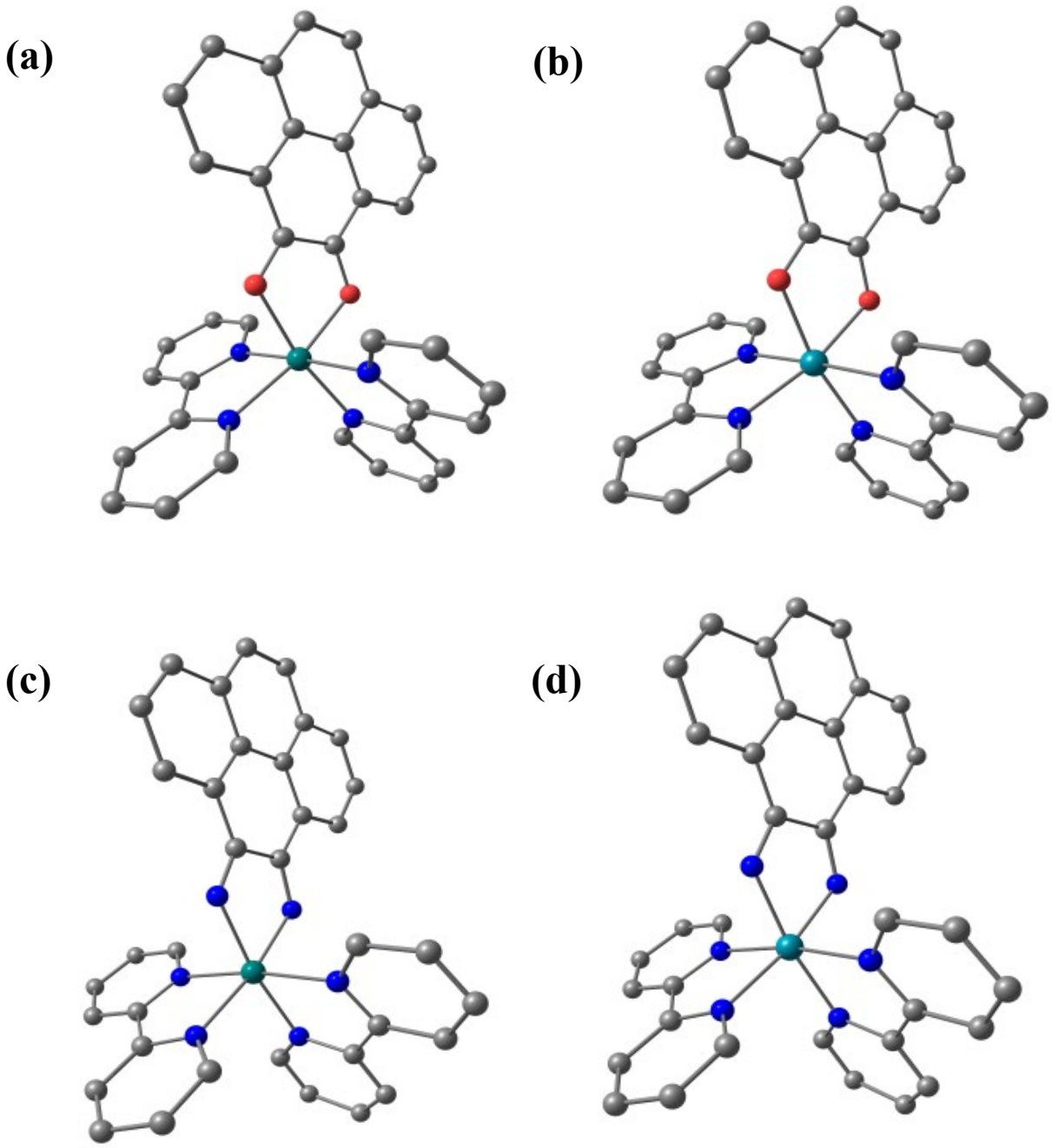


Fig. S6 DFT (M06L/LANL2DZ/6-31G*) optimised structure of (a) $\mathbf{1}^{+}$, (b) $\mathbf{2}^{+}$, (c) $\mathbf{3}^{2+}$ and (d) $\mathbf{4}^{2+}$.

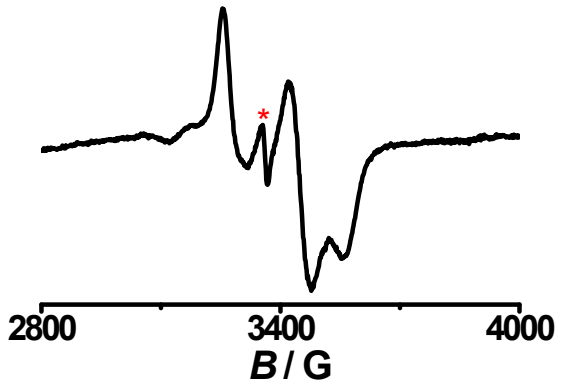


Fig. S7 EPR spectrum of [**4**]$(ClO_4)_2$ after *in situ* reduction at 4.5 K in CH_3CN/0.1 M Bu_4NClO_4.

*Signal from cavity.

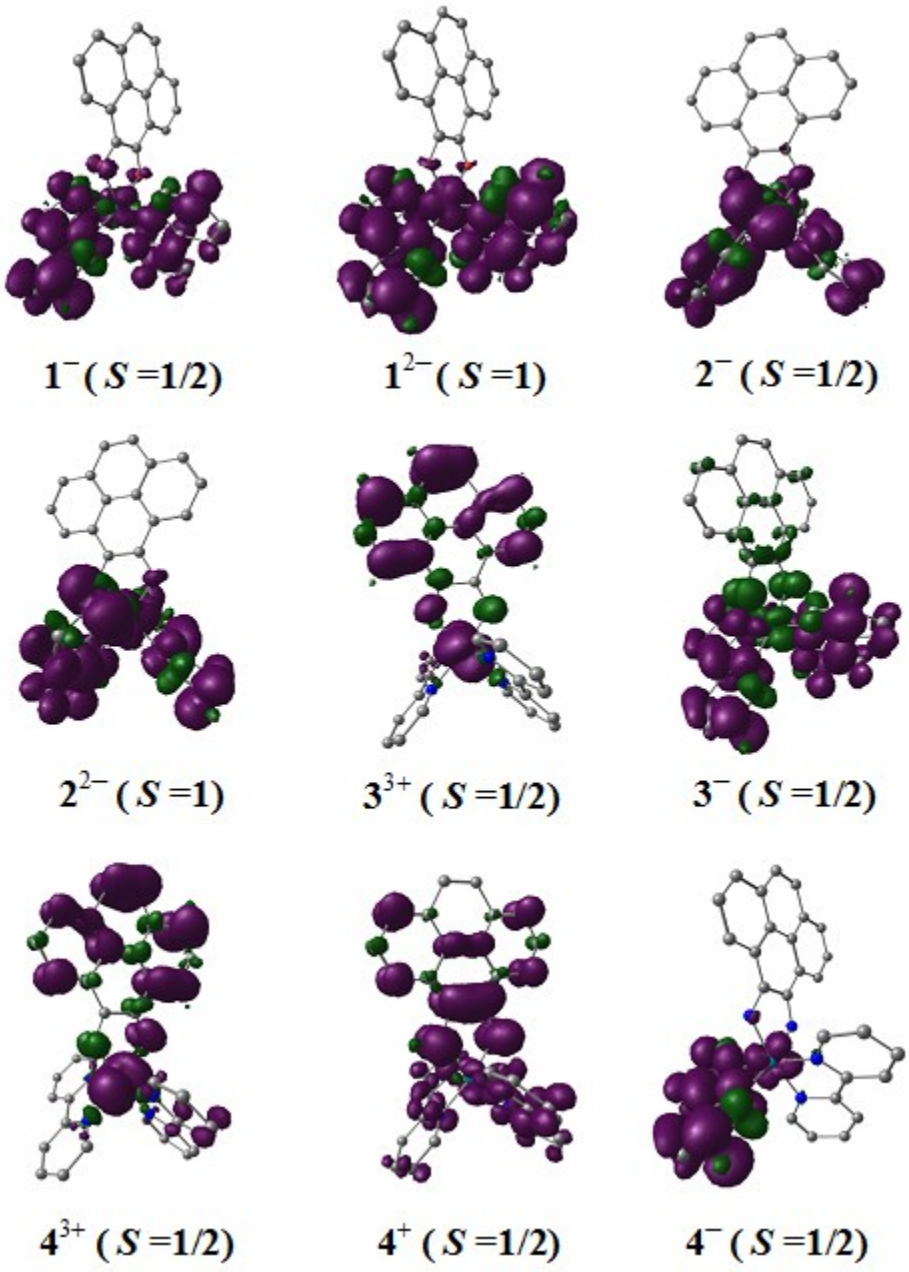


Fig. S8 DFT calculated Mulliken spin density plots.

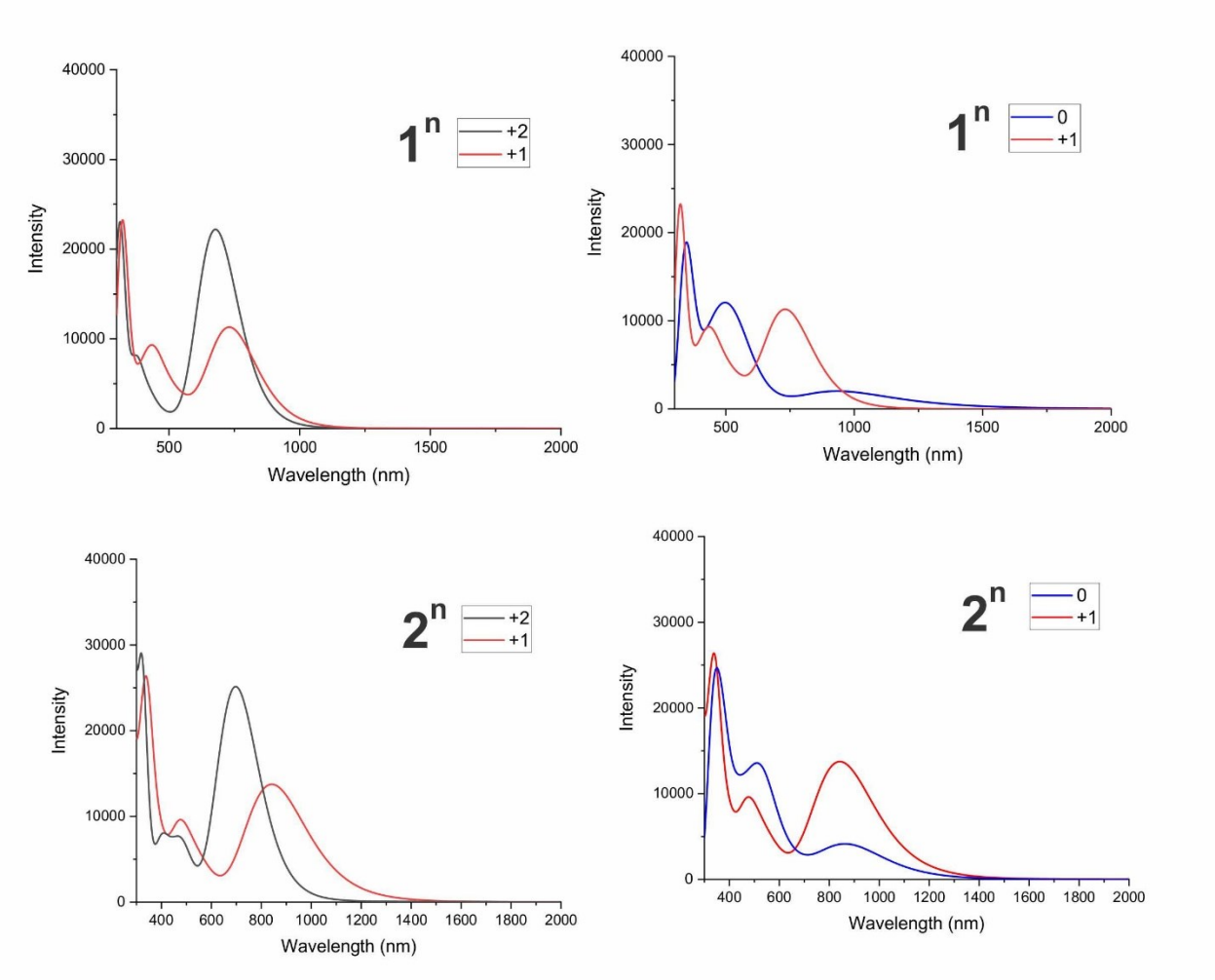


Fig. S9 TD-DFT simulated electronic spectra of redox series of complexes **1**^{n} and **2**^{n}.

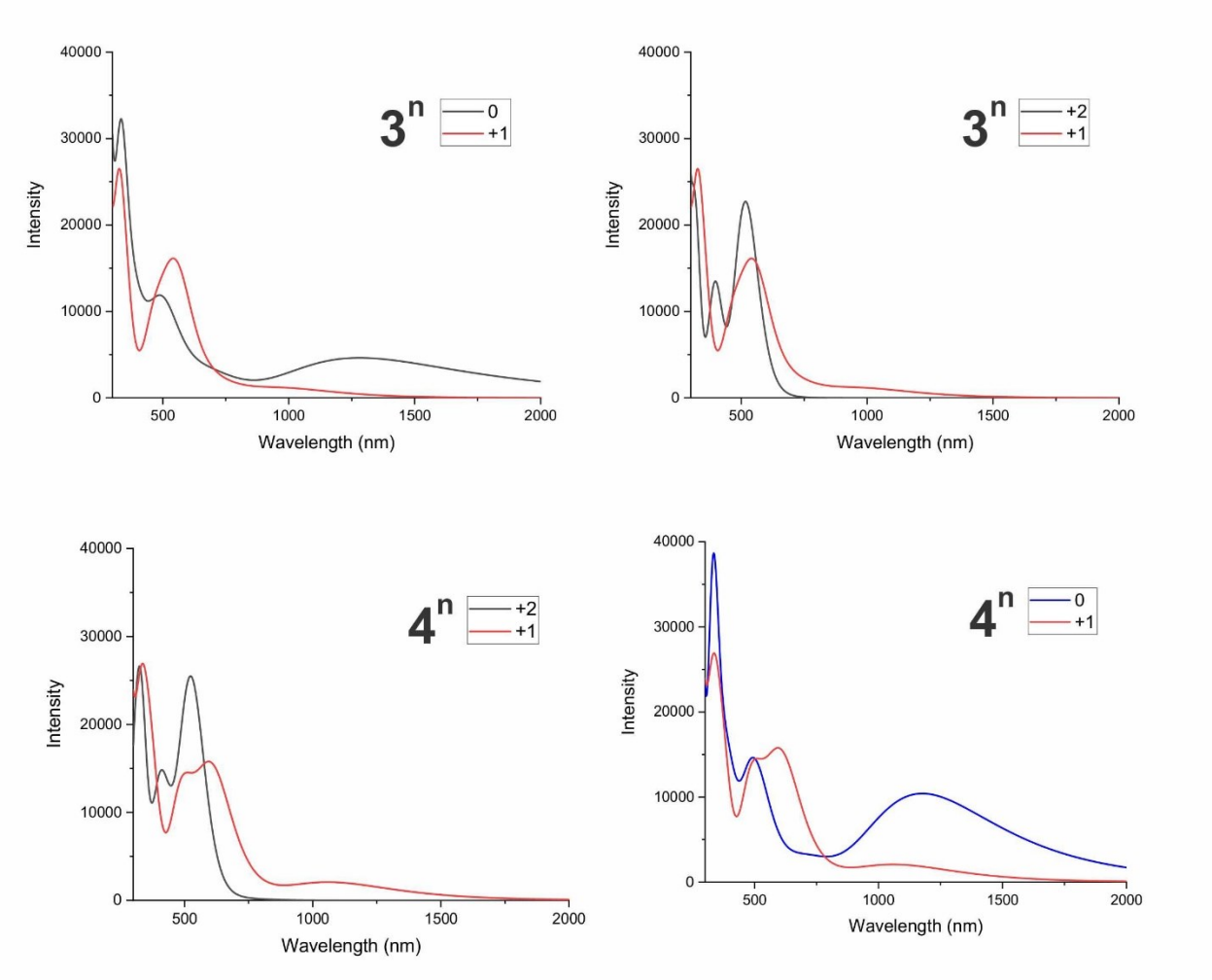


Fig. S10 TD-DFT simulated electronic spectra of redox series of complexes ***3***^{n} and **4**^{n}.

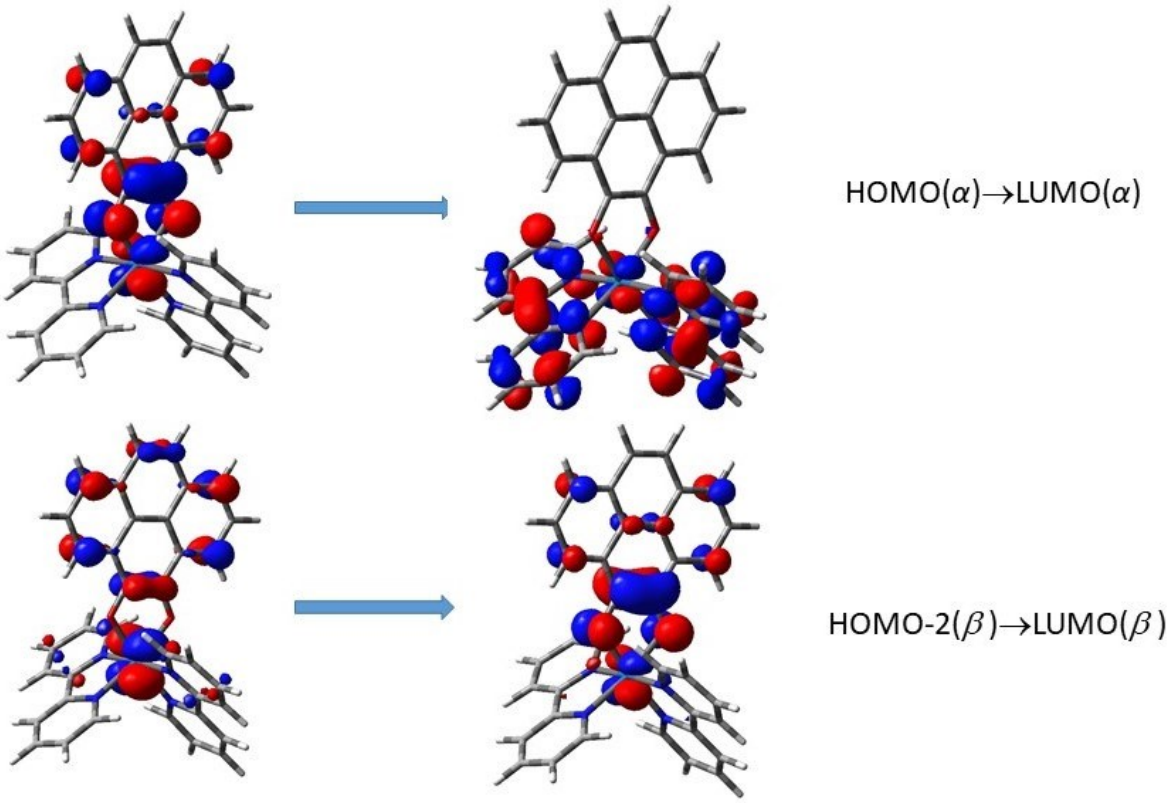


Fig. S11 Excitations assigned to the intense band around 900 nm of $\mathbf{2}^{+}$.

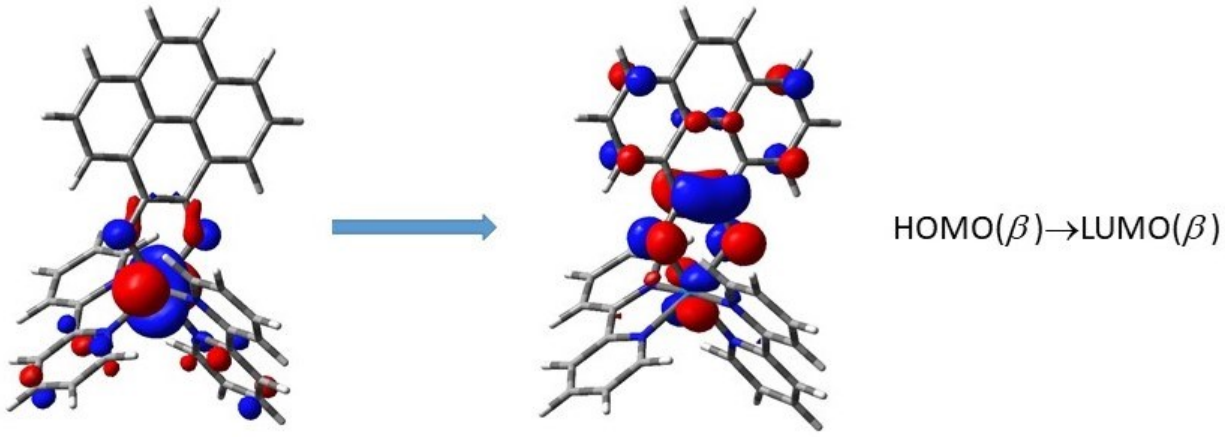


Fig. S12 Excitation assigned to the intense band around 1600 nm of $\mathbf{2}^{+}$.

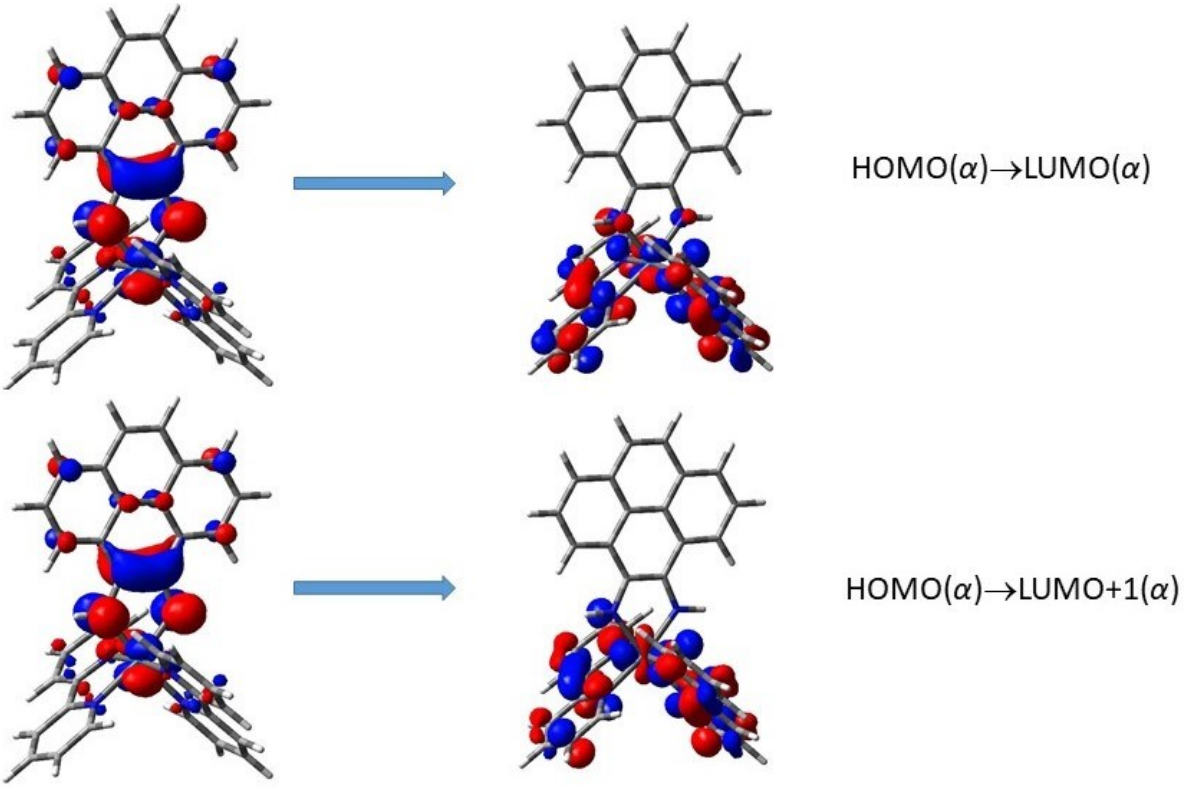


Fig. S13 Excitation assigned to NIR bands between 900 and 1200 nm of $\mathbf{4}^{+}$.

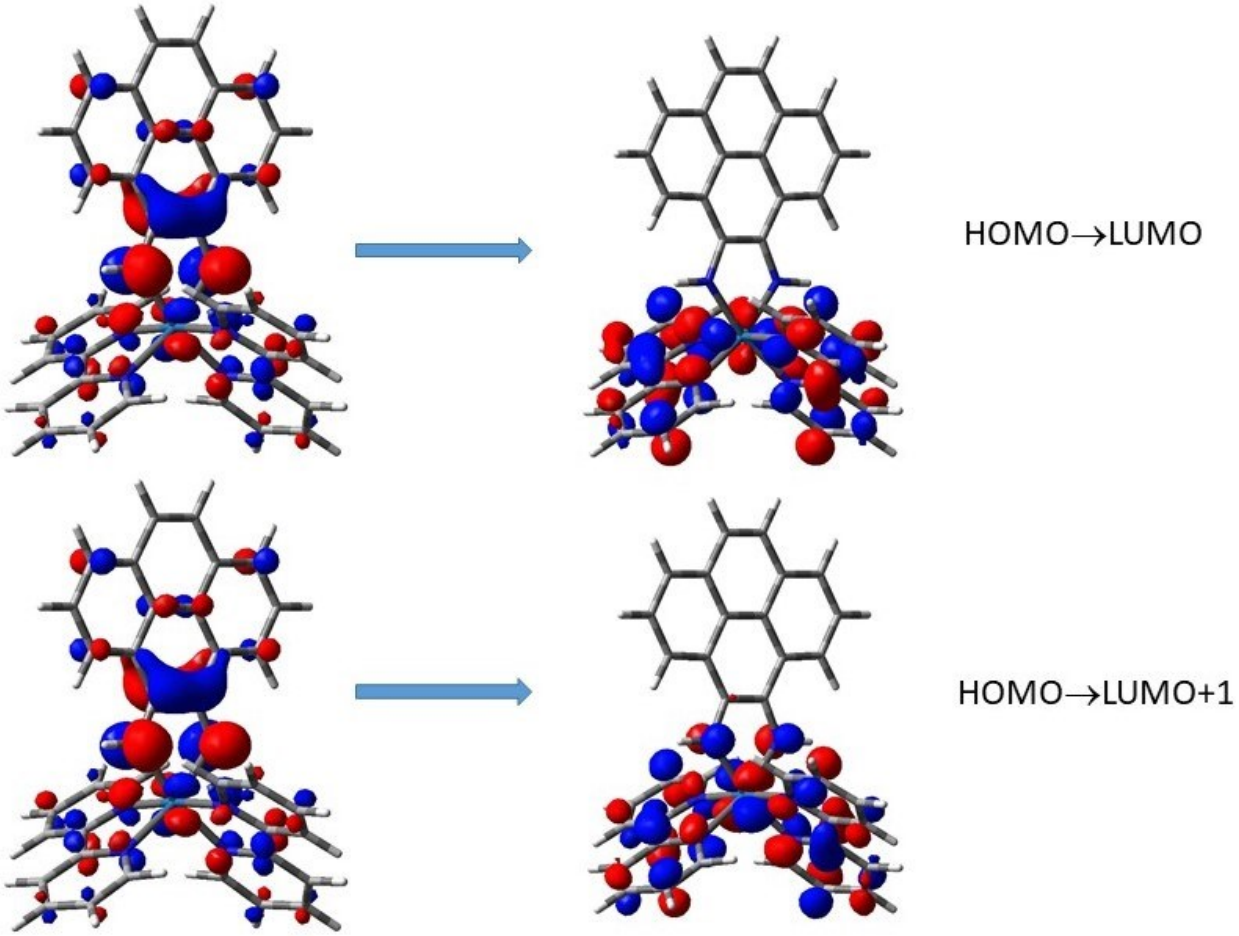


Fig. S14 Excitation assigned to NIR bands between 900 and 1200 nm of **4**.

Table S1 Selected crystallographic data

complex	2×[**1**]ClO_4·4C_6H_6	2×[**2**]ClO_4·C_6H_6	[**3**]$(ClO_4)_2$	[**4**]$(ClO_4)_2$
empirical formula	$C_{96}H_{72}N_8O_{12}Cl_2Ru_2$	$C_{78}H_{54}N_8O_{12}Cl_2Os_2$	$C_{36}H_{26}N_6O_8Cl_2Ru$	$C_{36}H_{26}N_6O_8Cl_2Os$
formula weight	1802.65	1746.59	842.61	931.73
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	16.1871(4)	16.2362(2)	9.7428(4)	9.7560(2)
b (Å)	25.7337(6)	25.7702(4)	16.1774(8)	16.2063(4)
c (Å)	19.8582(5)	19.8131(3)	20.8421(9)	20.8243(4)
α (deg)	90	90	90	90
β (deg)	92.578(2)	92.6620(10)	96.022(4)	95.821(2)
γ (deg)	90	90	90	90
V (Å^3)	8263.6(3)	8281.1(2)	3266.9(3)	3275.52(13)
Z	4	4	4	4
μ (mm^{-1})	0.500	3.190	0.711	4.123
T (K)	150(2)	150(2)	150(2)	150(2)
D_{calcd} (g cm^{-3})	1.449	1.401	1.7131	1.889
F (000)	3688	3440	1700	1832
θ range (deg)	1.886 to 25.00	1.886 to 25.00	1.97 to 25.00	1.966 to 25.00
data/restraints/parameters	14533/0/1081	14538/0/835	5731/0/486	5769/0/478
R_1, wR_2 [$I > 2\sigma(I)$]	0.0673, 0.1411	0.0669, 0.1465	0.0484, 0.1087	0.0327, 0.0760
R_1, wR_2 (all data)	0.0777, 0.1465	0.0746, 0.1496	0.0688, 0.1225	0.0426, 0.1039
GOF	1.225	1.311	1.0491	1.155
largest diff. peak/hole,(e Å^{-3})	0.915/-0.842	2.015/-2.837	0.8929/-1.2679	0.798/-0.868

Table S2 Selected experimental and DFT (M06L) calculated bond lengths (Å) for $\mathbf{1}^n$ (molecule **A**)

bond lengths (Å)	X-ray	DFT				
	$\mathbf{1}^+$	$\mathbf{1}^+$ (S=1/2)	$\mathbf{1}^{2+}$ (S=0)	**1** (S=0)	$\mathbf{1}^-$ (S=1/2)	$\mathbf{1}^{2-}$ (S=1)
Ru1-O1	2.051(4)	2.096	2.108	2.070	2.091	2.134
Ru1-O2	2.078(3)	2.094	2.112	2.062	2.104	2.132
Ru1-N2	2.028(4)	2.071	2.074	2.073	2.072	2.077
Ru1-N1	2.048(4)	2.078	2.097	2.058	2.074	2.079
Ru1-N3	2.024(4)	2.072	2.071	2.067	2.060	2.078
Ru1-N4	2.046(4)	2.076	2.099	2.066	2.059	2.079
O1-C1	1.298(6)	1.301	1.270	1.328	1.327	1.315
O2-C2	1.311(6)	1.301	1.270	1.329	1.325	1.315
C2-C1	1.420(7)	1.433	1.482	1.401	1.404	1.417
C2-C3	1.443(7)	1.439	1.435	1.434	1.433	1.434
C14-C1	1.452(7)	1.439	1.434	1.436	1.433	1.434

Table S3 Selected bond lengths (Å) for [**1**]ClO_4

bond lengths (Å)	**[1]**ClO_4 (molecule **A**)	bond lengths (Å)	**[1]**ClO_4 (molecule **B**)
	X-ray		X-ray
Ru1-O1	2.051(4)	Ru2-O3	2.073(3)
Ru1-O2	2.078(3)	Ru2-O4	2.052(4)
Ru1-N2	2.028(4)	Ru2-N5	2.026(4)
Ru1-N1	2.048(4)	Ru2-N6	2.049(4)
Ru1-N3	2.024(4)	Ru2-N7	2.047(4)
Ru1-N4	2.046(4)	Ru2-N8	2.027(4)
O1-C1	1.298(6)	O3-C37	1.294(6)
O2-C2	1.311(6)	O4-C38	1.293(6)
C2-C1	1.420(7)	C37-C38	1.426(8)
C2-C3	1.443(7)	C37-C50	1.449(7)
C14-C1	1.452(7)	C38-C39	1.451(8)

Table S4 Selected experimental and DFT (M06L) calculated bond lengths (Å) for $\mathbf{2}^n$ (molecule **A**)

bond lengths (Å)	X-ray	DFT				
	$\mathbf{2}^+$	$\mathbf{2}^+$ (S=1/2)	$\mathbf{2}^{2+}$ (S=0)	**2** (S=0)	$\mathbf{2}^-$ (S=1/2)	$\mathbf{2}^{2-}$ (S=1)
Os1-O1	2.062(7)	2.091	2.092	2.062	2.107	2.132
Os1-O2	2.051(7)	2.095	2.089	2.071	2.096	2.128
Os1-N2	2.031(10)	2.042	2.057	2.033	2.025	2.046
Os1-N1	2.053(8)	2.062	2.086	2.052	2.046	2.062
Os1-N3	2.015(8)	2.041	2.058	2.036	2.035	2.047
Os1-N4	2.064(8)	2.064	2.084	2.044	2.061	2.063
O1-C1	1.351(12)	1.305	1.280	1.333	1.327	1.319
O2-C2	1.304(12)	1.305	1.280	1.332	1.330	1.318
C2-C1	1.381(15)	1.427	1.465	1.395	1.399	1.412
C2-C3	1.447(14)	1.436	1.430	1.433	1.430	1.430
C14-C1	1.446(14)	1.435	1.430	1.431	1.431	1.430

Table S5 Selected bond lengths (Å) for [**2**]ClO_4

bond lengths (Å)	**[2]**ClO_4 (molecule **A**)	bond lengths (Å)	**[2]**ClO_4 (molecule **B**)
	X-ray		X-ray
Os1-O1	2.062(7)	Os2-O3	2.043(7)
Os1-O2	2.051(7)	Os2-O4	2.066(7)
Os1-N2	2.031(10)	Os2-N5	2.042(8)
Os1-N1	2.053(8)	Os2-N6	2.043(8)
Os1-N3	2.015(8)	Os2-N7	2.033(8)
Os1-N4	2.064(8)	Os2-N8	2.044(8)
O1-C1	1.351(12)	O3-C37	1.306(13)
O2-C2	1.304(12)	O4-C38	1.307(12)
C2-C1	1.381(15)	C37-C38	1.404(16)
C2-C3	1.447(14)	C37-C50	1.471(17)
C14-C1	1.446(14)	C38-C39	1.457(15)

Table S6 Selected experimental and DFT (M06L) calculated bond lengths (Å) for $\mathbf{3}^{n}$

bond	X-ray		DFT				
lengths (Å)	$\mathbf{3}^{2+}$	$\mathbf{3}^{2+}$ (S=0)	$\mathbf{3}^{3+}$ (S=1/2)	$\mathbf{3}^{+}$ (S=1/2)	**3** (S=0)	$\mathbf{3}^{-}$ (S=1/2)	$\mathbf{3}^{2-}$ (S=1)
Ru1-N1	2.001(4)	2.060	2.076	2.064	2.043	2.056	2.091
Ru1-N2	2.012(4)	2.057	2.029	2.063	2.051	2.060	2.095
Ru1-N3	2.071(3)	2.121	2.120	2.113	2.106	2.105	2.115
Ru1-N4	2.050(3)	2.107	2.105	2.088	2.079	2.076	2.092
Ru1-N5	2.081(4)	2.122	2.139	2.116	2.119	2.127	2.122
Ru1-N6	2.057(3)	2.108	2.123	2.088	2.076	2.094	2.090
N1-C1	1.303(6)	1.317	1.313	1.341	1.352	1.352	1.355
N2-C2	1.313(5)	1.316	1.325	1.340	1.354	1.352	1.359
C2-C1	1.458(6)	1.468	1.472	1.433	1.421	1.427	1.430
C2-C3	1.454(6)	1.446	1.438	1.444	1.437	1.435	1.429
C14-C1	1.460(6)	1.446	1.449	1.444	1.438	1.435	1.432
N1-H1	0.83(5)	1.019	1.019	1.015	1.015	1.015	1.014
N2-H2	0.81(4)	1.019	1.020	1.015	1.015	1.015	1.015

Table S7 Selected experimental and DFT (M06L) calculated bond lengths (Å) for $\mathbf{4}^{n}$

bond lengths (Å)	X-ray	DFT					
	$\mathbf{4}^{2+}$	$\mathbf{4}^{2+}$(S=0)	$\mathbf{4}^{3+}$ (S=1/2)	$\mathbf{4}^{+}$ (S=1/2)	**4** (S=0)	$\mathbf{4}^{-}$ (S=1/2)	$\mathbf{4}^{2-}$ (S=1)
Os1-N1	2.008(5)	2.041	2.007	2.054	2.047	2.047	2.085
Os1-N2	2.018(5)	2.043	2.058	2.053	2.036	2.049	2.077
Os1-N3	2.092(5)	2.112	2.134	2.097	2.091	2.112	2.096
Os1-N4	2.049(5)	2.092	2.112	2.072	2.057	2.106	2.071
Os1-N5	2.080(5)	2.111	2.117	2.094	2.082	2.055	2.093
Os1-N6	2.065(5)	2.091	2.094	2.073	2.066	2.031	2.076
N1-C1	1.310(8)	1.325	1.337	1.343	1.355	1.358	1.358
N2-C2	1.312(7)	1.325	1.322	1.344	1.357	1.358	1.357
C2-C1	1.454(8)	1.455	1.460	1.428	1.416	1.420	1.428
C2-C3	1.463(8)	1.443	1.443	1.441	1.435	1.431	1.428
C14-C1	1.456(8)	1.442	1.431	1.442	1.436	1.433	1.428
N1-H1	0.880(3)	1.019	1.020	1.016	1.014	1.015	1.014
N2-H2	0.881(4)	1.019	1.020	1.016	1.014	1.015	1.014

Table S8 Selected experimental and DFT (M06L) calculated bond angles (deg) for $\mathbf{1}^n$ (molecule **A**)

bond angle (deg)	X-ray	DFT				
	$\mathbf{1}^+$	$\mathbf{1}^+$ (S=1/2)	$\mathbf{1}^{2+}$ (S=0)	**1** (S=0)	$\mathbf{1}^-$ (S=1/2)	$\mathbf{1}^{2-}$ (S=1)
O1-Ru1-O2	79.88(14)	79.251	76.200	81.552	80.649	79.737
N3-Ru1-O2	169.52(15)	168.922	170.679	168.196	169.058	170.577
N3-Ru1-O1	91.75(15)	93.454	96.134	91.931	93.578	95.660
N3-Ru1-N1	97.20(16)	99.834	97.356	100.028	96.753	97.391
N3-Ru1-N2	92.57(17)	94.104	90.911	97.584	92.833	90.289
N3-Ru1-N4	79.46(16)	78.097	78.052	78.270	78.904	78.956
N1-Ru1-O2	89.81(14)	89.133	88.905	90.241	92.789	91.042
N1-Ru1-O1	94.61(15)	94.585	96.728	93.573	92.388	92.316
N2-Ru1-O2	96.42(15)	94.117	97.168	90.188	94.320	95.449
N2-Ru1-O1	172.77(15)	170.226	171.687	168.241	169.358	170.151
N2-Ru1-N1	79.11(17)	78.020	77.938	78.021	78.420	79.109
N2-Ru1-N4	97.71(16)	99.774	97.344	101.346	98.044	97.186
N4-Ru1-O2	93.96(15)	93.190	96.235	91.535	91.892	92.885
N4-Ru1-O1	88.77(15)	87.845	88.453	87.305	91.523	91.665
N4-Ru1-N1	175.34(17)	176.917	173.456	178.118	174.333	174.848

Table S9 Selected bond angles (deg) for [**1**]ClO_4

bond angle (deg)	**[1]**ClO_4 (molecule **A**)	bond angle (deg)	**[1]**ClO_4 (molecule **B**)
	X-ray		X-ray
O1-Ru1-O2	79.88(14)	O4-Ru2-O3	79.96(14)
N3-Ru1-O2	169.52(15)	N6-Ru2-O3	94.28(15)
N3-Ru1-O1	91.75(15)	N6-Ru2-O4	87.74(15)
N3-Ru1-N1	97.20(16)	N8-Ru2-O3	96.01(15)
N3-Ru1-N2	92.57(17)	N8-Ru2-O4	172.02(15)
N3-Ru1-N4	79.46(16)	N8-Ru2-N6	99.48(17)
N1-Ru1-O2	89.81(14)	N8-Ru2-N7	79.15(17)
N1-Ru1-O1	94.61(15)	N5-Ru2-O3	171.08(15)
N2-Ru1-O2	96.42(15)	N5-Ru2-O4	93.78(16)
N2-Ru1-O1	172.77(15)	N5-Ru2-N6	79.03(17)
N2-Ru1-N1	79.11(17)	N5-Ru2-N8	90.95(18)
N2-Ru1-N4	97.71(16)	N5-Ru2-N7	97.52(17)
N4-Ru1-O2	93.96(15)	N7-Ru2-O3	89.29(15)
N4-Ru1-O1	88.77(15)	N7-Ru2-O4	93.84(15)
N4-Ru1-N1	175.34(17)	N7-Ru2-N6	176.31(16)

Table S10 Selected experimental and DFT (M06L) calculated bond angles (deg) for $\mathbf{2}^{n}$ (molecule **A**)

bond	X-ray	DFT				
angle (deg)	$\mathbf{2}^{+}$	$\mathbf{2}^{+}$ (*S*=1/2)	$\mathbf{2}^{2+}$ (*S*=0)	**2** (*S*=0)	$\mathbf{2}^{-}$ (*S*=1/2)	$\mathbf{2}^{2-}$ (*S*=1)
O2-Os1-O1	79.2(3)	78.074	75.567	80.136	79.341	78.834
O2-Os1-N4	95.4(3)	94.860	97.028	93.785	92.396	92.948
O2-Os1-N1	88.7(3)	87.367	88.367	87.284	91.047	90.222
O1-Os1-N4	89.7(3)	88.696	88.690	90.170	92.026	91.054
N3-Os1-O2	172.3(3)	169.788	171.482	167.952	168.689	170.265
N3-Os1-O1	96.3(3)	94.383	97.482	101.196	98.495	95.568
N3-Os1-N4	78.2(3)	77.936	77.669	77.998	78.487	79.100
N3-Os1-N2	92.5(4)	94.732	90.699	98.143	94.244	91.797
N3-Os1-N1	98.0(3)	100.070	97.444	101.196	98.495	97.997
N2-Os1-O2	92.7(3)	93.652	96.640	91.922	93.544	94.872
N2-Os1-N1	78.4(3)	78.014	77.744	78.220	78.878	79.226
N1-Os1-O1	94.6(3)	93.456	96.719	91.643	92.156	92.170
N2-Os1-O2	92.7(3)	93.652	96.640	91.922	91.047	94.872
N2-Os1-O1	169.4(3)	168.477	170.696	167.470	168.522	169.394
N2-Os1-N4	97.8(3)	100.095	97.419	100.080	97.301	97.840
N1-Os1-N4	174.6(3)	177.184	173.182	178.031	175.013	175.862

Table S11 Selected bond angles (deg) for [**2**]ClO_4

bond angle (deg)	**[2]**ClO_4 (molecule **A**)	bond angle (deg)	**[2]**ClO_4 (molecule **B**)
	X-ray		X-ray
O2-Os1-O1	79.2(3)	O4-Os2-O3	79.9(3)
O2-Os1-N4	95.4(3)	O3-Os2-N8	87.7(3)
O2-Os1-N1	88.7(3)	O3-Os2-N6	94.1(3)
O1-Os1-N4	89.7(3)	N8-Os2-O4	94.3(3)
N3-Os1-O2	172.3(3)	N5-Os2-O3	171.4(3)
N3-Os1-O1	96.3(3)	N5-Os2-O4	95.7(3)
N3-Os1-N4	78.2(3)	N5-Os2-N8	100.2(3)
N3-Os1-N2	92.5(4)	N5-Os2-N6	78.3(3)
N3-Os1-N1	98.0(3)	N7-Os2-O3	93.6(3)
N2-Os1-O2	92.7(3)	N7-Os2-O4	170.9(3)
N2-Os1-N1	78.4(3)	N7-Os2-N8	79.0(3)
N1-Os1-O1	94.6(3)	N7-Os2-N5	91.5(3)
N2-Os1-O2	92.7(3)	N7-Os2-N6	97.4(3)
N2-Os1-O1	169.4(3)	N6-Os2-O4	89.4(3)
N2-Os1-N4	97.8(3)	N6-Os2-N8	176.1(3)

Table S12 Selected experimental and DFT (M06L) calculated bond angles (deg) for $\mathbf{3}^{n}$

bond angle (deg)	X-ray	DFT					
	$\mathbf{3}^{2+}$	$\mathbf{3}^{2+}$ (*S*=0)	$\mathbf{3}^{3+}$ (*S*=1/2)	$\mathbf{3}^{+}$ (*S*=1/2)	**3** (*S*=0)	$\mathbf{3}^{-}$ (*S*=1/2)	$\mathbf{3}^{2-}$ (*S*=1)
N1-Ru1-N2	76.30(15)	74.910	75.309	76.131	77.034	76.911	76.121
N1-Ru1-N5	96.86(15)	98.628	98.966	97.559	94.969	96.353	97.518
N1-Ru1-N3	170.16(14)	171.432	172.701	169.179	167.731	169.029	169.233
N3-Ru1-N5	90.87(14)	88.740	87.961	90.756	94.512	92.038	90.409
N3-Ru1-N2	96.40(14)	98.095	97.913	96.414	94.556	95.577	96.968
N5-Ru1-N2	171.96(14)	171.948	173.291	170.546	168.753	170.208	169.885
N6-Ru1-N2	97.59(14)	97.920	99.615	95.719	95.216	95.498	94.265
N6-Ru1-N5	78.46(14)	77.008	76.470	77.076	77.160	77.383	77.926
N6-Ru1-N3	93.70(13)	96.176	95.663	98.440	96.421	97.380	96.872
N6-Ru1-N1	93.81(13)	89.773	88.241	90.195	93.265	91.357	91.924
N4-Ru1-N2	92.33(14)	89.935	91.162	89.419	89.990	89.177	90.868
N4-Ru1-N5	92.49(14)	95.769	93.296	98.205	98.477	98.461	97.446
N4-Ru1-N3	78.41(13)	77.075	77.365	77.149	77.377	77.809	78.051
N4 -Ru1-N1	95.11(14)	97.718	99.803	94.740	93.522	93.926	93.637
N4-Ru1-N6	167.99(13)	170.349	167.939	173.607	172.230	173.626	173.200

Table S13 Selected experimental and DFT (M06L) calculated bond angles (deg) for $\mathbf{4}^{n}$

bond	X-ray	DFT					
angle (deg)	$\mathbf{4}^{2+}$	$\mathbf{4}^{2+}$(*S*=0)	$\mathbf{4}^{3+}$ (*S*=0)	$\mathbf{4}^{+}$ (*S*=1/2)	**4** (*S*=0)	$\mathbf{4}^{-}$ (*S*=1/2)	$\mathbf{4}^{2-}$ (*S*=1)
N1-Os1-N2	75.72(19)	74.603	75.161	75.491	76.243	76.684	75.484
N1-Os1-N5	94.4(2)	98.646	98.676	97.071	95.114	94.537	97.188
N1-Os1-N6	94.4(2)	90.451	90.865	89.942	90.206	88.533	90.456
N1-Os1-N4	95.4(2)	98.014	99.579	95.961	95.530	96.204	94.651
N1-Os1-N3	169.91(19)	171.832	173.555	170.308	168.494	169.740	169.864
N5-Os1-N3	90.59(19)	88.195	86.772	90.470	94.470	93.899	90.760
N6-Os1-N5	77.67(19)	76.765	77.055	76.933	77.111	78.320	78.137
N6-Os1-N3	93.6(2)	95.485	93.725	97.717	98.133	98.894	97.352
N2-Os1-N5	171.3(2)	171.473	173.300	169.167	167.532	168.685	169.139
N2-Os1-N6	97.79(19)	97.824	100.152	94.973	93.742	94.143	93.726
N2-Os1-N4	93.05(19)	90.293	87.258	90.784	93.430	92.354	91.944
N2-Os1-N3	97.08(18)	98.970	99.543	97.827	95.216	95.616	97.474
N4-Os1-N5	92.48(19)	95.881	96.478	97.903	96.376	95.726	96.693
N4-Os1-N6	166.9(2)	169.590	168.502	172.632	171.713	172.702	173.171
N4-Os1-N3	77.7(2)	76.727	76.266	76.900	77.072	77.135	78.116

Table S14 Energies of DFT (M06L/LANL2DZ/6-31G*) optimised structures

complex	*E* (Hartrees)		$\Delta E_{(HE\text{-}LE)}$[a]
	S = 0	*S* = 1	
1^{2+}	−1849.1687906	−1849.1411220	0.0276686 Hartrees 6072.5557476 cm^{-1} 72.643914834 kJ/mol
1	−1849.6084753	−1849.5963629	0.0121124 Hartrees 2658.3645084 cm^{-1} 31.801108622 kJ/mol
1^{2-}	−1849.5777020	−1849.5794476	0.0017456 Hartrees 383.11491413 cm^{-1} 4.5830731491 kJ/mol
2^{2+}	−1846.3145693	−1846.2932997	0.0212696 Hartrees 4668.1375902 cm^{-1} 55.843339054 kJ/mol
2	−1846.7619364	−1846.7451543	0.0167821 Hartrees 3683.2451881 cm^{-1} 44.061406906 kJ/mol
2^{2-}	−1846.7285563	−1846.7257949	0.0027614 Hartrees 606.05724328 cm^{-1} 7.2500562523 kJ/mol
3^{4+}	−1808.4684218	−1808.4789299	0.0105081 Hartrees 2306.2613595 cm^{-1} 27.589018652 kJ/mol
3	−1809.8474799	−1809.8453289	0.002151 Hartrees 472.0899291cm^{-1} 5.64745093 kJ/mol
3^{2-}	−1809.7982225	−1809.8057036	0.0074811 Hartrees 1641.9116545 cm^{-1} 19.641629546 kJ/mol
4	−1807.0080052	−1807.0013954	0.0066098 Hartrees 1450.6834094 cm^{-1} 17.354031222 kJ/mol

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

Table S15 DFT calculated (M06L/LanL2DZ/6-31G*) Mulliken spin densities

complex	Ru/Os	L^1/H_2L^2	bpy
$\mathbf{1}^{-}$ (*S*=1/2)	0.039	0.037	0.924
$\mathbf{1}^{2-}$ (*S*=1)	0.218	0.022	1.762
$\mathbf{2}^{-}$ (*S*=1/2)	0.101	0.057	0.843
$\mathbf{2}^{2-}$ (*S*=1)	0.333	0.063	1.603
$\mathbf{3}^{3+}$ (*S*=1/2)	0.489	0.517	-0.004
$\mathbf{3}^{-}$ (*S*=1/2)	-0.78	-0.330	1.408
$\mathbf{3}^{2-}$ (*S*=1)	0.258	0.057	1.685
$\mathbf{4}^{3+}$ (*S*=1/2)	0.599	0.410	-0.010
$\mathbf{4}^{-}$ (*S*=1/2)	0.104	0.022	0.874
$\mathbf{4}^{2-}$ (*S*=1)	0.389	0.135	1.477

Table S16 Experimental and TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions for $\mathbf{1}^n$

λ_{max}/nm (expt.)[a] (ε/dm^{3}cm^{-1} mol^{-1})[b]	λ/nm (DFT) (f)[c]	transitions	character
		$\mathbf{1}^+$ (S=1/2)	
904(912)	19200(0.03)	HOMO(α)→LUMO(α)(0.97)	L^1(π)→bpy(π*)
798(837)	11400(0.15)	HOMO-2(β)→LUMO(β)(0.95)	Ru(dπ)/L^1(π)/bpy(π)→L^1(π*)/bpy(π*)
628(617)	4820(0.03)	HOMO(α)→LUMO+2(α)(0.92)	L^1(π)→bpy(π*)
580(546)	9100(0.04)	HOMO-2(α)→LUMO(α)(0.70)	L^1(π)/Ru(dπ)→bpy(π*)
494(507)	20600(0.055)	HOMO-3(α)→LUMO+1(α)(0.85)	Ru(dπ)/L^1(π)/bpy(π)→bpy(π*)
430(433)	17800(0.03)	HOMO(α)→LUMO+7(α)(0.76)	L^1(π)→Ru(dπ)/L^1(π*)/bpy(π*)
(395)	17800(0.052)	HOMO-2(β)→LUMO+5(β)(0.58)	Ru(dπ)/L^1(π)/bpy(π)→bpy(π*)
345(369)	37000(0.070)	HOMO-3(α)→LUMO+4(α)(0.83)	Ru(dπ)/L^1(π)/bpy(π)→bpy(π*)
(349)	37000(0.065)	HOMO-3(α)→LUMO+5(α)(0.38)	Ru(dπ)/L^1(π)/bpy(π)→bpy(π*)Ru(dπ)
		HOMO-3(β)→LUMO+3(β)(0.38)	L^1(π)/Ru(dπ)→bpy(π*)
(311)	37000(0.087)	HOMO-4(α)→LUMO+4(α)(0.58)	L^1(π)/Ru(dπ)→bpy(π*)
		$\mathbf{1}^{2+}$ (S=0)	
915(773)	19300(0.33)	HOMO-2→LUMO(0.68)	Ru(dπ)/L^1(π)→L^1(π*)
805(773)	19300(0.33)	HOMO-2→LUMO(0.68)	Ru(dπ)/L^1(π)→L^1(π*)
623(588)	6550(0.38)	HOMO-3→LUMO(0.60)	L^1(π)→L^1(π*)
578(556)	9130(0.03)	HOMO-5→LUMO(0.57)	bpy(π)→L^1(π*)
487(482)	15000(0.048)	HOMO-1→LUMO+1(0.66)	Ru(dπ)/L^1(π)→bpy(π*)
----(452)	15000(0.052)	HOMO-2→LUMO+2(0.66)	Ru(dπ)/L^1(π)→bpy(π*)
421(415)	19400(0.05)	HOMO-1→LUMO+3(0.67)	Ru(dπ)/L^1(π)→L^1(π*)
400(373)	20490(0.05)	HOMO-2→LUMO+3(0.50)	Ru(dπ)/L^1(π)→L^1(π*)
		HOMO-3→LUMO+3(0.25)	L^1(π)→L^1(π*)

345(361)	32200(0.087)	HOMO-1→LUMO+4(0.53)	$L^1(\pi)\rightarrow L^1(\pi^*)$
---(315)	32200(0.076)	HOMO-3→LUMO+3(0.47)	$L^1(\pi)\rightarrow L^1(\pi^*)$
		HOMO-2→LUMO+6(0.15)	$Ru(d\pi)/L^1(\pi)\rightarrow bpy(\pi^*)$
		1 (*S*=0)	
858(1323)	7600(0.062)	HOMO→LUMO+1(0.65)	$L^1(\pi)/bpy(\pi)\rightarrow bpy(\pi^*)$
-----(662)	---(0.043)	HOMO→LUMO+3(0.52)	$L^1(\pi)/bpy(\pi)\rightarrow bpy(\pi^*)$
588(565)	10160(0.11)	HOMO-3→LUMO+1(0.44)	$Ru(d\pi)/L^1(\pi)\rightarrow bpy(\pi^*)$
484(490)	24700(0.03)	HOMO→LUMO+7(0.66)	$L^1(\pi)/bpy(\pi)\rightarrow Ru(d\pi)/bpy(\pi^*)$
----(482)	24700(0.04)	HOMO-1→LUMO+4(0.67)	$Ru(d\pi)\rightarrow bpy(\pi^*)$
334(365)	37500(0.102)	HOMO-3→LUMO+5(0.33)	$Ru(d\pi)/L^1(\pi)\rightarrow bpy(\pi^*)$
		HOMO-1→LUMO+7(0.26)	$Ru(d\pi)\rightarrow L^1(\pi^*)$
----(344)	37500(0.03)	HOMO→LUMO+12(0.62)	$L^1(\pi)/bpy(\pi)\rightarrow L^1(\pi^*)$
320(309)	38700(0.124)	HOMO-1→LUMO+9(0.55)	$Ru(d\pi)\rightarrow L^1(\pi^*)$

[a] Experimental absorption maxima (λ_{max} > 300 nm) from OTTLE spectroelectrochemistry in CH_3CN/0.1M Bu_4NClO_4. [b] Molar extinction coefficients in dm^3cm^{-1} mol^{-1}. [c] Calculated oscillator strengths.

Table S17. Experimental and TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions for $\mathbf{2}^n$

λ_{max}/nm (expt.)[a] (ε/dm^{3}cm^{-1} mol^{-1})[b]	λ/nm (DFT) (f)[c]	transitions	character
		$\mathbf{2}^+$ (S=1/2)	
2107(2003)[d]	2800(0.00088)	HOMO→LUMO(0.99)	Os(dπ)/bpy(π)→L^1(π*)/bpy(π*)
1625(1503)	1700(0.0012)	HOMO(β)→LUMO(β)(0.99)	Os(dσ)→L^1(π*)/bpy(π*)
935(920)	16900(0.082)	HOMO(α)→LUMO(α)(0.90)	L^1(π)/Os(dπ)→bpy(π*)
(890)	16900(0.13)	HOMO-2(β)→LUMO(β)(0.41)	Os(dπ)/bpy(π)/L^1(π)→L^1(π*)/bpy(π*)
707(679)	4300(0.013)	HOMO-1(α)→LUMO(α)(0.72)	Os(dπ)/bpy(π)→bpy(π*)
639(623)	4300(0.024)	HOMO(α)→LUMO+2(α)(0.92)	L^1(π)/Os(dπ)→bpy(π*)
490(505)	9600(0.043)	HOMO-3(α)→LUMO+1(α)(0.74)	Os(dπ)/bpy(π)/L^1(π)→bpy(π*)
(433)	9600(0.052)	HOMO-1(β)→LUMO+3(β)(0.58)	L^1(π)/Os(dπ)→bpy(π*)
(411)	9600(0.064)	HOMO-2(α)→LUMO+3(α)(0.48)	L^1(π)/Os(dπ)→bpy(π*)
		HOMO-4(α)→LUMO+1(α)(0.44)	L^1(π)→bpy(π*)
385(385)	14100(0.078)	HOMO-3(α)→LUMO+2(α)(0.45)	Os(dπ)/L^1(π)/bpy(π)→bpy(π*)
		HOMO-7(β)→LUMO(β)(0.45)	bpy(π)→L^1(π*)/bpy(π*)
(369)	14100 (0.105)	HOMO-3(α)→LUMO+4(α)(0.75)	Os(dπ)/L^1(π)/bpy(π)→bpy(π*)
343(342)	16900(0.083)	HOMO-3(β)→LUMO+4(β)(0.38)	L^1(π)→bpy(π*)
		HOMO-1(α)→LUMO+6(α)(0.25)	Os(dπ)/bpy(π)→L^1(π*)
(311)	16900(0.078)	HOMO-4(α)→LUMO+2(α)(0.52)	L^1(π)→bpy(π*)
		$\mathbf{2}^{2+}$ (S=0)	
2230(2533)	2100(0.000)	HOMO→LUMO(0.71)	Os(dσ)→L^1(π*)
720(795)	20200(0.34)	HOMO-2→LUMO(0.68)	Os(dπ)/L^1(π)→L^1(π*)
----(602)	20200(0.025)	HOMO→LUMO+1(0.69)	Os(dπ)/bpy(π)→bpy(π*)

492(540)	7300(0.064)	HOMO-5→LUMO(0.55)	bpy(π)→L^1(π*)/Os(dπ)
---(506)	7300(0.074)	HOMO-1→LUMO+1(0.66)	Os(dπ)/L^1(π)→bpy(π*)
---(485)	7300(0.050)	HOMO→LUMO+3(0.62)	Os(dπ)/bpy(π)→L^1(π*)
---(463)	7300(0.054)	HOMO-2→LUMO+2(0.67)	Os(dπ)/L^1(π)→bpy(π*)
400(422)	13840(0.089)	HOMO-1→LUMO+3(0.67)	Os(dπ)/L^1(π)→L^1(π*)
385(391)	14100(0.050)	HOMO→LUMO+6(0.64)	Os(dπ)/bpy(π)→bpy(π*)
364(366)	13400(0.080)	HOMO-3→LUMO+2(0.58)	L^1(π)→bpy(π*)
341(348)	13500(0.085)	HOMO-2→LUMO+5(0.58)	Os(dπ)/L^1(π)→bpy(π*)
---(313)	13500(0.105)	HOMO-3→LUMO+3(0.64)	L^1(π)→L^1(π*)
		2 (*S*=0)	
886(914)	4900(0.059)	HOMO→LUMO(0.61)	L^1(π)/bpy(π)→bpy(π*)
755(672)	5300(0.03)	HOMO-1→LUMO(0.63)	Os(dπ)/bpy(π)→bpy(π*)
587(579)	10880(0.07)	HOMO-2→LUMO(0.57)	L^1(π)/Os(dπ)→bpy(π*)
490(500)	16800(0.075)	HOMO→LUMO+6(0.50)	L^1(π)/bpy(π)→L^1(π*)
		HOMO-3→LUMO+1(0.38)	Os(dπ)/L^1(π)→bpy(π*)
---(493)	16800(0.07)	HOMO→LUMO+6(0.48)	L^1(π)/bpy(π)→L^1(π*)
432(434)	15200(0.07)	HOMO→LUMO+7(0.69)	L^1(π)/bpy(π)→L^1(π*)
---(396)	15200(0.15)	HOMO-2→LUMO+3(0.45)	L^1(π)/Os(dπ)→bpy(π*)
346(349)	18560(0.03)	HOMO-3→LUMO+4(0.60)	Os(dπ)/L^1(π)→bpy(π*)
---(320)	18560(0.07)	HOMO-3→LUMO+5(0.39)	Os(dπ)/L^1(π)→bpy(π*)
		HOMO→LUMO+9(0.35)	L^1(π)/bpy(π)→bpy(π*)

[a] Experimental absorption maxima (λ_{max} > 300 nm) from OTTLE spectroelectrochemistry in CH_3CN/0.1M Bu_4NClO_4. [b] Molar extinction coefficients in $dm^3cm^{-1}mol^{-1}$. [c] Calculated oscillator strengths. [d] Calculations using ORCA indicated such a transition at 2003 nm.

Table S18. Experimental and TD-DFT (M06L/CPCM/CH_3CN) calculated electronic Transitions for $\mathbf{3}^n$

λ_{max}/nm (expt.)[a] (ε/dm^{3}cm^{-1} mol^{-1})[b]	λ/nm (DFT) (f)[c]	transitions	character
		$\mathbf{3}^{2+}$ (S=0)	
560(608)	17500(0.263)	HOMO-2→LUMO(0.66)	Ru(dπ)/bpy(π)→H_2L^2(π*)
428(462)	4700(0.17)	HOMO-3→LUMO(0.66)	H_2L^2(π)/Ru(dπ) →H_2L^2(π*)
(429)	4890(0.08)	HOMO→LUMO+3(0.52)	Ru(dπ)→bpy(π*)
(421)	4890(0.05)	HOMO-5→LUMO(0.52)	H_2L^2(π)→H_2L^2(π*)
387(394)	4200(0.03)	HOMO-3→LUMO+1(0.51)	H_2L^2(π)/Ru(dπ)→bpy(π*)
(376)	4200(0.033)	HOMO-2→LUMO+3(0.51)	Ru(dπ)/bpy(π)→bpy(π*)
352(376)	5900(0.05)	HOMO-1→LUMO+4(0.62)	Ru(dπ)/H_2L^2(π)→bpy(π*)
----(352)	5900(0.065)	HOMO-2→LUMO+5(0.51)	Ru(dπ)/bpy(π)→bpy(π*)
		$\mathbf{3}^{3+}$ (S=1/2)	
415(441)	6400(0.063)	HOMO-14(β)→LUMO(β)(0.85)	bpy(π)/H_2L^2(π)→Ru(dπ)/H_2L^2(π*)
---(436)	6400(0.080)	HOMO-14(β)→LUMO(β)(0.57)	H_2L^2(π)/bpy(π)→Ru(dπ)/H_2L^2(π*)
394(377)	6600(0.040)	HOMO-19(β)→LUMO(β)(0.54)	H_2L^2(π)/bpy(π)→Ru(dπ)/H_2L^2(π*)
---(340)	6600(0.087)	HOMO(β)→LUMO+4(β)(0.40)	Ru(dπ)/H_2L^2(π)→H_2L^2(π*)
		HOMO-3(β)→LUMO+4(β)(0.25)	Ru(dπ)/H_2L^2(π)→H_2L^2 (π*)
		$\mathbf{3}^{+}$ (S=1/2)	
638(651)	2800(0.024)	HOMO-2(β)→LUMO(β)(0.85)	Ru(dπ)→bpy(π*)
---(643)	2800(0.101)	HOMO-1(β)→LUMO(β)(0.76)	H_2L^2(π)/Ru(dπ)→bpy(π*)
550(595)	12700(0.025)	HOMO-1(β)→LUMO+2(β)(0.65)	H_2L^2(π)/Ru(dπ)→H_2L^2(π*)
---(544)	12700(0.067)	HOMO-3(α)→LUMO(α)(0.62)	Ru(dπ)/bpy(π)→bpy(π*)
---(528)	12700(0.064)	HOMO-3(α)→LUMO+1(α)(0.67)	Ru(dπ)/bpy(π)→bpy(π*)
450(477)	4300(0.035)	HOMO(β)→LUMO+5(β)(0.65)	Ru(dπ)/H_2L^2(π)→bpy(π*)

405(401)	5700(0.038)	HOMO-1(β)→LUMO+5(β)(0.65)	H_2L^2(π)/Ru(dπ)→bpy(π*)
---(389)	5700(0.046)	HOMO-1(β)→LUMO+4(β)(0.62)	H_2L^2(π)/Ru(dπ)→bpy(π*)
356(357)	7000(0.13)	HOMO(α)→LUMO+13(α)(0.68)	H_2L^2(π)/bpy(π)→H_2L^2(π*)/Ru(dπ)
		3 (*S*=0)	
1000(965)	1000(0.022)	HOMO→LUMO+3(0.70)	H_2L^2(π)/bpy(π)→bpy(π*)
625(629)	5100(0.032)	HOMO→LUMO+7(0.70)	H_2L^2(π)/bpy(π)→ H_2L^2(π*)
592(558)	5100(0.06)	HOMO-2→LUMO(0.42)	Ru(dπ)/H_2L^2(π)→bpy(π*)
		HOMO-2→LUMO+1(0.36)	Ru(dπ)/H_2L^2(π)→bpy(π*)
546(542)	5680(0.094)	HOMO-2→LUMO+1(0.39)	Ru(dπ)/H_2L^2(π)→bpy(π*)
		HOMO-3→LUMO(0.38)	Ru(dπ)→bpy(π*)
486(501)	7300(0.036)	HOMO-3→LUMO+1(0.40)	Ru(dπ)/bpy(π)→bpy(π*)/H_2L^2(π*)
		HOMO-2→LUMO(0.20)	Ru(dπ)/H_2L^2(π)→bpy(π*)
----(442)	7300(0.050)	HOMO→LUMO+10(0.64)	H_2L^2(π)/bpy(π)→bpy(π*)
396(414)	6200(0.045)	HOMO-5→LUMO(0.42)	H_2L^2(π)→bpy(π*)
		HOMO-2→LUMO+3(0.41)	Ru(dπ)/H_2L^2(π)→bpy(π*)
----(388)	6200(0.145)	HOMO-3→LUMO+4(0.56)	Ru(dπ)/bpy(π)→bpy(π*)/H_2L^2(π*)
360(358)	7400(0.21)	HOMO→LUMO+13(0.57)	H_2L^2(π)/bpy(π)→Ru(dπ)
		3$^-$ (*S*=1/2)	
1286(1327)	1800(0.098)	HOMO(β)→LUMO+1(β)(0.60)	H_2L^2(π)→bpy(π*)
619(628)	6200(0.12)	HOMO-1(β)→LUMO+2(β)(0.65)	Ru(dπ)→H_2L^2(π*)
587(564)	6200(0.038)	HOMO-2(β)→LUMO+1(β)(0.90)	Ru(dπ)/bpy(π)→bpy(π*)
558(516)	5590(0.025)	HOMO-3(β)→LUMO(β)(0.58)	Ru(dπ)/H_2L^2(π)→bpy(π*)
508(477)	4920(0.03)	HOMO(α)→LUMO+10(α)(0.51)	bpy(π)→bpy(π*)
432(428)	6730(0.05)	HOMO(β)→LUMO+9(β)(0.38)	H_2L^2(π)→bpy(π*)/Ru(dπ)
		HOMO-1(α)→LUMO+9(α)(0.51)	bpy(π)/H_2L^2(π)→bpy(π*)/Ru(dπ)
368(382)	11200(0.035)	HOMO-4(β)→LUMO(β)(0.42)	H_2L^2(π)→bpy(π*)
		HOMO(β)→LUMO+13(β)(0.35)	H_2L^2(π)→bpy(π*)/Ru(dπ)
368(375)	11200(0.083)	HOMO-3(β)→LUMO+5(β)(0.46)	Ru(dπ)/H_2L^2(π)→H_2L^2 (π*)/bpy(π*)
		HOMO-1(α)→LUMO+12(α)(0.44)	bpy(π)/H_2L^2(π)→H_2L^2(π*)/Ru(dπ)

[a] Experimental absorption maxima (λ_{max} > 300 nm) from OTTLE spectroelectrochemistry in CH_3CN/0.1M Bu_4NClO_4. [b] Molar extinction coefficients in dm^3cm^{-1} mol^{-1}. [c] Calculated oscillator strengths.

Table S19. Experimental and TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions for $\mathbf{4}^n$

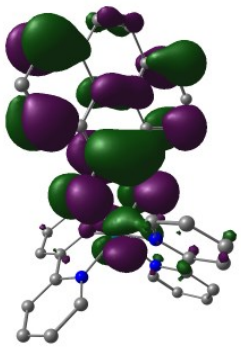
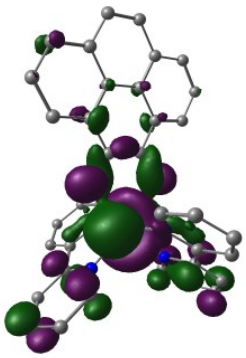
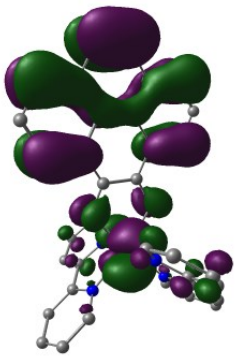
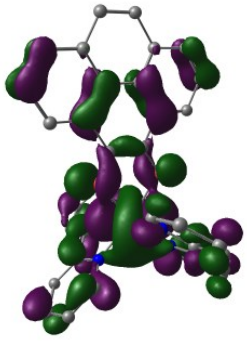
λ_{max}/nm (expt.)[a] (ε/dm^{3}cm^{-1} mol^{-1})[b]	λ/nm (DFT) (f)[c]	transitions	character
		$\mathbf{4}^{2+}$ (S=0)	
1031(899)	1110(0.003)	HOMO→LUMO(0.70)	$H_2L^2(\pi)$/Os(dπ)→ $H_2L^2(\pi^*)$/bpy(π*)
718(721)	800(0.012)	HOMO-1→LUMO(0.70)	Os(dπ)/$H_2L^2(\pi)$→$H_2L^2(\pi^*)$/bpy(π*)
550(623)	24100(0.26)	HOMO-2→LUMO(0.65)	Os(dπ)/bpy(π)→$H_2L^2(\pi^*)$/bpy(π*)
(516)	24100(0.063)	HOMO-1→LUMO+1(0.61)	Os(dπ)/$H_2L^2(\pi)$→bpy(π*)
(492)	24100(0.052)	HOMO-2→LUMO+2(0.57)	Os(dπ)/bpy(π)→bpy(π*)
416(436)	11400(0.24)	HOMO-3→LUMO(0.38)	$H_2L^2(\pi)$→$H_2L^2(\pi^*)$/bpy(π*)
		HOMO-2→LUMO(0.16)	Os(dπ)/bpy(π)→$H_2L^2(\pi^*)$/bpy(π*)
(420)	11400(0.15)	HOMO-3→LUMO(0.50)	$H_2L^2(\pi)$/Os(dπ)→$H_2L^2(\pi^*)$/bpy(π*)
340(365)	11100(0.07)	HOMO-2→LUMO+5(0.63)	Os(dπ)/bpy(π)→bpy(π*)
(348)	11100(0.108)	HOMO-7→LUMO(0.44)	bpy(π)→$H_2L^2(\pi^*)$/bpy(π*)
		HOMO-2→LUMO+3(0.34)	Os(dπ)/bpy(π)→bpy(π*)
		$\mathbf{4}^{3+}$ (S=1/2)	
1890(1525)[d]	900(0.0024)	HOMO-1(β)→LUMO(β)(0.88)	Os(dπ)/bpy(π)→Os(dπ)/$H_2L^2(\pi^*)$
544(636)	10400(0.121)	HOMO-6(β)→LUMO(β)(0.87)	$H_2L^2(\pi)$→Os(dπ)/$H_2L^2(\pi^*)$
495(433)	7120(0.051)	HOMO-1(β)→LUMO+3(β)(0.77)	Os(dπ)/bpy(π)→bpy(π*)
400(426)	11400(0.243)	HOMO-10(β)→LUMO(β)(0.46)	$H_2L^2(\pi)$/bpy(π)→Os(dπ)/$H_2L^2(\pi^*)$
		HOMO-3(β)→LUMO+1(β)(0.42)	Os(dπ)/$H_2L^2(\pi)$→$H_2L^2(\pi^*)$/Os(dπ)
---(422)	11400(0.094)	HOMO-10(β)→LUMO(β)(0.83)	$H_2L^2(\pi)$/bpy(π)→Os(dπ)/$H_2L^2(\pi^*)$
---(388)	11400(0.030)	HOMO-13(β)→LUMO(β)(0.84)	$H_2L^2(\pi)$→Os(dπ)/$H_2L^2(\pi^*)$
333(380)	12400(0.030)	HOMO-8(α)→LUMO(α)(0.54)	$H_2L^2(\pi)$→$H_2L^2(\pi^*)$
333(337)	12400(0.133)	HOMO(β)→LUMO+4(β)(0.42)	$H_2L^2(\pi)$/Os(dπ)→$H_2L^2(\pi^*)$

		HOMO(α)→LUMO+3(α)(0.41)	H_2L^2(π)/Os(dπ)→H_2L^2 (π*)
		4$^+$ (*S*=1/2)	
1031(1592)	1400(0.02)	HOMO(α)→LUMO+1(α)(0.98)	H_2L^2(π)/bpy(π)→bpy(π*)
----(873)	1400(0.015)	HOMO(α)→LUMO+2(α)(0.98)	H_2L^2(π)/bpy(π)→bpy(π*)
720(699)	3900(0.022)	HOMO-1(β)→LUMO(β)(0.86)	H_2L^2(π)/bpy(π)→bpy(π*)
640(679)	4600(0.141)	HOMO-2(β)→LUMO+2(β)(0.87)	H_2L^2(π)/bpy(π)→bpy(π*)
550(571)	18000(0.022)	HOMO(α)→LUMO+7(α)(0.98)	H_2L^2(π)/bpy(π)→H_2L^2(π*)
---(539)	18000(0.05)	HOMO-3(α)→LUMO(α)(0.58)	Os(dπ)/bpy(π)→bpy(π*)/H_2L^2(π*)
---(522)	18000(0.066)	HOMO-3(α)→LUMO+1(α)(0.61)	Os(dπ)/bpy(π)→bpy(π*)
448(484)	13200(0.053)	HOMO-1(α)→LUMO+4(α)(0.70)	Os(dπ)→bpy(π*)
423(451)	11800(0.051)	HOMO-1(α)→LUMO+5(α)(0.65)	Os(dπ)→bpy(π*)
343(381)	11200(0.112)	HOMO-1(β)→LUMO+6(β)(0.37)	H_2L^2(π)/Os(dπ)→bpy(π*)
		HOMO-1(α)→LUMO+7(α)(0.36)	Os(dπ)→H_2L^2(π*)
---(357)	11200(0.111)	HOMO(α)→LUMO+11(α)(0.86)	H_2L^2(π)/bpy(π)→bpy(π*)/Os(dπ)
		4 (*S*=0)	
1152(1247)	3900(0.16)	HOMO→LUMO+1(0.71)	bpy(π)/H_2L^2(π)→bpy(π*)
771(779)	4800(0.02)	HOMO→LUMO+4(0.65)	bpy(π)/H_2L^2(π)→bpy(π*)
590(538)	8600(0.15)	HOMO-2→LUMO(0.54)	H_2L^2(π)/Os((dπ)→bpy(π*)
474(496)	15700(0.063)	HOMO-3→LUMO+1(0.50)	Os(dπ)/bpy(π)→bpy(π*)
----(459)	15700(0.067)	HOMO-1→LUMO+5(0.64)	Os(dπ)→bpy(π*)
364(380)	13200(0.091)	HOMO-5→LUMO+1(0.53)	H_2L^2(π)→bpy(π*)
		4$^-$ (*S*=1/2)	
1123(1088)	6600(0.014)	HOMO-1(α)→LUMO+1(α)(0.69)	bpy(π)/H_2L^2(π)→H_2L^2(π*)
----(994)	6600(0.093)	HOMO-1(α)→LUMO+5(α)(0.54)	bpy(π)/H_2L^2(π)→bpy(π*)/H_2L^2(π*)
716(662)	4810(0.083)	HOMO-1(α)→LUMO+5(α)(0.51)	bpy(π)/H_2L^2(π)→bpy(π*)/H_2L^2(π*)
542(561)	10700(0.056)	HOMO-2(β)→LUMO+2(β)(0.73)	Os(dπ)/bpy(π)→bpy(π*)/H_2L^2(π*)
434(455)	13100(0.049)	HOMO(α)→LUMO+9(α)(0.64)	bpy(π)→H_2L^2(π*)
362(376)	19500(0.092)	HOMO(α)→LUMO+12(α)(0.51)	H_2L^2(π)/bpy(π)→bpy(π*)

[a] Experimental absorption maxima (λ_{max} > 300 nm) from OTTLE spectroelectrochemistry in CH_3CN/0.1M Bu_4NClO_4. [b] Molar extinction coefficients in dm^3cm^{-1} mol^{-1}. [c] Calculated oscillator strengths. [d] Calculations using ORCA indicated such a transition at 1525 nm.

Table S20 DFT calculated MO composition for $\mathbf{1}^{+}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Ru	bpy	L^1
α-MO				
LUMO+5	-4.177	6	93	1
LUMO+4	-4.205	3	96	1
LUMO+3	-4.314	4	96	1
LUMO+2	-4.512	2	97	1
LUMO+1	-5.153	11	87	1
LUMO	-5.253	8	91	2
SOMO	-6.186	13	9	78
HOMO-1	-7.014	73	15	12
HOMO-2	-7.212	37	9	54
HOMO-3	-7.285	62	19	19
HOMO-4	-7.644	17	4	80
HOMO-5	-7.837	43	10	47
β-MO				
LUMO+5	-4.198	3	96	1
LUMO+4	-4.311	4	96	1
LUMO+3	-4.510	2	97	1
LUMO+2	-5.140	11	87	2
LUMO+1	-5.209	11	80	9
LUMO	-5.595	6	20	74
HOMO	-6.947	71	15	14
HOMO-1	-7.061	37	9	54
HOMO-2	-7.208	60	20	21
HOMO-3	-7.610	19	4	77
HOMO-4	-7.647	45	10	45
HOMO-5	-8.498	5	3	92

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

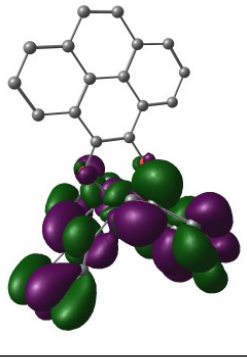
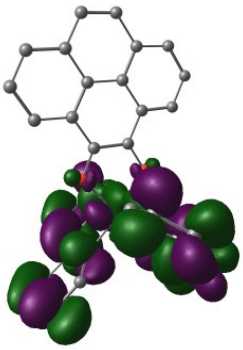
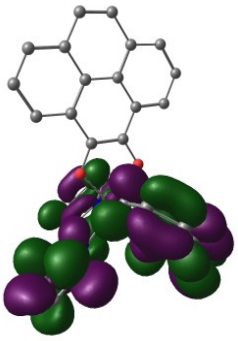
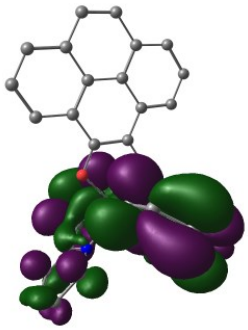
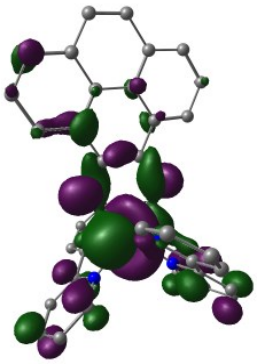
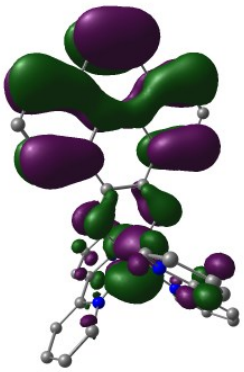
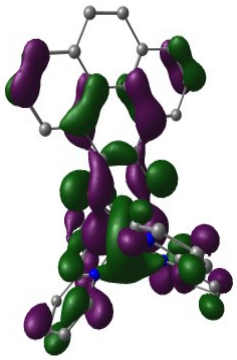
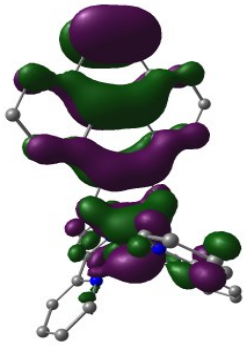
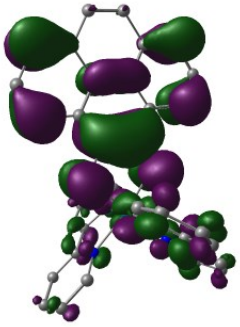
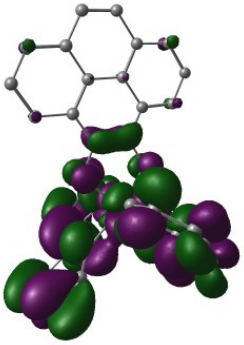
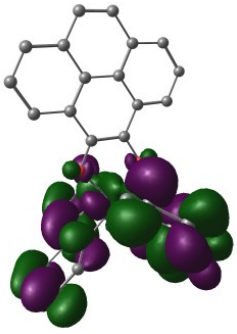
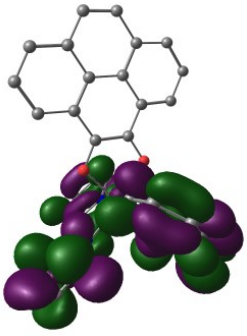
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 DFT Calculated MO Composition for $\mathbf{1}^{2+}$ in $S = 0$ State

MO	energy (eV)	% composition		
		Ru	bpy	L^1
LUMO+5	-6.943	3	95	2
LUMO+4	-7.061	3	95	2
LUMO+3	-7.220	1	2	97
LUMO+2	-7.859	8	91	1
LUMO+1	-7.920	6	93	1
LUMO	-9.488	16	6	78
HOMO	-10.132	78	13	9
HOMO-1	-10.365	64	13	24
HOMO-2	-10.371	58	11	31
HOMO-3	-10.990	7	2	91
HOMO-4	-10.994	35	9	56
HOMO-5	-11.608	1	98	1

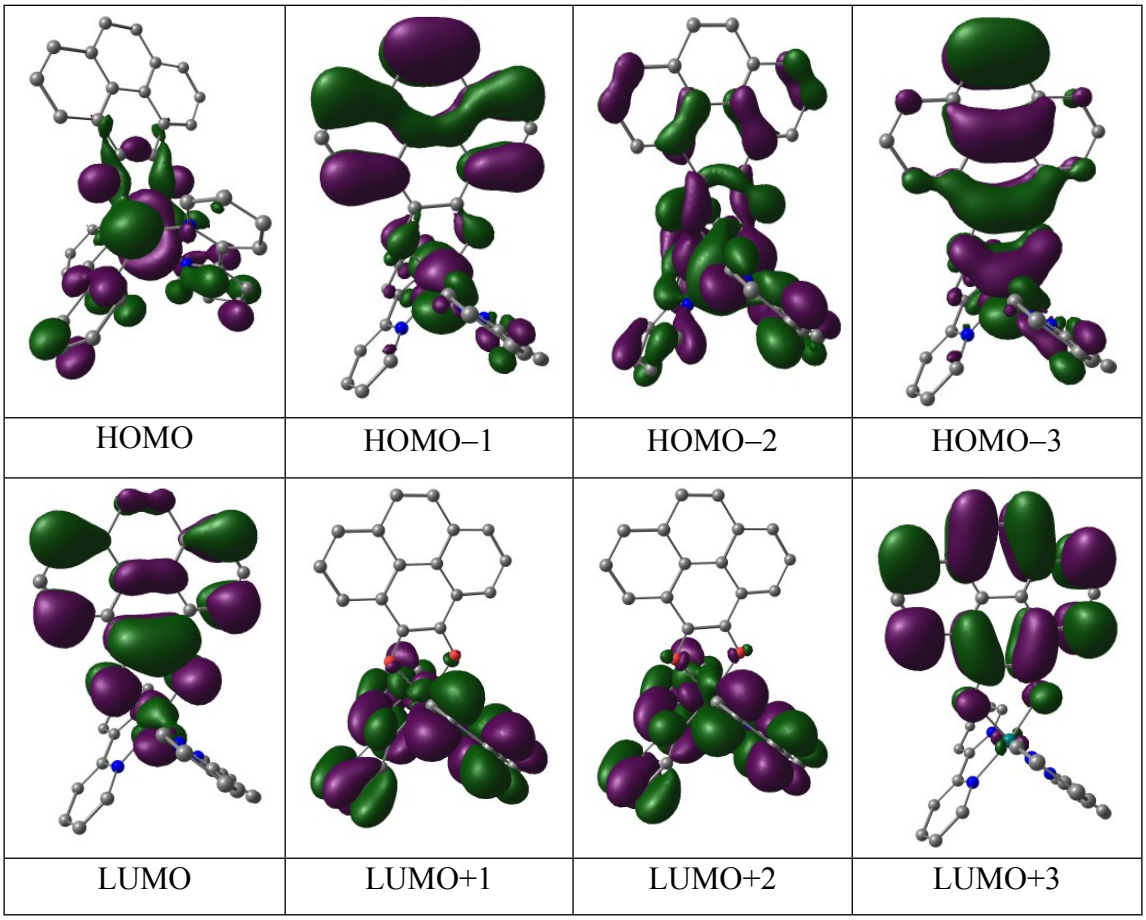


Table S22 DFT calculated MO composition for **1** in *S* = 0 state

MO	energy (eV)	% composition		
		Ru	bpy	L^1
LUMO+5	-1.425	4	95	1
LUMO+4	-1.462	5	94	1
LUMO+3	-1.531	5	94	1
LUMO+2	-1.753	2	97	1
LUMO+1	-2.381	11	83	5
LUMO	-2.450	11	77	12
HOMO	-2.721	4	28	68
HOMO-1	-4.050	71	15	14
HOMO-2	-4.252	41	10	50
HOMO-3	-4.297	59	18	23
HOMO-4	-4.788	43	9	48
HOMO-5	-4.794	19	4	77

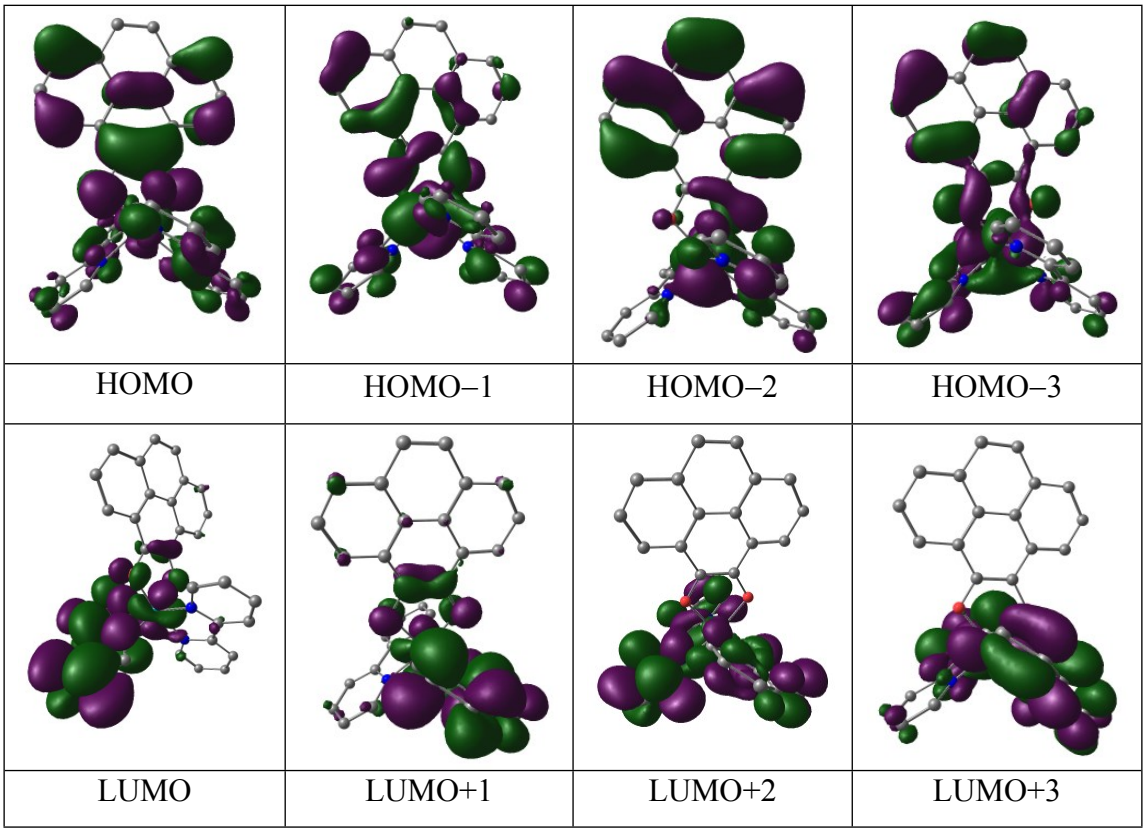
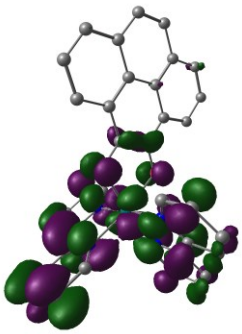
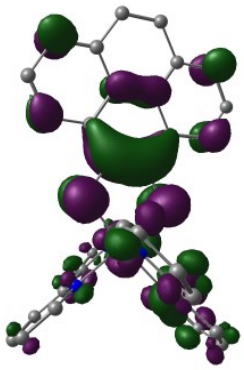
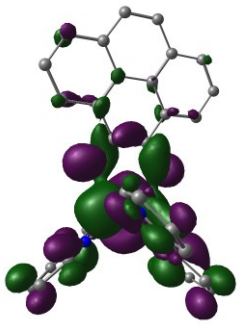
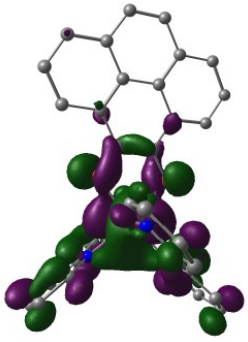


Table S23 DFT calculated MO composition for $\mathbf{1}^{-}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Ru	bpy	L^1
α-MO				
LUMO+5	1.647	7	91	1
LUMO+4	1.601	4	94	2
LUMO+3	1.513	5	93	2
LUMO+2	1.406	0	3	96
LUMO+1	1.328	2	96	2
LUMO	0.558	13	84	3
SOMO	0.541	14	78	8
HOMO-1	-0.027	8	23	68
HOMO-2	-0.861	75	14	11
HOMO-3	-1.121	62	23	15
HOMO-4	-1.362	59	16	25
HOMO-5	-2.189	12	4	84
β-MO				
LUMO+5	1.673	5	94	1
LUMO+4	1.561	4	94	2
LUMO+3	1.414	0	2	97
LUMO+2	1.387	3	95	2
LUMO+1	0.869	11	86	3
LUMO	0.771	12	83	4
HOMO	0.054	12	19	69
HOMO-1	-0.803	75	14	11
HOMO-2	-1.061	64	21	15
HOMO-3	-1.219	58	16	25
HOMO-4	-2.162	9	4	88
HOMO-5	-2.251	5	2	93

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

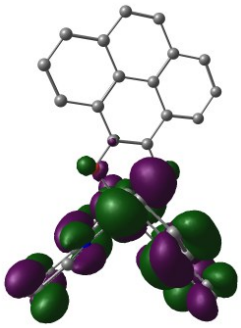
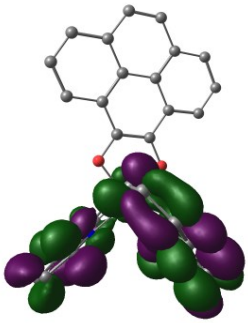
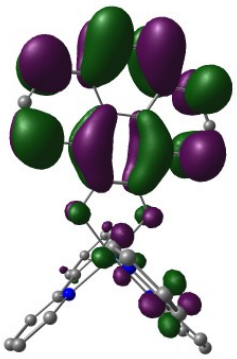
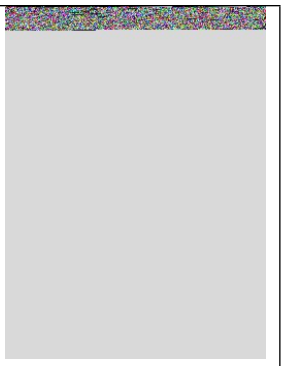
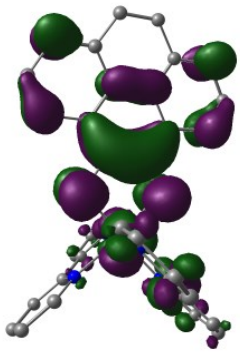
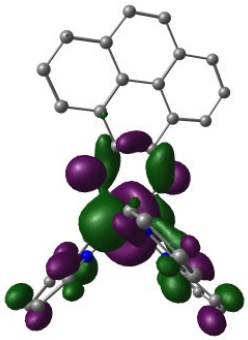
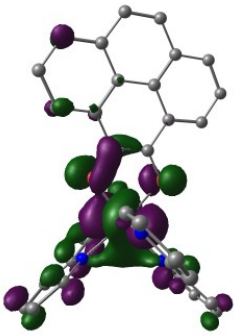
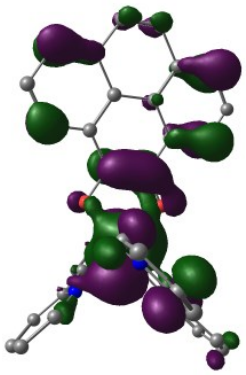
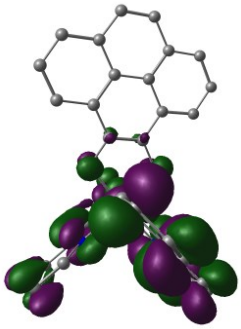
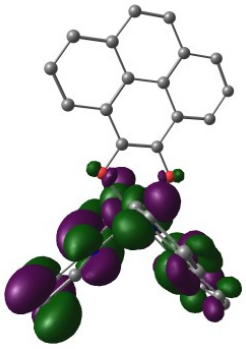
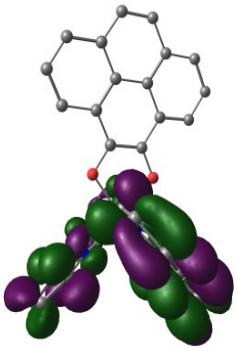
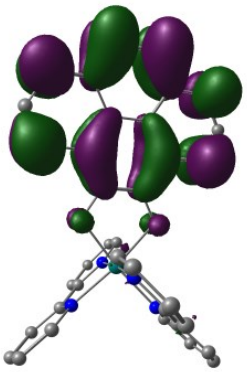
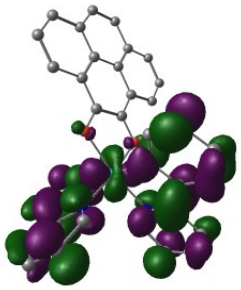
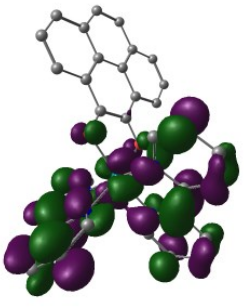
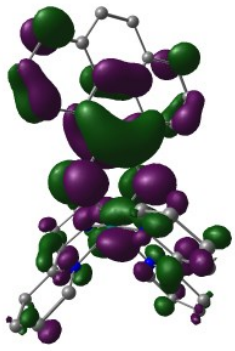
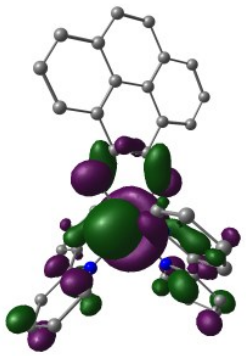
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S24 DFT calculated MO composition for $\mathbf{1}^{2-}$ in $S = 1$ state

MO	energy (eV)	% composition		
		Ru	bpy	L^1
α-MO				
LUMO+5	4.685	7	92	1
LUMO+4	4.655	4	94	1
LUMO+3	4.591	6	92	1
LUMO+2	4.509	1	4	95
LUMO+1	4.382	3	93	4
LUMO	3.669	1	3	96
SOMO1	3.503	16	79	5
SOMO2	3.299	12	83	5
HOMO-2	2.760	21	21	59
HOMO-3	2.253	78	14	8
HOMO-4	1.841	61	28	11
HOMO-5	1.619	55	13	32
β-MO				
LUMO+5	4.706	7	92	1
LUMO+4	4.521	1	25	74
LUMO+3	4.481	3	72	24
LUMO+2	4.070	13	84	2
LUMO+1	3.859	8	90	2
LUMO	3.681	1	2	98
HOMO	2.875	30	15	55
HOMO-1	2.373	76	15	8
HOMO-2	2.108	64	26	9
HOMO-3	1.757	49	12	39
HOMO-4	0.222	1	39	60
HOMO-5	0.212	2	23	76

α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3

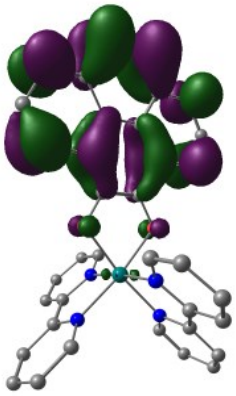
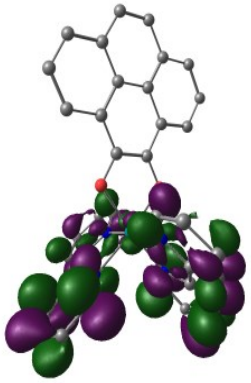
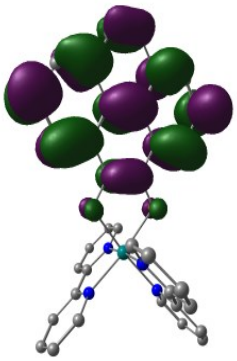
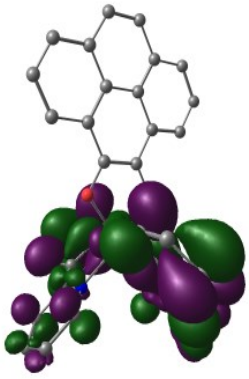
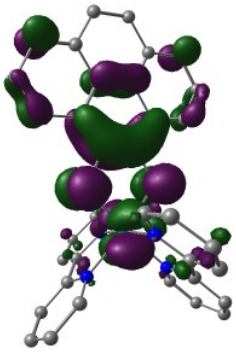
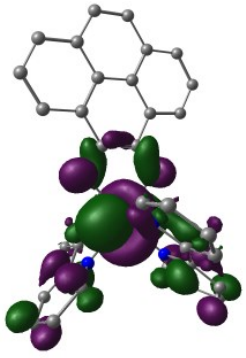
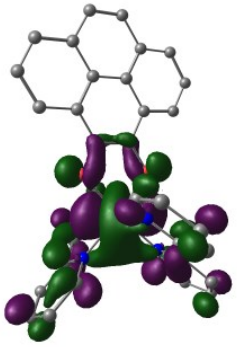
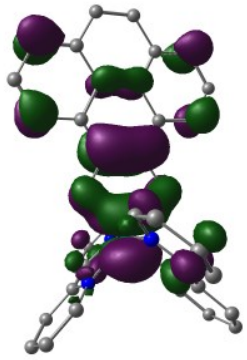
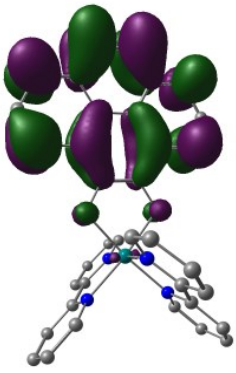
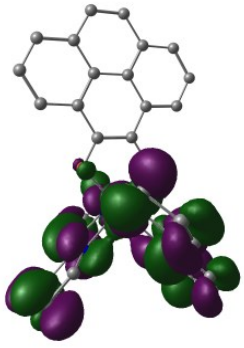
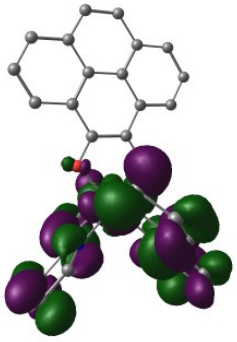
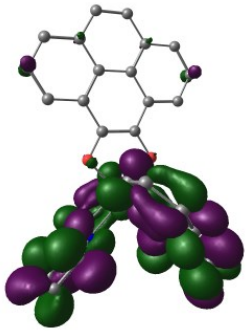
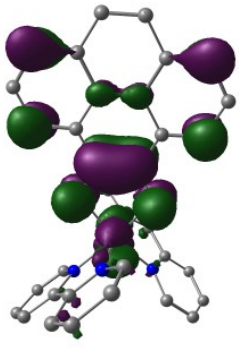
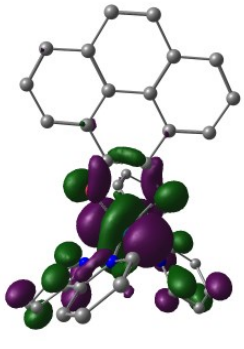
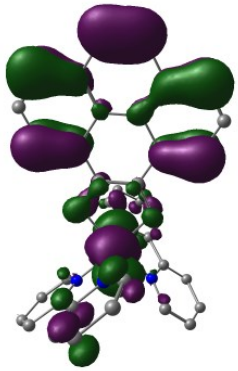
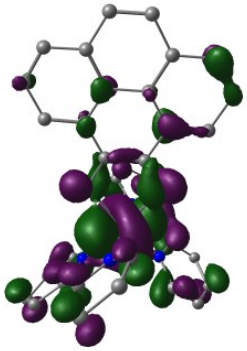
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25 DFT Calculated MO Composition for $\mathbf{2}^{+}$ in $S = 1/2$ State

MO	energy (eV)	% composition		
		Os	bpy	L^1
α-MO				
LUMO+5	-4.137	9	90	1
LUMO+4	-4.269	4	95	1
LUMO+3	-4.328	4	96	1
LUMO+2	-4.531	2	97	1
LUMO+1	-5.057	14	84	2
LUMO	-5.236	10	87	3
SOMO	-6.332	18	13	69
HOMO-1	-6.890	69	20	12
HOMO-2	-7.198	41	15	44
HOMO-3	-7.228	53	22	25
HOMO-4	-7.670	10	3	87
HOMO-5	-7.973	31	10	59
β-MO				
LUMO+5	-4.249	5	94	1
LUMO+4	-4.317	4	96	1
LUMO+3	-4.526	2	97	1
LUMO+2	-5.034	14	84	2
LUMO+1	-5.176	13	79	8
LUMO	-5.826	10	21	69
HOMO	-6.811	68	19	13
HOMO-1	-7.021	37	13	49
HOMO-2	-7.135	55	26	18
HOMO-3	-7.642	10	3	88
HOMO-4	-7.744	33	10	58
HOMO-5	-8.535	5	3	92

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

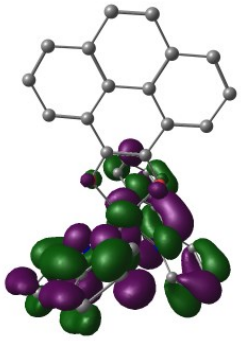
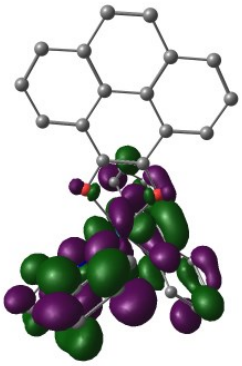
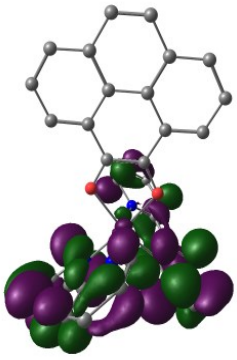
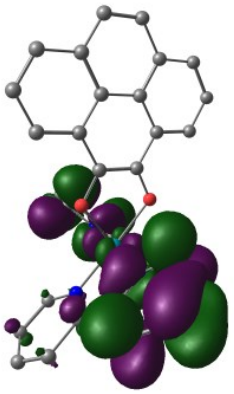
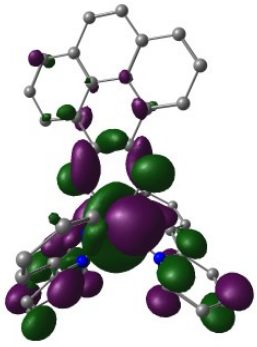
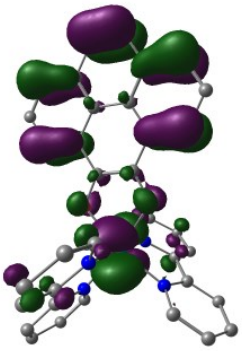
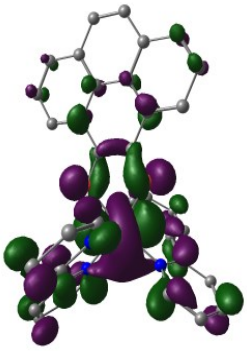
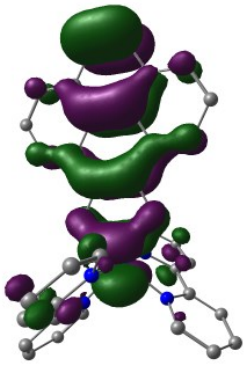
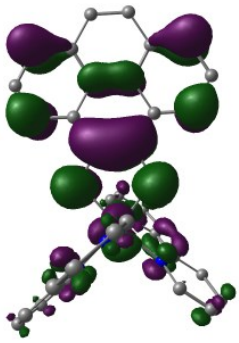
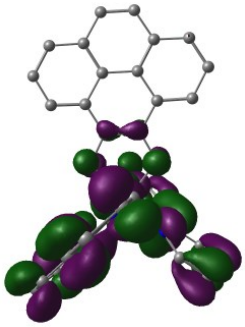
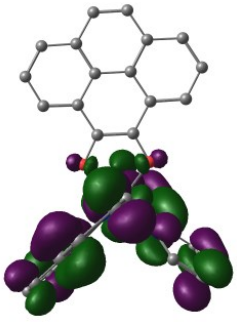
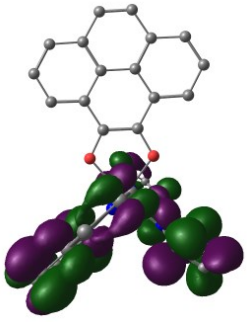
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26 DFT calculated MO composition for $\mathbf{2}^{2+}$ in $S = 0$ state

MO	energy (eV)	% composition		
		Os	bpy	L^1
LUMO+5	-7.002	3	95	2
LUMO+4	-7.102	2	96	2
LUMO+3	-7.190	1	3	96
LUMO+2	-7.893	11	87	2
LUMO+1	-7.987	9	90	1
LUMO	-9.463	18	9	73
HOMO	-9.993	71	19	9
HOMO-1	-10.286	59	17	24
HOMO-2	-10.297	50	14	35
HOMO-3	-10.961	5	2	93
HOMO-4	-11.011	29	11	60
HOMO-5	-11.653	1	98	1

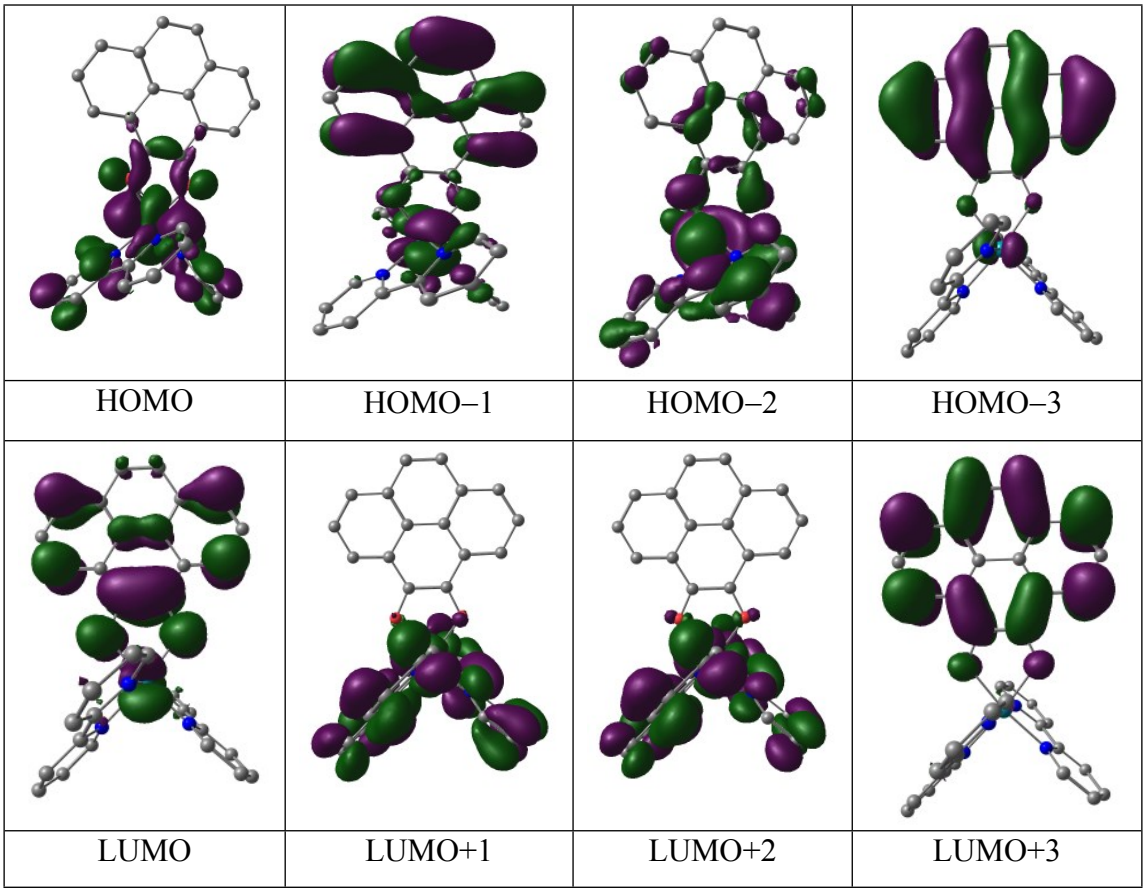


Table S27 DFT calculated MO composition for **2** in $S = 0$ state

MO	energy (eV)	% composition		
		Os	bpy	L^1
LUMO+5	-1.362	10	88	1
LUMO+4	-1.450	4	94	2
LUMO+3	-1.513	4	95	1
LUMO+2	-1.743	2	97	1
LUMO+1	-2.331	14	82	4
LUMO	-2.412	15	73	12
HOMO	-2.857	4	29	67
HOMO-1	-3.981	67	20	14
HOMO-2	-4.256	40	14	46
HOMO-3	-4.285	54	26	20
HOMO-4	-4.859	30	10	61
HOMO-5	-4.863	17	5	77

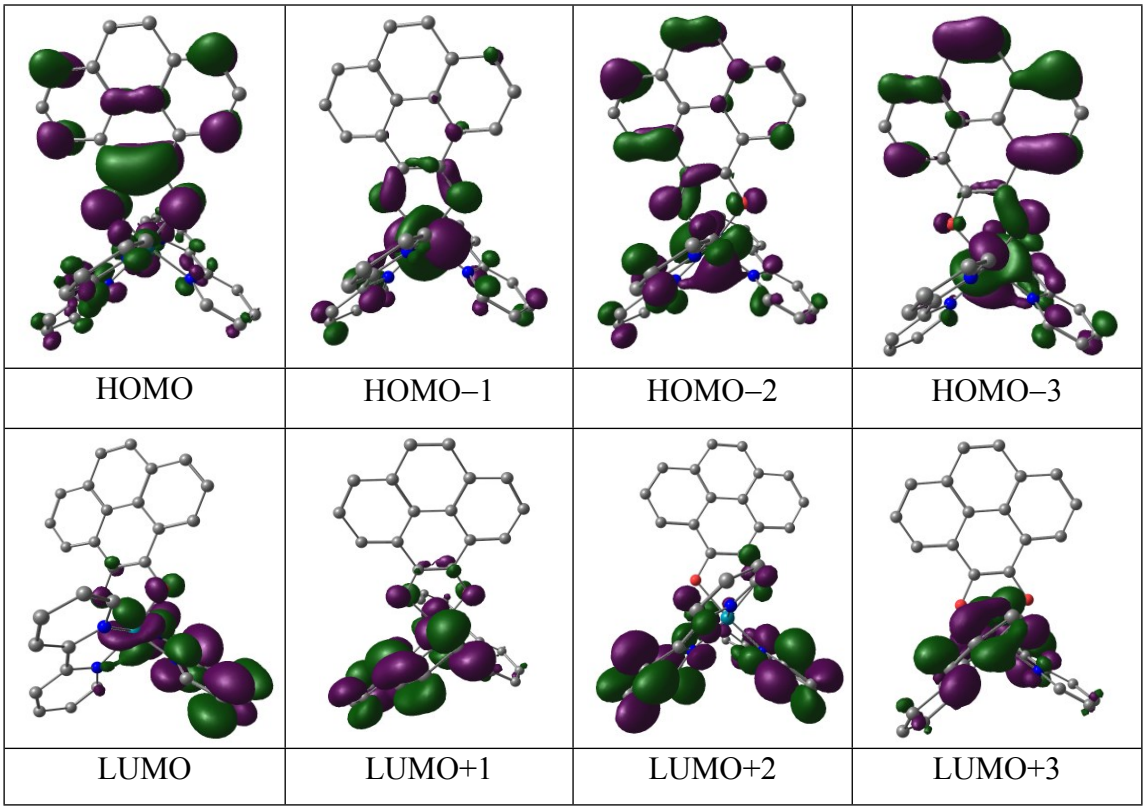
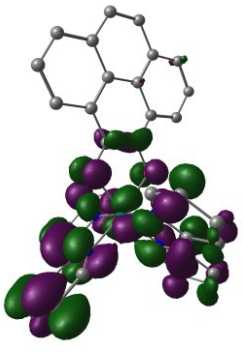
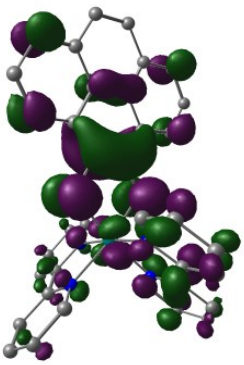
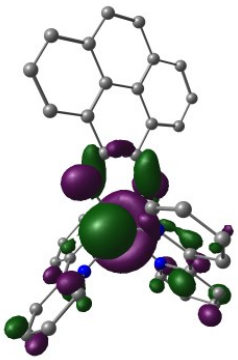
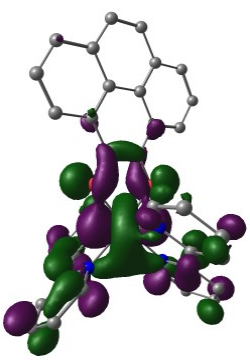


Table S28 DFT calculated MO composition for **2**$^{-}$ in S = 1/2 state

MO	energy (eV)	% composition		
		Os	bpy	L[1]
α-MO				
LUMO+5	1.784	12	86	2
LUMO+4	1.642	6	92	2
LUMO+3	1.551	4	94	1
LUMO+2	1.373	2	96	2
LUMO+1	1.287	1	2	98
LUMO	0.670	16	81	4
SOMO	0.620	17	76	8
HOMO-1	-0.186	10	26	64
HOMO-2	-0.787	69	20	11
HOMO-3	-1.103	55	32	14
HOMO-4	-1.423	50	20	31
HOMO-5	-2.336	10	5	85
β-MO				
LUMO+5	1.715	7	91	3
LUMO+4	1.602	4	95	1
LUMO+3	1.439	3	95	2
LUMO+2	1.295	1	2	97
LUMO+1	0.940	15	80	5
LUMO	0.849	14	81	5
HOMO	-0.086	14	26	61
HOMO-1	-0.721	69	20	11
HOMO-2	-1.026	57	29	14
HOMO-3	-1.266	47	20	33
HOMO-4	-2.305	7	4	89
HOMO-5	-2.305	4	2	94

α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3

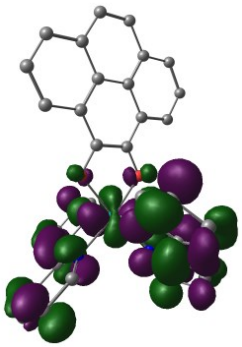
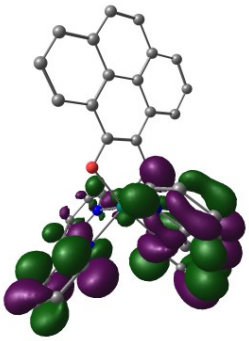
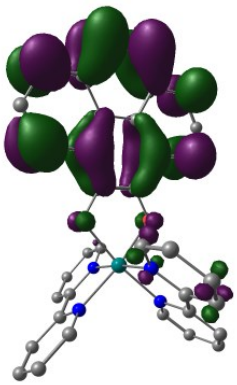
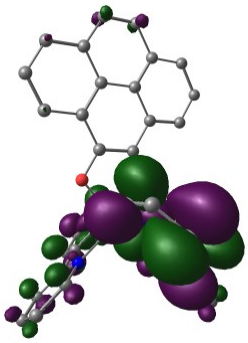
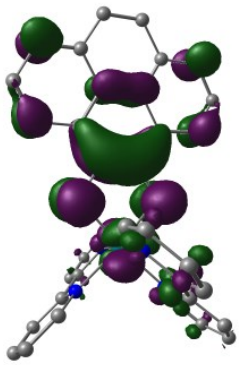
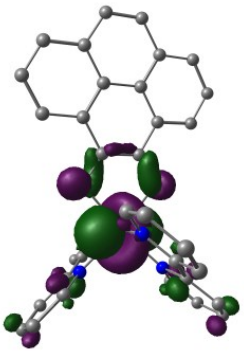
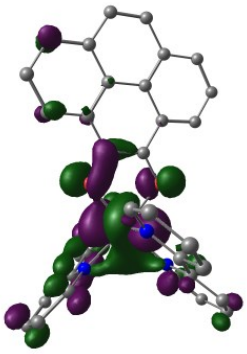
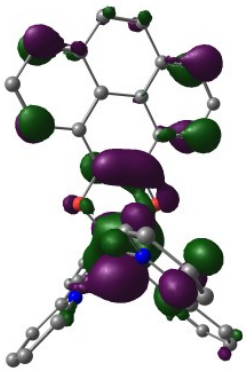
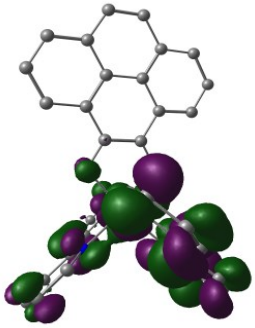
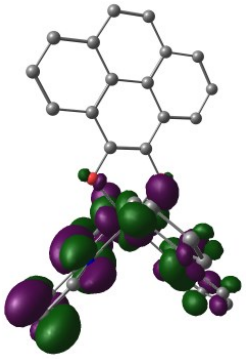
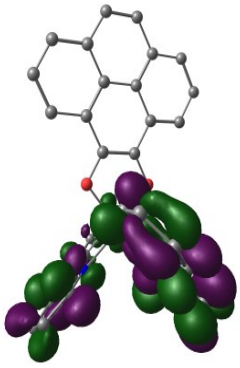
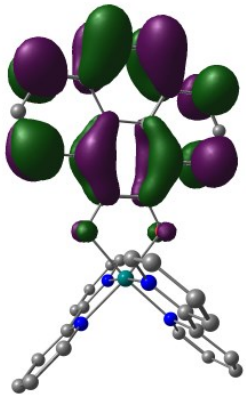
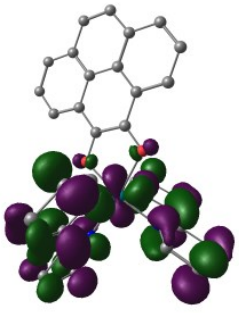
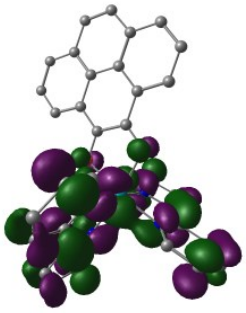
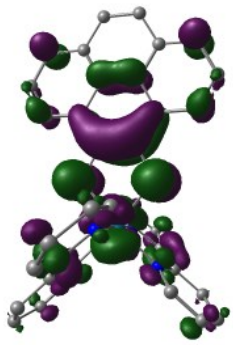
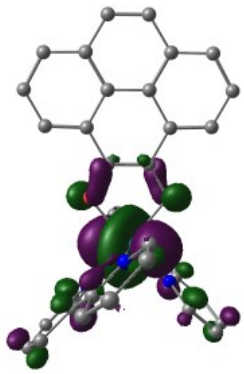
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S29 DFT calculated MO composition for $\mathbf{2}^{2-}$ in $S = 1$ state

MO	energy (eV)	% composition		
		Os	bpy	L^1
α-MO				
LUMO+5	4.736	13	86	2
LUMO+4	4.615	5	93	2
LUMO+3	4.564	5	93	1
LUMO+2	4.512	1	3	97
LUMO+1	4.331	2	96	2
LUMO	3.674	3	10	86
SOMO1	3.566	16	71	14
SOMO2	3.295	16	77	7
HOMO-2	2.664	19	28	53
HOMO-3	2.270	71	20	9
HOMO-4	1.766	52	37	11
HOMO-5	1.496	46	16	38
β-MO				
LUMO+5	4.670	6	93	1
LUMO+4	4.525	1	5	94
LUMO+3	4.449	2	93	5
LUMO+2	4.080	15	82	4
LUMO+1	3.786	12	80	8
LUMO	3.732	1	6	93
HOMO	2.830	27	24	49
HOMO-1	2.398	69	22	9
HOMO-2	2.034	55	36	10
HOMO-3	1.667	39	15	46
HOMO-4	0.221	2	14	83
HOMO-5	0.159	1	15	84

α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3

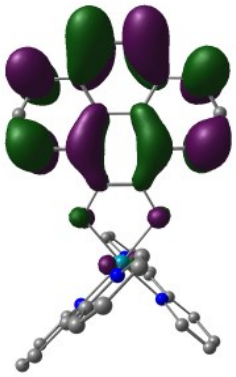
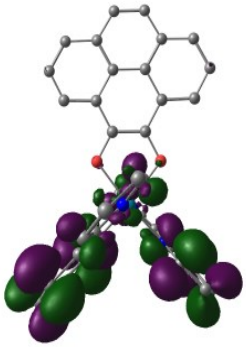
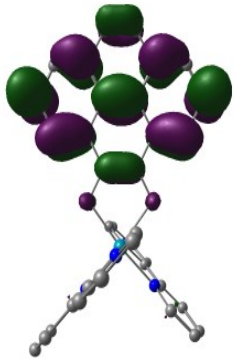
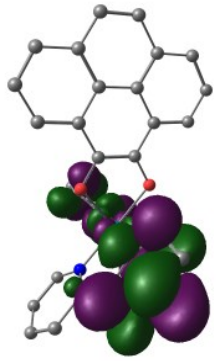
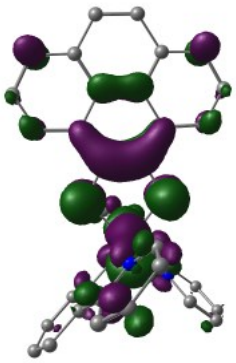
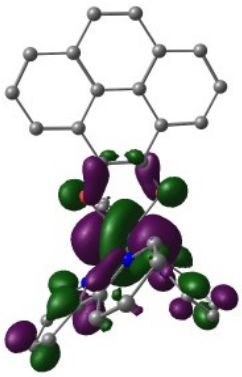
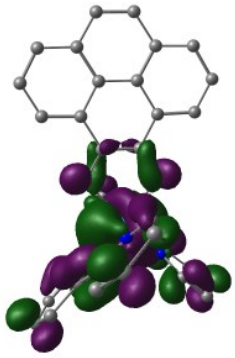
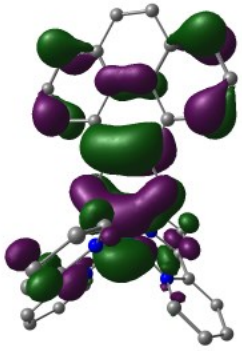
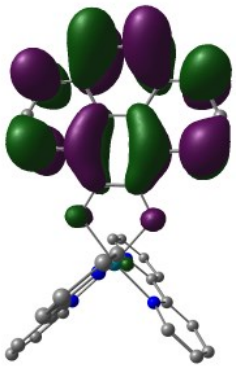
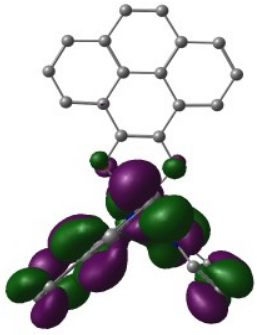
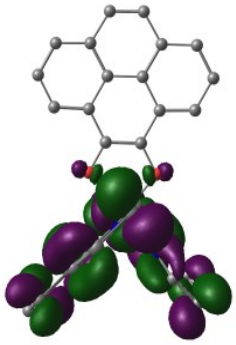
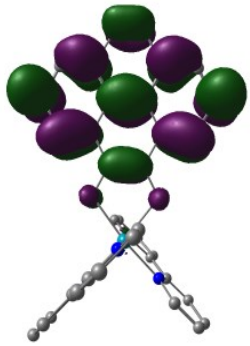
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S30 DFT calculated MO composition for $\mathbf{3}^{2+}$ in $S = 0$ state

MO	energy (eV)	% composition		
		Ru	bpy	H_2L^2
LUMO+5	-6.964	3	97	0
LUMO+4	-7.079	2	97	1
LUMO+3	-7.202	2	97	1
LUMO+2	-7.826	10	88	2
LUMO+1	-7.979	6	91	3
LUMO	-8.598	16	10	75
HOMO	-10.046	23	5	72
HOMO-1	-10.116	69	10	21
HOMO-2	-10.420	74	18	9
HOMO-3	-10.696	18	4	78
HOMO-4	-10.826	51	11	38
HOMO-5	-11.554	8	4	89

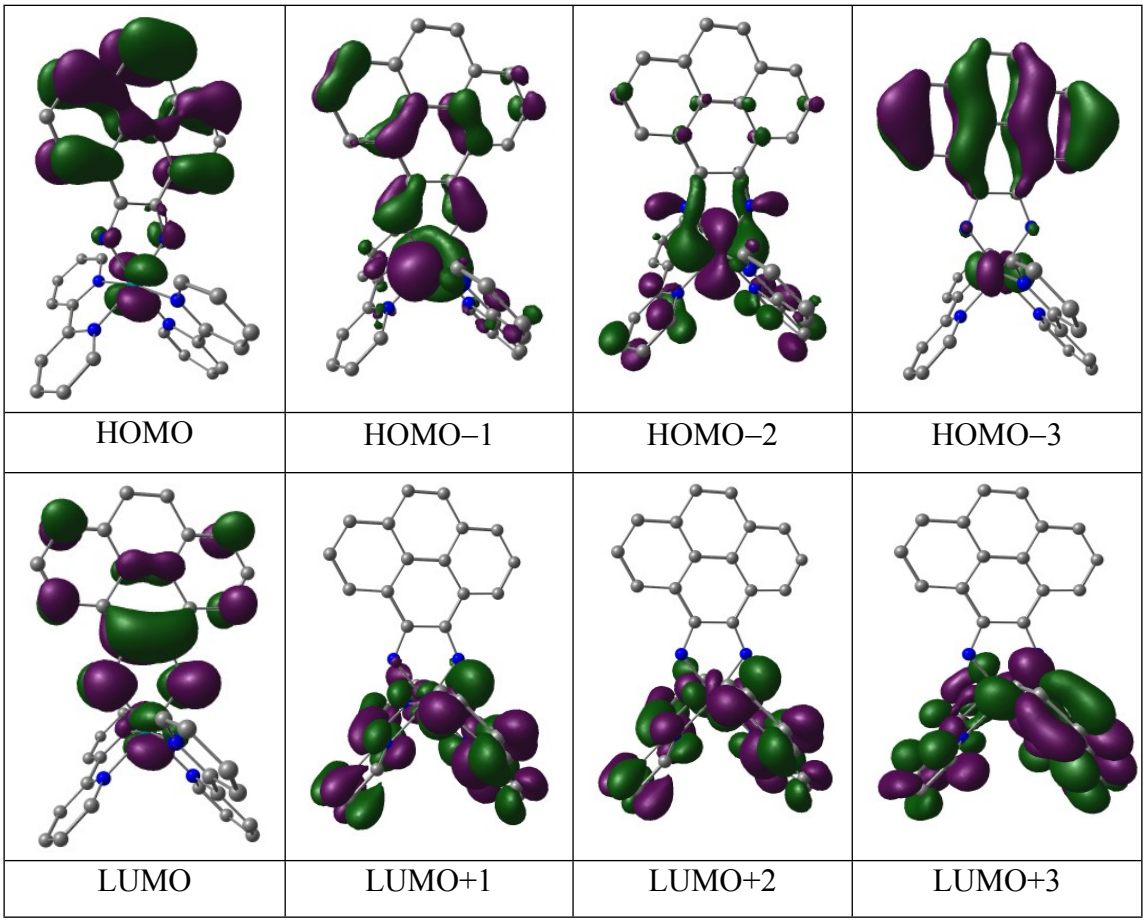
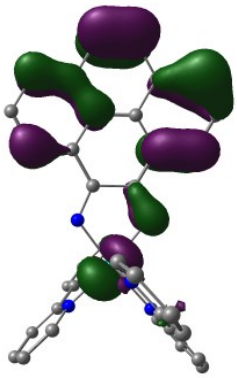
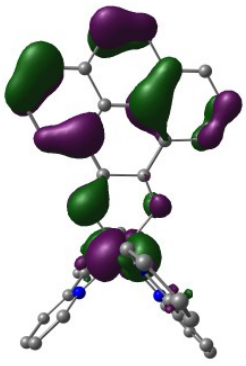
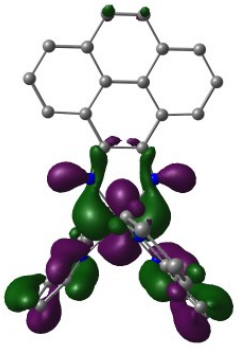
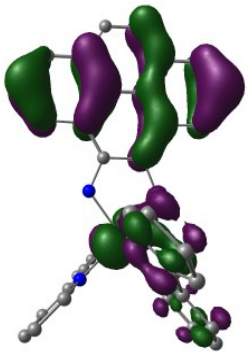


Table S31 DFT calculated MO composition for $\mathbf{3}^{3+}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Ru	bpy	H_2L^2
α-MO				
LUMO+5	-9.693	48	24	28
LUMO+4	-9.949	52	39	9
LUMO+3	-10.230	98	98	98
LUMO+2	-10.493	8	92	1
LUMO+1	-10.551	3	96	1
LUMO	-11.904	14	4	82
SOMO	-13.452	35	5	60
HOMO-1	-13.664	52	10	38
HOMO-2	-13.741	66	16	19
HOMO-3	-14.002	31	12	57
HOMO-4	-14.151	7	88	5
HOMO-5	-14.213	9	87	4
β-MO				
LUMO+5	-9.682	50	41	8
LUMO+4	-10.016	1	1	98
LUMO+3	-10.475	8	91	1
LUMO+2	-10.535	3	95	1
LUMO+1	-11.777	18	5	78
LUMO	-13.164	47	6	46
HOMO	-13.221	59	8	33
HOMO-1	-13.480	75	16	9
HOMO-2	-13.900	15	4	81
HOMO-3	-13.958	47	17	36
HOMO-4	-14.185	7	90	4
HOMO-5	-14.206	2	97	1

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

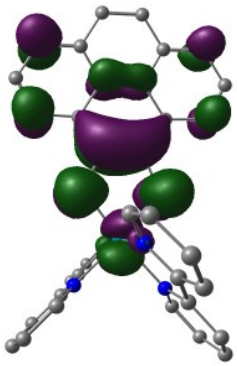
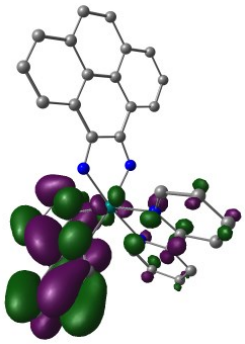
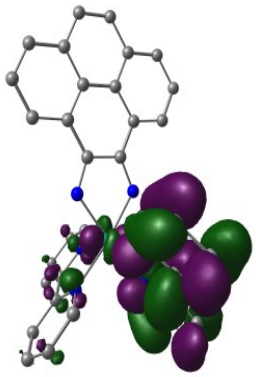
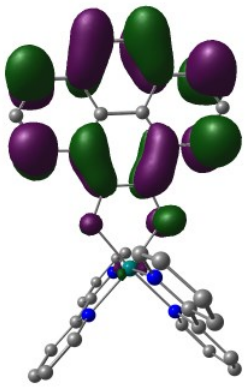
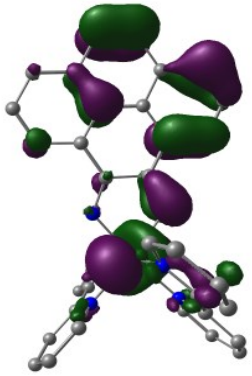
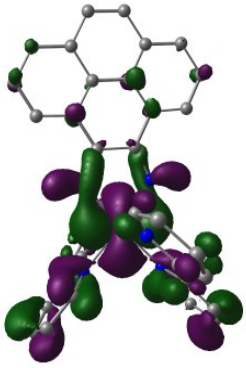
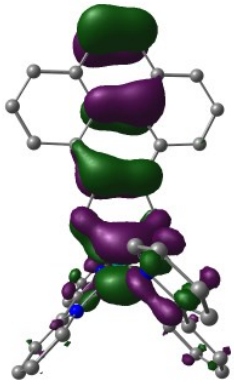
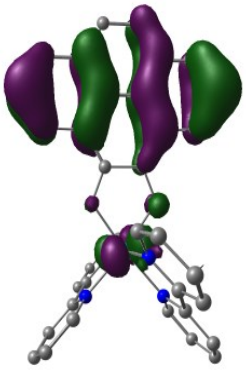
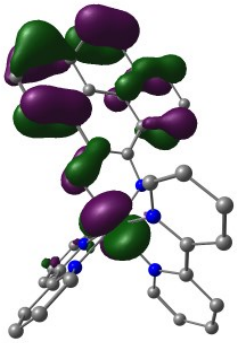
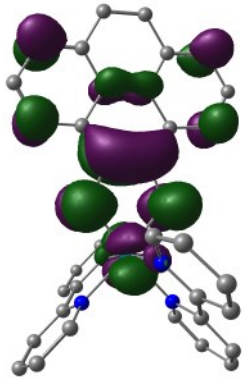
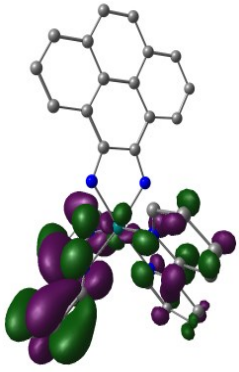
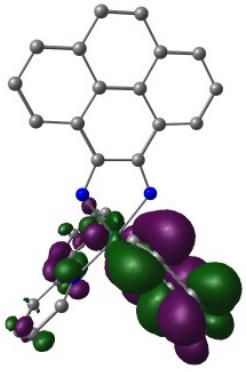
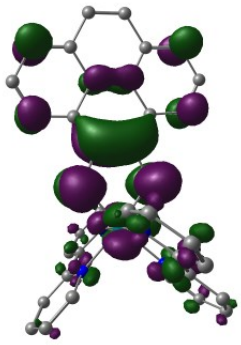
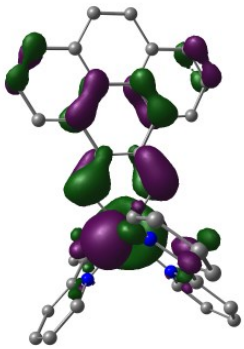
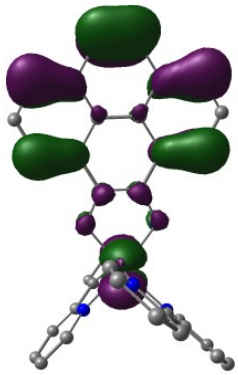
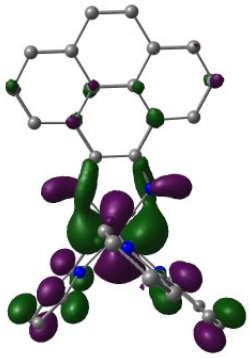
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S32 DFT calculated MO composition for $\mathbf{3}^{+}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Ru	bpy	H_2L^2
α-MO				
LUMO+5	-4.147	2	98	0
LUMO+4	-4.171	3	96	0
LUMO+3	-4.226	5	94	1
LUMO+2	-4.429	2	97	1
LUMO+1	-5.134	11	88	1
LUMO	-5.214	11	73	16
SOMO	-5.446	9	28	63
HOMO-1	-6.899	74	9	17
HOMO-2	-7.064	34	6	61
HOMO-3	-7.297	73	17	10
HOMO-4	-7.704	16	3	80
HOMO-5	-7.711	47	8	45
β-MO				
LUMO+5	-4.138	3	97	0
LUMO+4	-4.209	6	94	1
LUMO+3	-4.413	2	97	1
LUMO+2	-4.908	16	13	72
LUMO+1	-5.062	10	88	1
LUMO	-5.211	1	91	8
HOMO	-6.815	69	9	22
HOMO-1	-6.959	34	6	60
HOMO-2	-7.266	73	16	11
HOMO-3	-7.591	50	8	42
HOMO-4	-7.660	20	4	76
HOMO-5	-8.413	9	4	87

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

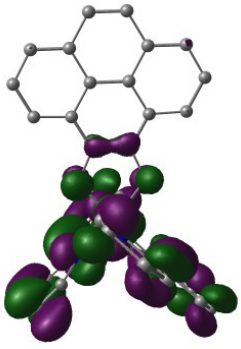
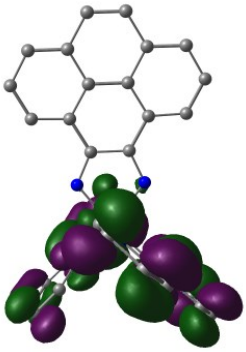
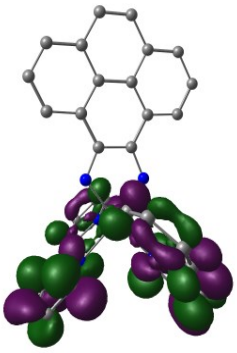
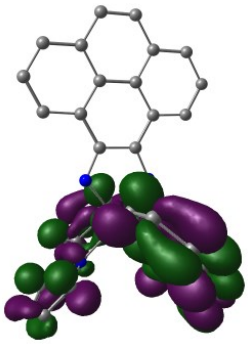
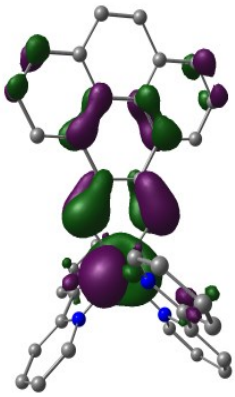
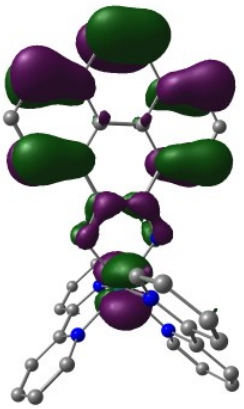
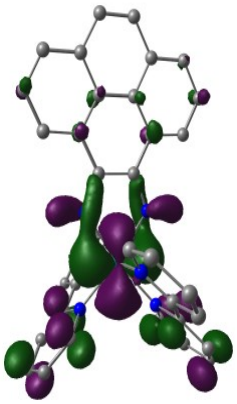
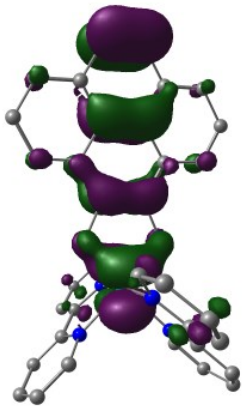
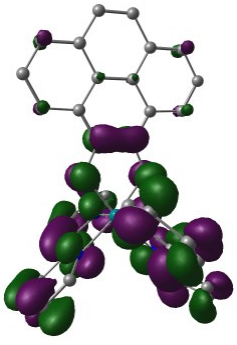
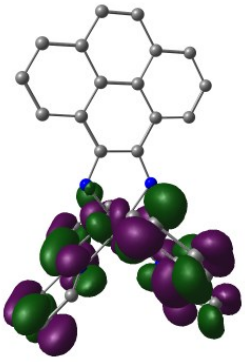
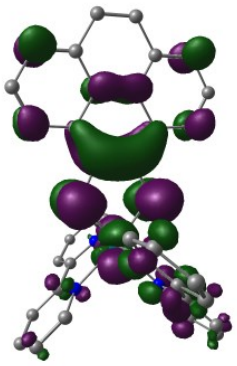
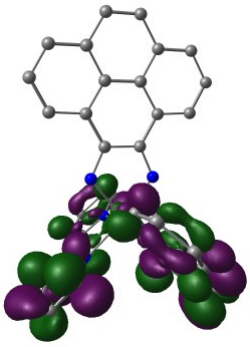
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S33 DFT calculated MO composition for **3** in $S = 0$ state

MO	energy (eV)	% composition		
		Ru	bpy	H_2L^2
LUMO+5	-1.199	2	61	36
LUMO+4	-1.227	2	55	44
LUMO+3	-1.290	6	92	2
LUMO+2	-1.496	3	96	1
LUMO+1	-2.140	13	70	17
LUMO	-2.180	12	76	12
HOMO	-2.429	5	45	50
HOMO-1	-3.828	72	10	18
HOMO-2	-4.246	51	10	39
HOMO-3	-4.282	74	18	8
HOMO-4	-4.880	28	6	66
HOMO-5	-4.966	13	4	84

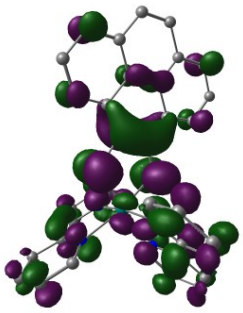
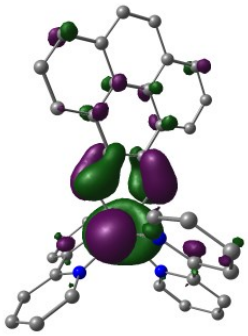
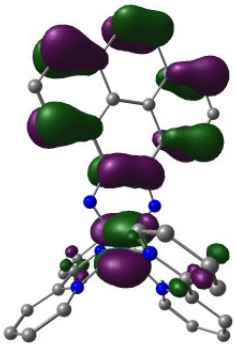
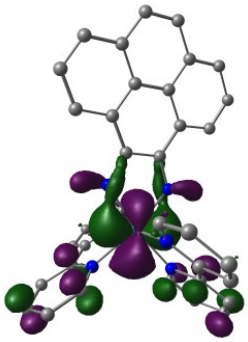
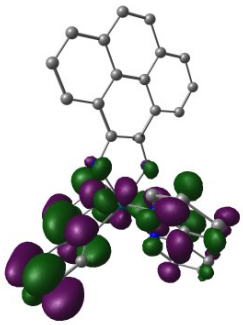
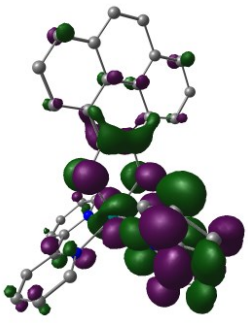
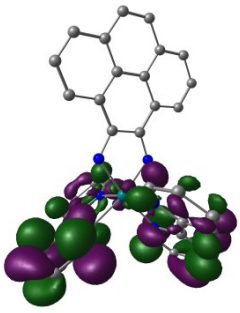
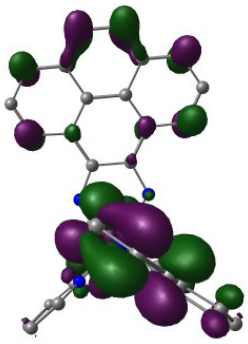
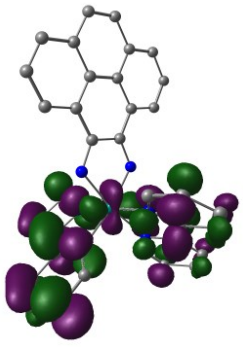
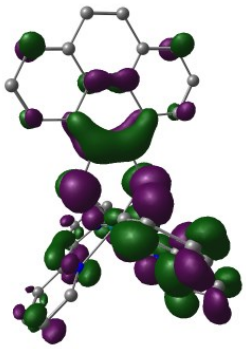
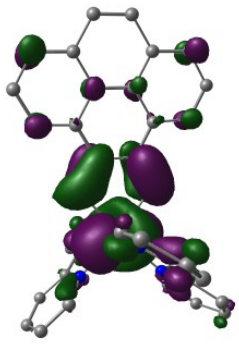
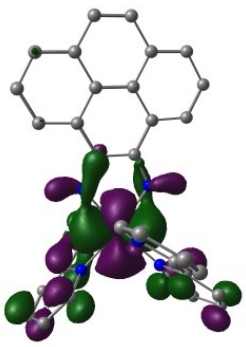
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S34 DFT calculated MO composition for $\mathbf{3}^{-}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Ru	bpy	H_2L^2
α-MO				
LUMO+5	1.824	4	95	1
LUMO+4	1.784	5	94	1
LUMO+3	1.736	6	93	1
LUMO+2	1.528	3	95	2
LUMO+1	1.170	1	1	98
LUMO	0.765	22	46	32
SOMO	0.647	12	86	2
HOMO-1	0.313	4	57	39
HOMO-2	-0.674	73	10	16
HOMO-3	-1.172	72	21	7
HOMO-4	-1.265	58	14	28
HOMO-5	-2.348	9	4	87
β-MO				
LUMO+5	1.902	3	47	50
LUMO+4	1.822	7	92	2
LUMO+3	1.605	3	95	2
LUMO+2	1.137	3	15	82
LUMO+1	1.086	8	76	16
LUMO	1.005	10	85	5
HOMO	0.264	17	15	68
HOMO-1	-0.718	75	11	14
HOMO-2	-1.080	74	20	6
HOMO-3	-1.397	58	13	29
HOMO-4	-2.404	7	5	87
HOMO-5	-2.438	7	7	86

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

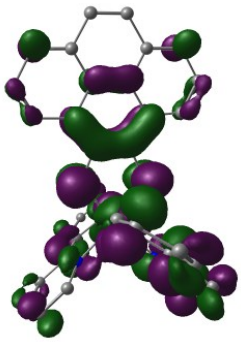
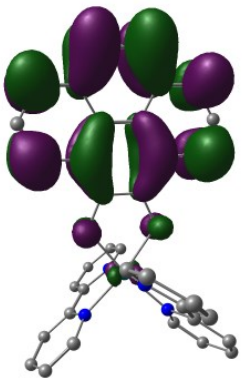
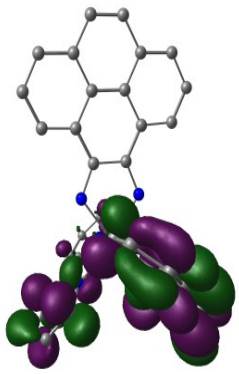
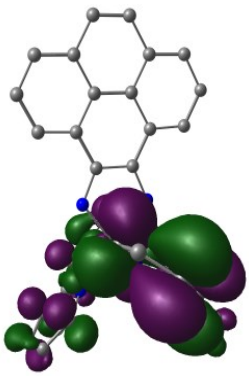
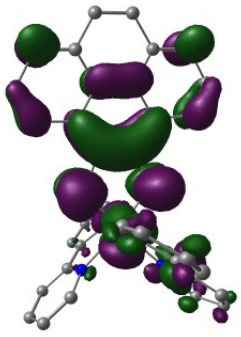
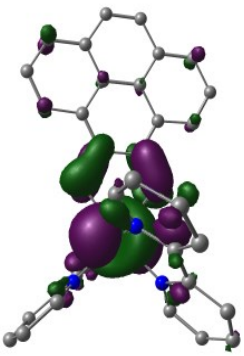
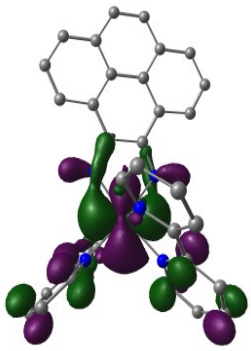
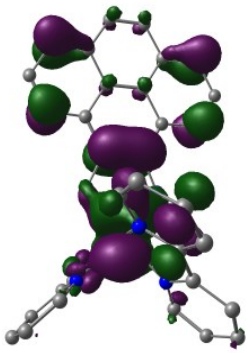
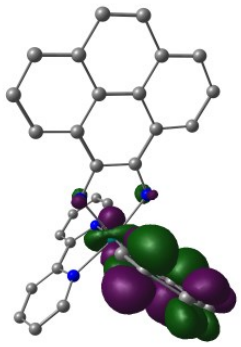
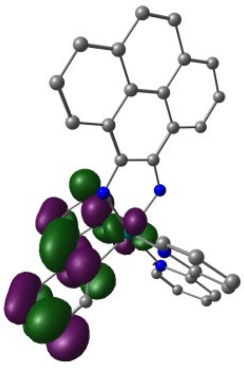
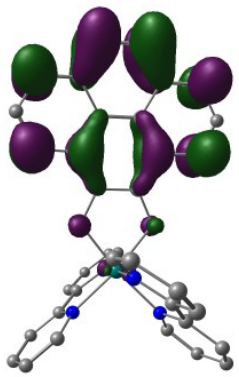
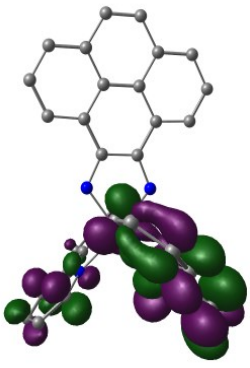
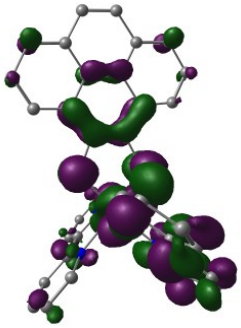
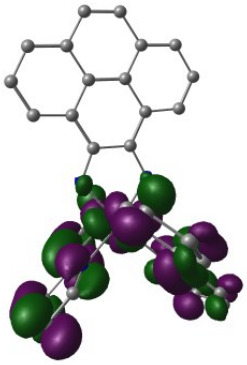
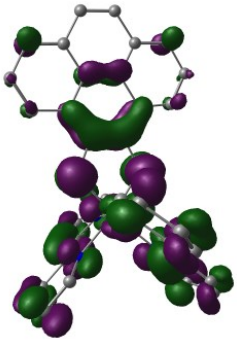
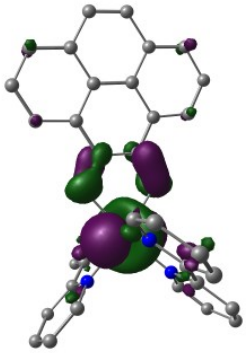
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S35 DFT calculated MO composition for $\mathbf{3}^{2-}$ in $S = 1$ state

MO	energy (eV)	% composition		
		Ru	bpy	H_2L^2
α-MO				
LUMO+5	4.757	4	95	1
LUMO+4	4.711	5	93	1
LUMO+3	4.626	8	91	1
LUMO+2	4.549	2	2	96
LUMO+1	4.432	6	92	2
LUMO	3.726	1	1	98
SOMO1	3.559	20	55	25
SOMO2	3.357	13	81	6
HOMO-2	3.093	5	52	43
HOMO-3	2.318	75	11	14
HOMO-4	1.776	72	22	6
HOMO-5	1.559	59	15	26
β-MO				
LUMO+5	4.735	8	91	1
LUMO+4	4.567	3	3	94
LUMO+3	4.533	6	91	3
LUMO+2	4.022	14	77	9
LUMO+1	3.901	12	84	4
LUMO	3.737	2	2	96
HOMO	3.325	15	26	58
HOMO-1	2.453	75	11	14
HOMO-2	2.053	73	22	6
HOMO-3	1.801	54	15	32
HOMO-4	0.495	7	16	77
HOMO-5	0.304	1	22	77

α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3

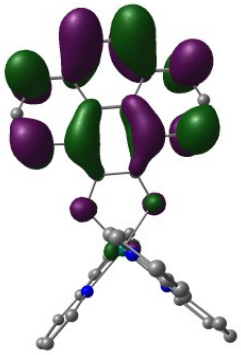
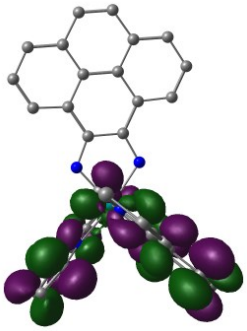
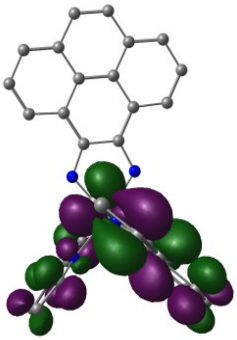
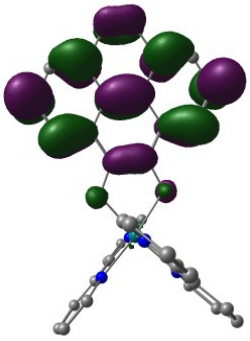
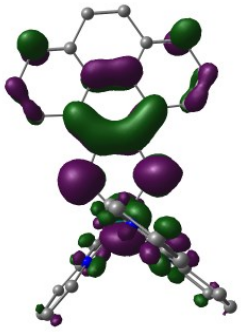
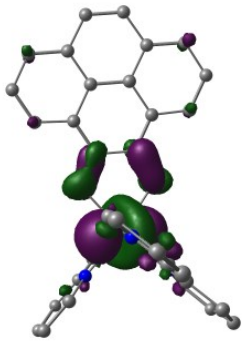
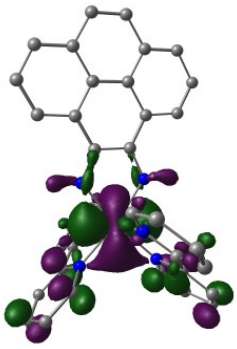
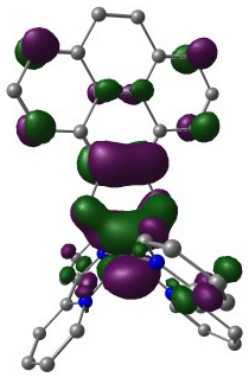
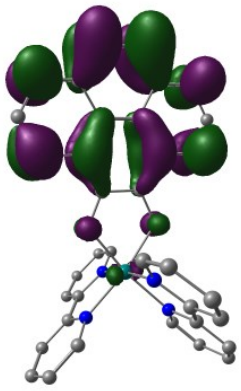
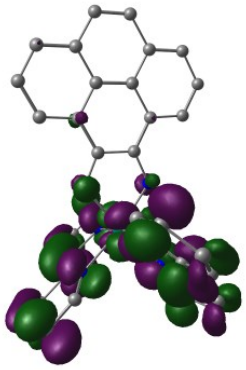
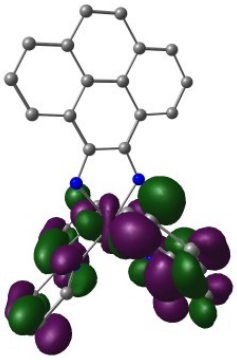
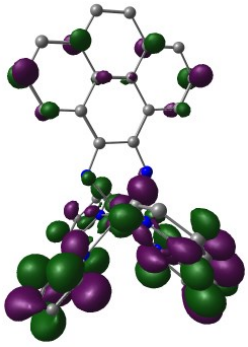
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S36 DFT calculated MO composition for $\mathbf{4}^{2+}$ in $S = 0$ state

MO	energy (eV)	% composition		
		Os	bpy	H_2L^2
LUMO+5	-7.011	3	96	1
LUMO+4	-7.164	2	97	1
LUMO+3	-7.255	3	96	1
LUMO+2	-7.830	13	85	3
LUMO+1	-8.017	11	80	9
LUMO	-8.544	15	21	64
HOMO	-9.928	21	7	72
HOMO-1	-9.965	65	13	22
HOMO-2	-10.317	67	23	11
HOMO-3	-10.581	16	5	79
HOMO-4	-10.769	42	12	46
HOMO-5	-11.494	7	4	89

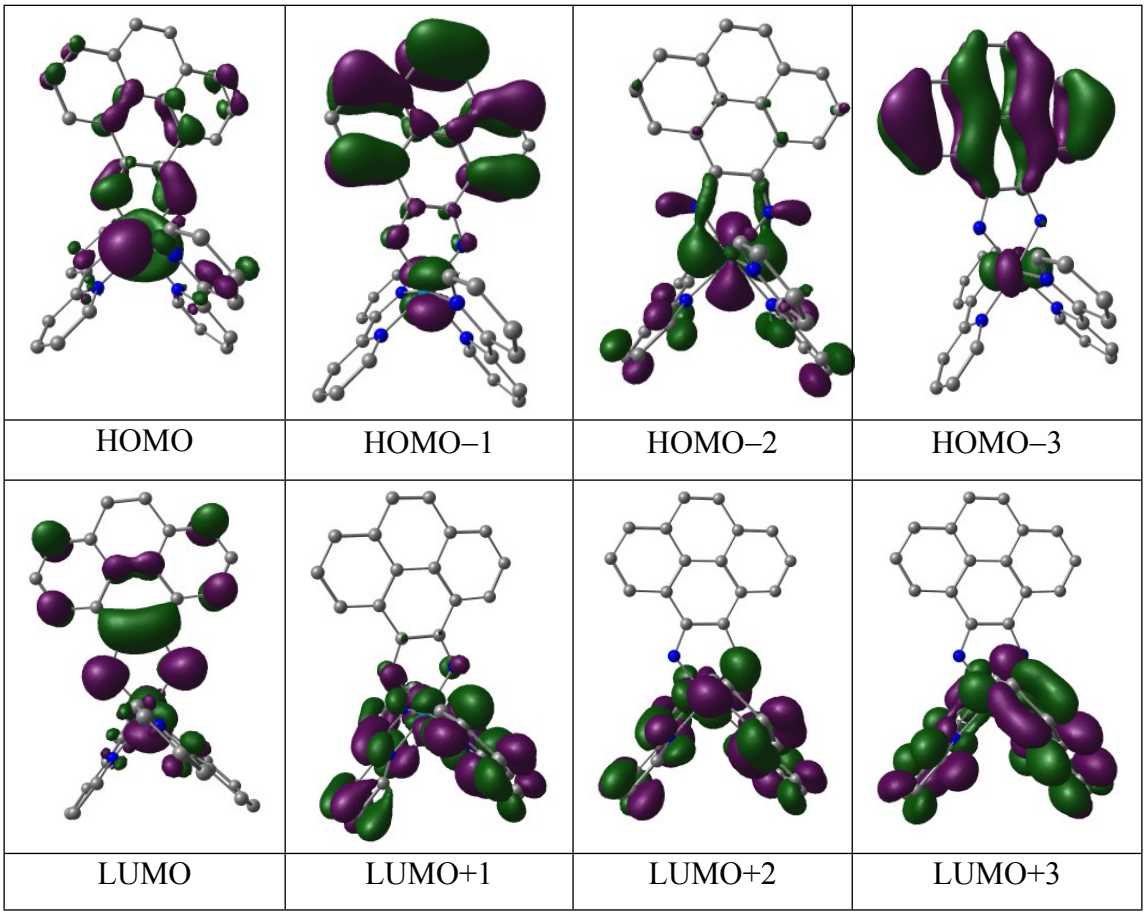
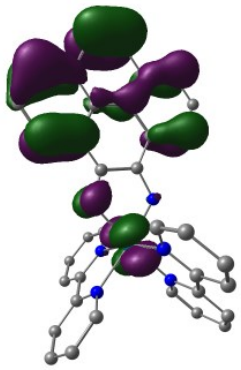
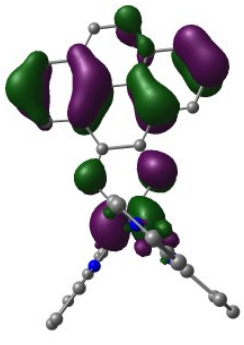
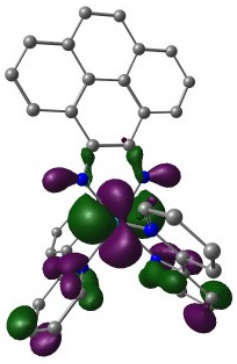
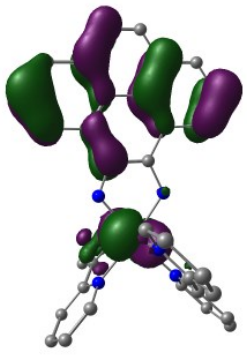


Table S37 DFT calculated MO composition for $\mathbf{4}^{3+}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Os	bpy	H_2L^2
α-MO				
LUMO+5	-9.704	2	97	1
LUMO+4	-9.823	2	97	1
LUMO+3	-10.017	1	2	97
LUMO+2	-10.637	9	89	2
LUMO+1	-10.768	5	94	2
LUMO	-11.827	17	7	76
SOMO	-13.211	22	5	73
HOMO-1	-13.536	36	9	55
HOMO-2	-13.673	68	20	12
HOMO-3	-13.912	42	11	46
HOMO-4	-14.202	42	30	28
HOMO-5	-14.351	7	89	5
β-MO				
LUMO+5	-9.804	2	95	3
LUMO+4	-9.862	1	9	90
LUMO+3	-10.613	10	88	2
LUMO+2	-10.743	5	92	2
LUMO+1	-11.694	20	8	71
LUMO	-12.947	51	9	39
HOMO	-13.033	43	8	48
HOMO-1	-13.444	68	20	12
HOMO-2	-13.735	15	4	81
HOMO-3	-13.946	45	14	41
HOMO-4	-14.338	2	96	2
HOMO-5	-14.374	1	98	1

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

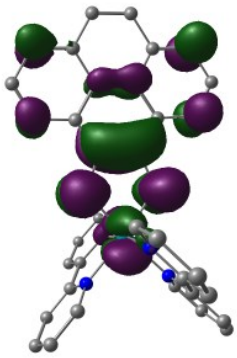
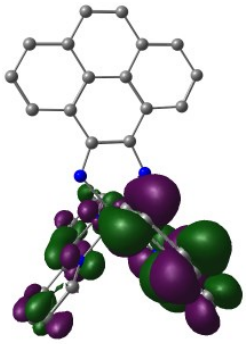
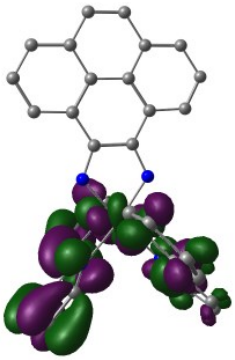
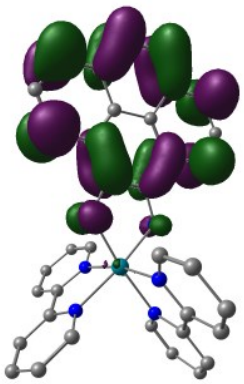
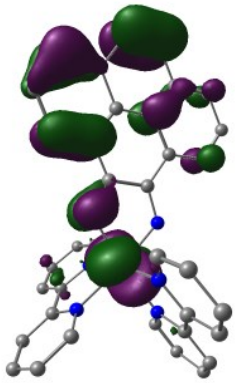
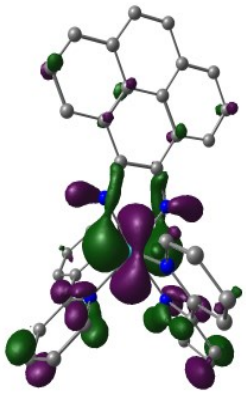
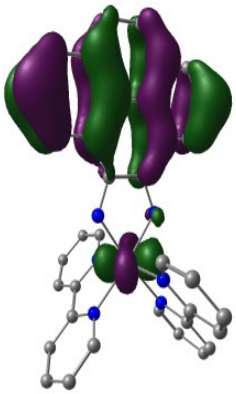
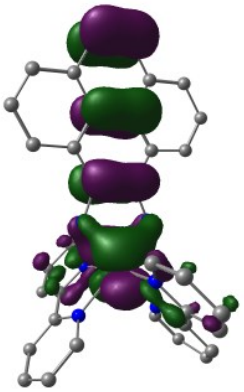
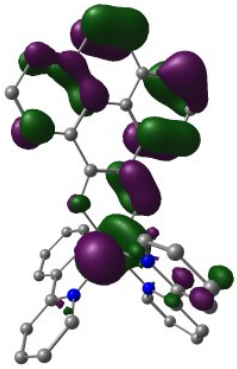
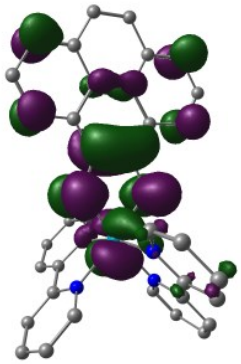
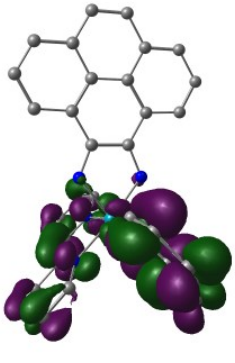
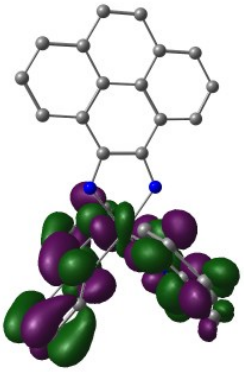
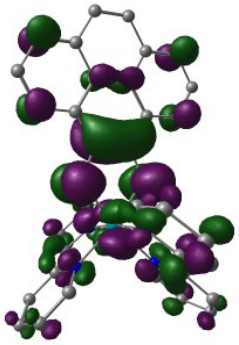
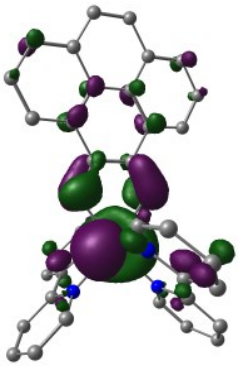
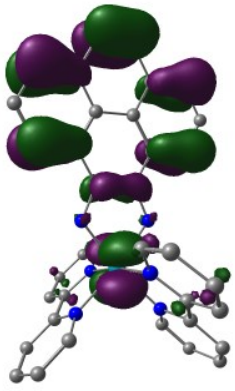
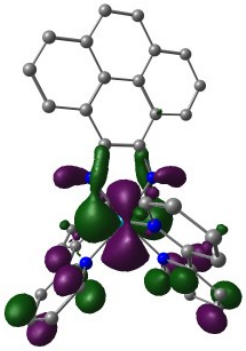
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S38 DFT calculated MO composition for $\mathbf{4}^{+}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Os	bpy	H_2L^2
α-MO				
LUMO+5	-4.153	7	92	1
LUMO+4	-4.158	3	97	1
LUMO+3	-4.189	3	94	3
LUMO+2	-4.414	2	97	1
LUMO+1	-5.067	14	84	2
LUMO	-5.194	16	64	20
SOMO	-5.538	10	38	52
HOMO-1	-6.802	70	13	17
HOMO-2	-7.070	31	8	61
HOMO-3	-7.258	66	24	10
HOMO-4	-7.786	10	3	87
HOMO-5	-7.806	37	9	55
β-MO				
LUMO+5	-4.119	5	94	1
LUMO+4	-4.139	5	93	2
LUMO+3	-4.388	3	96	1
LUMO+2	-4.967	19	32	49
LUMO+1	-4.974	13	85	2
LUMO	-5.279	2	74	24
HOMO	-6.730	67	13	20
HOMO-1	-6.969	33	8	58
HOMO-2	-7.231	67	23	10
HOMO-3	-7.687	38	9	53
HOMO-4	-7.749	12	4	84
HOMO-5	-8.546	7	5	88

α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3

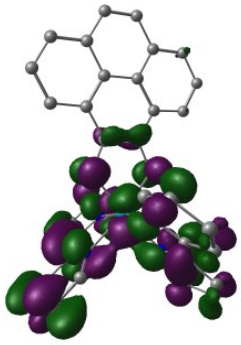
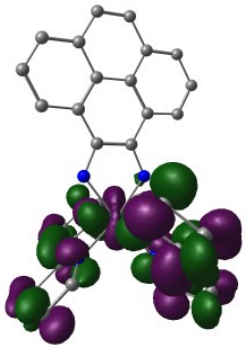
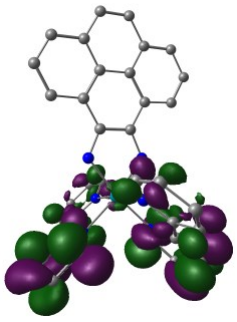
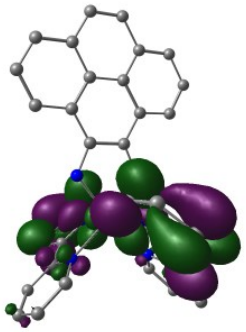
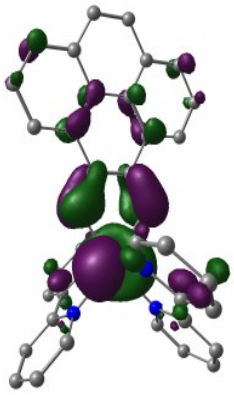
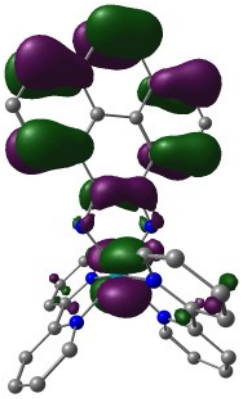
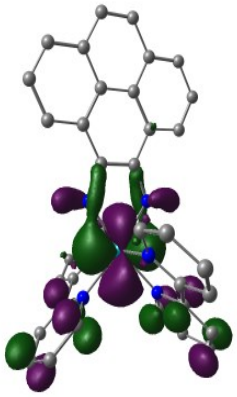
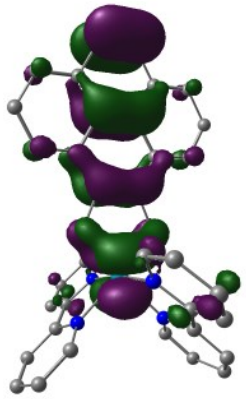
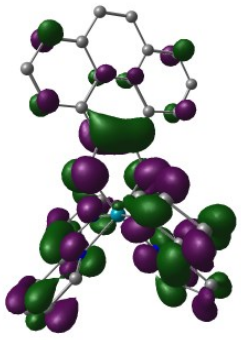
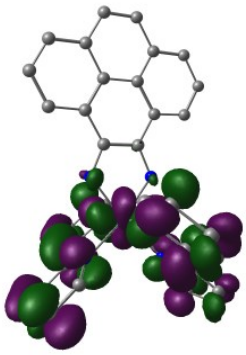
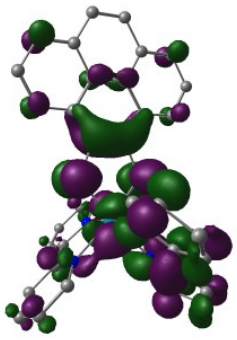
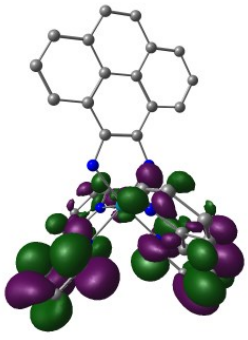
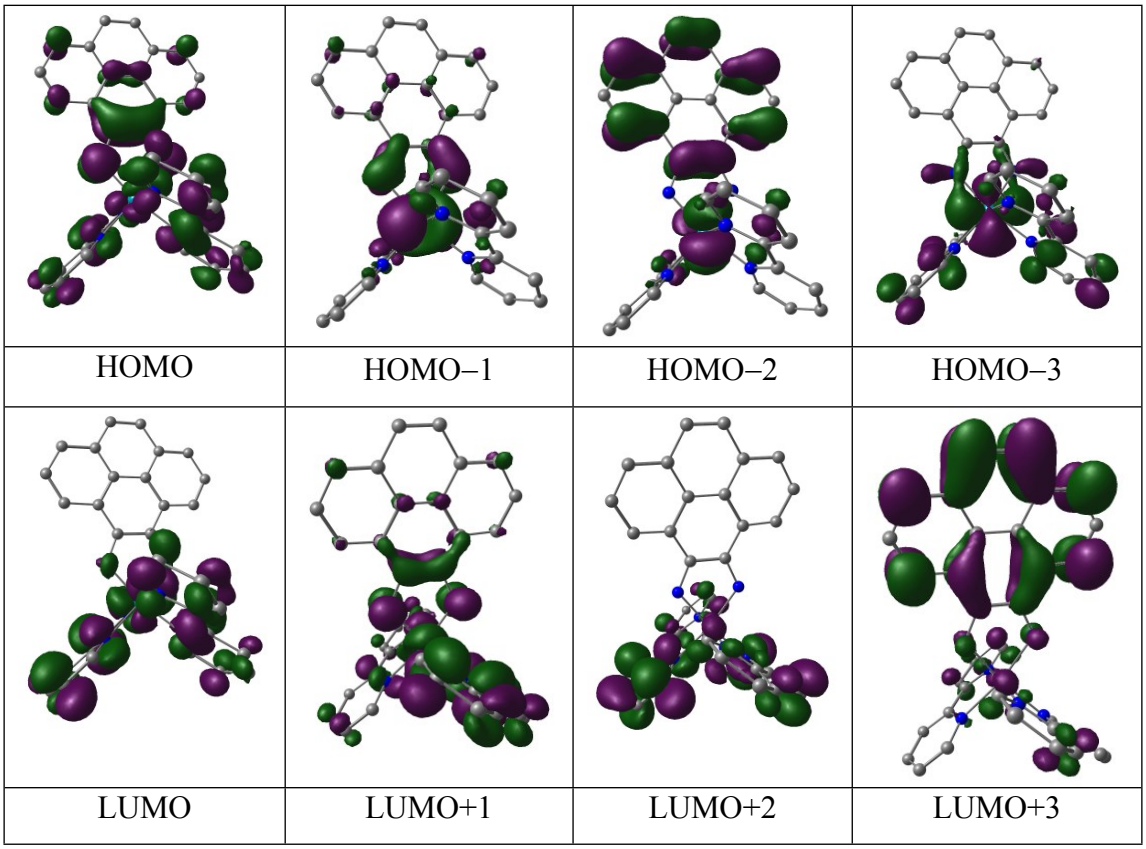
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S39 DFT calculated MO composition for **4** in $S = 0$ state

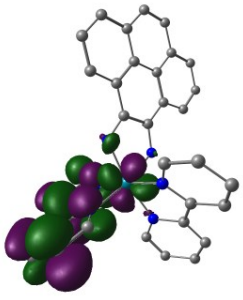
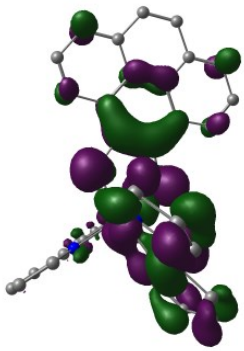
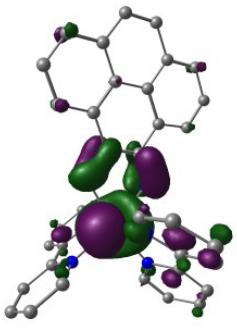
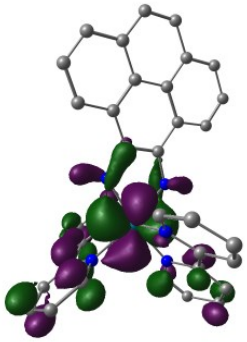
MO	energy (eV)	% composition		
		Os	bpy	H_2L^2
LUMO+5	-1.193	6	92	2
LUMO+4	-1.211	6	80	13
LUMO+3	-1.295	0	21	79
LUMO+2	-1.483	3	96	2
LUMO+1	-2.089	16	68	16
LUMO	-2.126	15	71	13
HOMO	-2.539	6	49	46
HOMO-1	-3.741	68	14	17
HOMO-2	-4.243	48	15	38
HOMO-3	-4.253	63	24	13
HOMO-4	-4.976	22	7	71
HOMO-5	-5.059	9	4	87



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

Table S40. DFT calculated MO composition for $\mathbf{4}^{-}$ in $S = 1/2$ state

MO	energy (eV)	% composition		
		Os	bpy	H_2L^2
α-MO				
LUMO+5	1.851	4	75	20
LUMO+4	1.836	8	90	2
LUMO+3	1.766	4	94	1
LUMO+2	1.528	3	95	2
LUMO+1	1.119	1	2	97
LUMO	0.856	23	51	27
SOMO	0.716	14	83	3
HOMO-1	0.221	5	56	39
HOMO-2	-0.615	69	15	17
HOMO-3	-1.189	63	29	8
HOMO-4	-1.343	46	17	37
HOMO-5	-2.447	7	4	89
β-MO				
LUMO+5	1.868	8	90	2
LUMO+4	1.851	5	84	11
LUMO+3	1.601	3	95	2
LUMO+2	1.144	10	57	33
LUMO+1	1.072	4	31	64
LUMO	1.023	14	76	10
HOMO	0.254	15	28	57
HOMO-1	-0.619	70	15	15
HOMO-2	-1.037	64	29	7
HOMO-3	-1.407	47	16	38
HOMO-4	-2.472	6	7	86
HOMO-5	-2.520	6	9	86

α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3

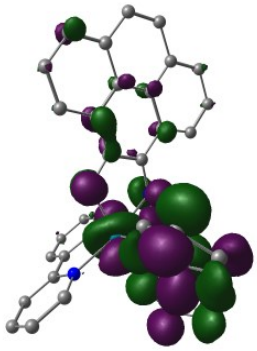
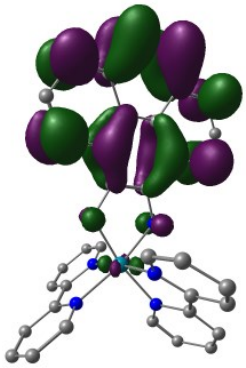
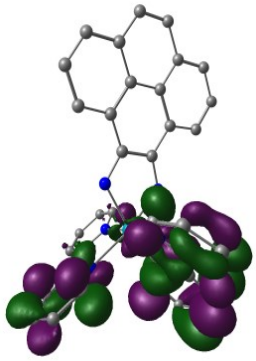
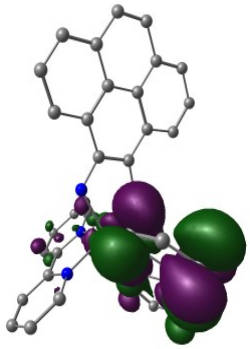
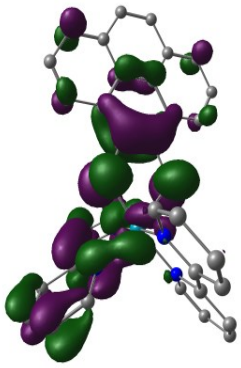
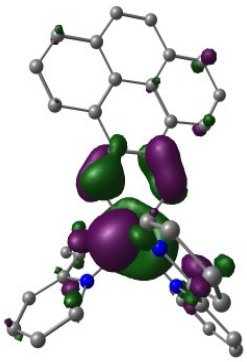
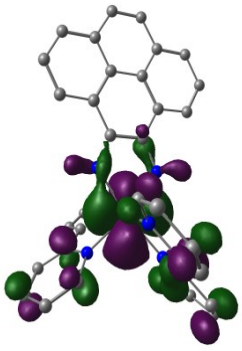
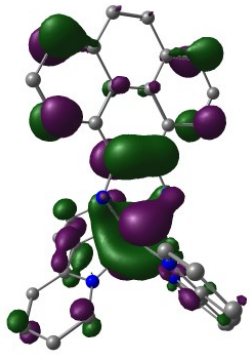
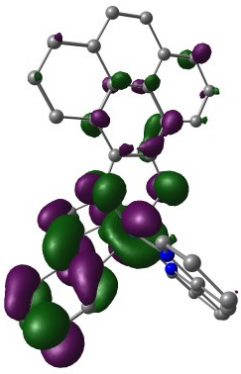
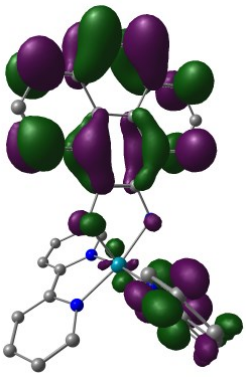
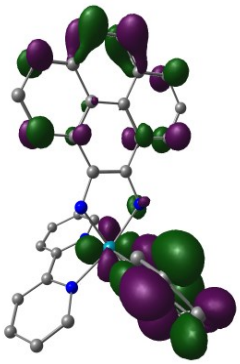
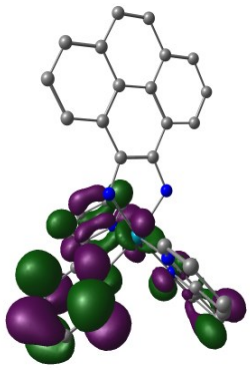
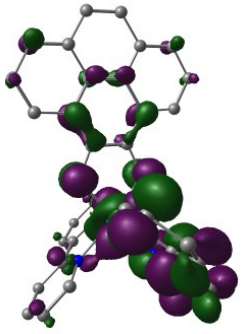
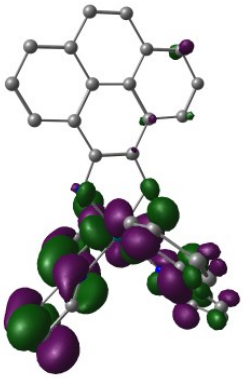
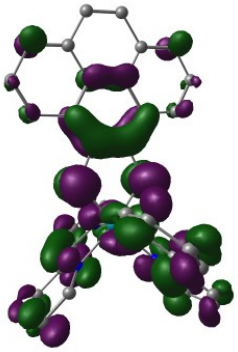
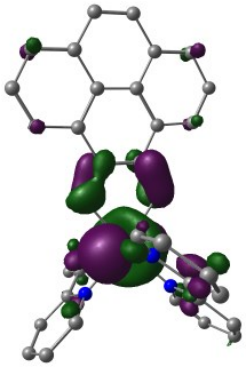
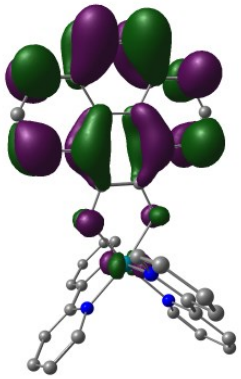
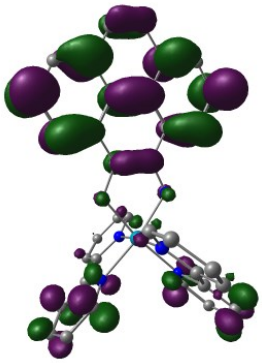
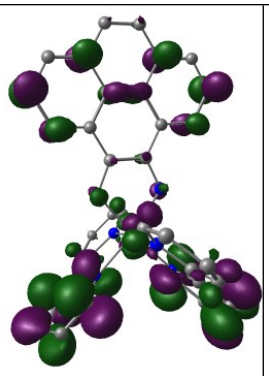
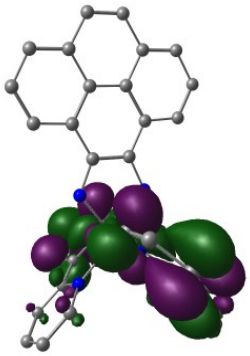
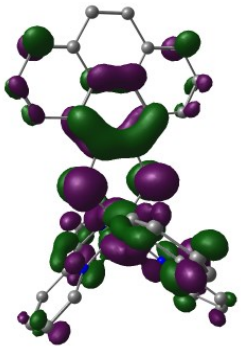
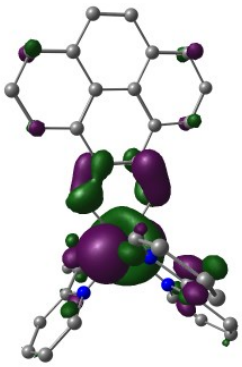
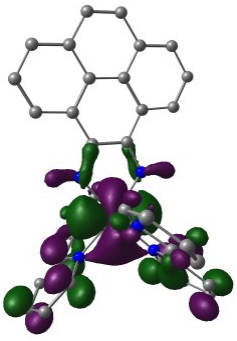
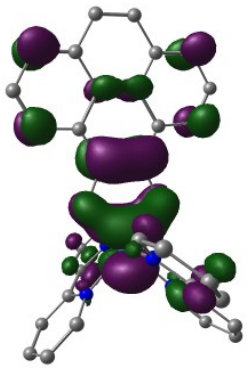
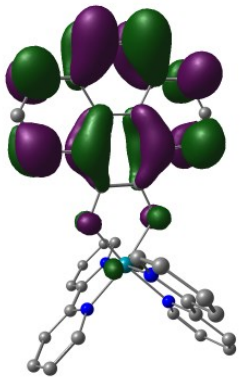
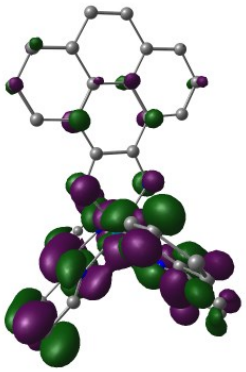
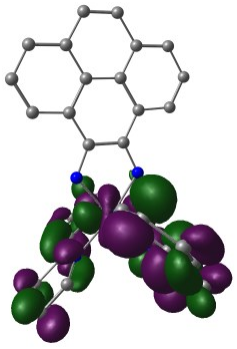
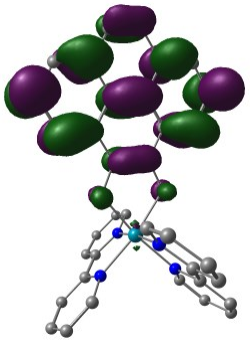
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S41 DFT calculated MO composition for $\mathbf{4}^{2-}$ in $S = 1$ state

MO	energy (eV)	% composition		
		Os	bpy	H_2L^2
α-MO				
LUMO+5	4.731	7	88	6
LUMO+4	4.722	10	83	7
LUMO+3	4.598	2	11	87
LUMO+2	4.526	4	93	2
LUMO+1	4.329	5	93	3
LUMO	3.779	6	14	80
SOMO1	3.727	15	49	35
SOMO2	3.217	16	75	9
HOMO-2	2.973	6	52	42
HOMO-3	2.288	68	15	16
HOMO-4	1.678	62	30	8
HOMO-5	1.431	47	18	35
β-MO				
LUMO+5	4.665	6	89	5
LUMO+4	4.636	1	11	87
LUMO+3	4.438	5	93	3
LUMO+2	4.065	17	65	18
LUMO+1	3.917	3	9	87
LUMO	3.744	12	78	10
HOMO	3.177	11	41	48
HOMO-1	2.417	67	16	16
HOMO-2	1.959	62	30	8
HOMO-3	1.655	43	18	39
HOMO-4	0.466	7	8	85
HOMO-5	0.343	4	15	81

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