Supporting Information

Unsymmetric (μ-oxido)/(μ-pz) and Symmetric (μ-pz)$_2$ Bridged Diosmium Frameworks (pz=pyrazolato): Electronic Structure and Magnetic Properties

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Table S1. Experimental and DFT Calculated Selected Bond Angles (deg) for [1]$^{3+}$ in 2x[1](ClO$_4$)$_3$

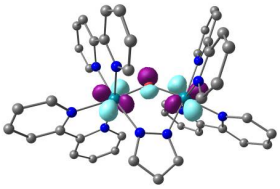
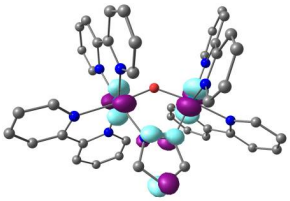
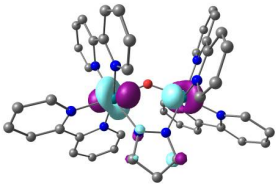
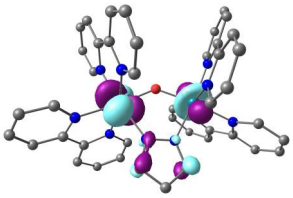
molecule A [**1**]$^{3+}$				molecule B [**1**]$^{3+}$		
bond angle	exp.	DFT		bond angle	exp.	DFT
		meso	*rac*			
N1-Os1-O1	83.68(18)	81.661	83.341	N11-Os3-O2	83.25(19)	-
N1-Os1-N3	81.7(2)	99.696	93.936	N11-Os3-N13	94.5(2)	-
N1-Os1-N4	102.17(19)	91.825	93.125	N11-Os3-N14	91.9(2)	-
N1-Os1-N5	173.2(2)	167.489	171.002	N11-Os3-N15	168.3(2)	-
N1-Os1-N6	100.5(2)	90.686	92.514	N11-Os3-N16	92.1(2)	-
N3-Os1-O1	104.65(19)	91.519	97.044	N13-Os3-O2	92.56(18)	-
N4-Os1-O1	174.13(18)	165.520	170.100	N14-Os3-O2	168.53(19)	-
N5-Os1-O1	89.54(18)	95.015	93.451	N15-Os3-O2	90.70(18)	-
N6-Os1-O1	85.72(18)	100.269	94.254	N16-Os3-O2	98.22(19)	-
N3-Os1-N4	77.0(2)	76.769	92.413	N13-Os3-N14	77.4(2)	-
N3-Os1-N5	100.4(2)	92.424	78.073	N13-Os3-N15	95.8(2)	-
N3-Os1-N6	169.59(19)	165.338	167.566	N13-Os3-N16	168.0(2)	-
N4-Os1-N5	84.61(19)	93.976	91.357	N14-Os3-N15	95.80(19)	-
N4-Os1-N6	92.63(19)	92.688	76.617	N14-Os3-N16	92.3(2)	-
N5-Os1-N6	78.6(2)	77.988	96.114	N15-Os3-N16	78.8(2)	-
N2-Os2-O1	83.56(18)	82.236	83.276	N12-Os4-O2	83.27(18)	-
N7-Os2-O1	98.30(19)	88.359	96.995	N17-Os4-O2	85.12(19)	-
N8-Os2-O1	90.94(19)	91.056	93.566	N18-Os4-O2	90.01(19)	-
N9-Os2-O1	169.72(19)	179.450	170.024	N19-Os4-O2	175.05(19)	-
N10-Os2-O1	93.38(19)	104.074	94.243	N20-Os4-O2	106.35(19)	-
N2-Os2-N7	91.4(2)	102.637	94.057	N12-Os4-N17	102.7(2)	-
N2-Os2-N8	168.7(2)	173.288	171.053	N12-Os4-N18	173.0(2)	-
N2-Os2-N9	92.57(19)	98.310	93.108	N12-Os4-N19	101.2(2)	-
N2-Os2-N10	95.4(2)	82.273	92.454	N12-Os4-N20	81.6(2)	-
N7-Os2-N8	79.5(2)	77.301	77.976	N17-Os4-N18	78.5(2)	-
N7-Os2-N9	91.3(2)	91.578	92.525	N17-Os4-N19	91.7(2)	-
N7-Os2-N10	167.1(2)	167.226	167.596	N17-Os4-N20	168.2(2)	-
N8-Os2-N9	94.4(2)	88.397	91.324	N18-Os4-N19	85.6(2)	-
N8-Os2-N10	94.7(2)	99.214	96.135	N18-Os4-N20	98.5(2)	-
N9-Os2-N10	77.5(2)	75.961	76.575	N19-Os4-N20	76.6(2)	-
Os1-O1-Os2	130.3(2)	132.26	131.191	Os3-O2-Os4	130.7(2)	-

Table S2. Experimental and DFT Calculated Selected Bond Angles (deg) for $[2]^{2+}$ in $[2](ClO_4)_2$

	$[\mathbf{2}]^{2+}$		
bond angle	exp.	DFT	
		meso	*rac*
N1-Os1-N4	96.9(3)	93.010	94.246
N1-Os1-N5	93.4(3)	91.936	94.164
N1-Os1-N6	168.2(3)	169.313	171.058
N1-Os1-N7	89.7(3)	90.132	91.068
N1-Os1-N8	91.0(3)	93.969	89.281
N4-Os1-N5	89.9(3)	93.178	94.269
N4-Os1-N6	91.2(3)	90.311	90.082
N5-Os1-N6	78.1(3)	77.702	77.691
N5-Os1-N7	98.6(3)	96.052	95.907
N5-Os1-N8	175.2(3)	171.814	172.875
N6-Os1-N7	83.7(3)	88.384	86.169
N6-Os1-N8	97.3(4)	96.638	98.423
N7-Os1-N8	79.2(3)	77.732	77.771
N7-Os1-N4	168.9(3)	169.313	168.145
N8-Os1-N4	91.8(3)	91.936	91.689
N2-Os2-N3	96.7(3)	92.315	94.174
N2-Os2-N9	93.2(3)	98.709	91.665
N2-Os2-N10	168.8(3)	174.943	168.112
N2-Os2-N11	89.7(3)	90.936	90.119
N2-Os2-N12	90.8(3)	90.896	94.277
N3-Os2-N9	92.6(3)	90.709	89.335
N3-Os2-N10	91.6(3)	90.875	91.139
N3-Os2-N11	169.6(3)	174.742	171.005
N3-Os2-N12	93.0(3)	98.891	94.075
N9-Os2-N10	78.9(4)	77.454	77.754
N9-Os2-N11	95.3(4)	98.287	98.450
N9-Os2-N12	172.7(3)	174.089	172.913
N10-Os2-N11	83.2(3)	86.173	86.154
N10-Os2-N12	96.3(3)	98.285	95.946
N11-Os2-N12	78.7(3)	77.453	77.703

Table S3. Composition and Energies of Selected Molecular Orbitals of 1^{3+} (BS (1,1) *S*=0) (*meso*, Molecule A)

MO	energy(eV)	composition			
		Os	pz	bpy	O
		α-spin			
HOMO–5	–7.457	0.01	0.00	0.99	0.00
HOMO–4	–6.461	0.74	0.02	0.23	0.00
HOMO–3	–6.278	0.71	0.14	0.14	0.01
HOMO–2	–6.193	0.71	0.09	0.20	0.01
HOMO–1	–6.035	0.58	0.27	0.15	0.01
SOMO	–5.550	0.63	0.03	0.19	0.15
LUMO	–3.932	0.47	0.00	0.32	0.21
LUMO+1	–2.920	0.06	0.00	0.93	0.00
LUMO+2	–2.704	0.16	0.00	0.81	0.03
LUMO+3	–2.637	0.08	0.01	0.92	0.00
LUMO+4	–2.478	0.09	0.01	0.90	0.01
LUMO+5	–2.005	0.03	0.01	0.95	0.00
		β-spin			
HOMO–5	–7.457	0.01	0.00	0.99	0.00
HOMO–4	–6.461	0.74	0.02	0.23	0.00
HOMO–3	–6.278	0.71	0.14	0.14	0.01
HOMO–2	–6.193	0.71	0.09	0.20	0.01
HOMO–1	–6.035	0.58	0.27	0.15	0.01
HOMO	–5.550	0.63	0.03	0.19	0.15
LUMO	–3.932	0.47	0.00	0.32	0.21
LUMO+1	–2.920	0.06	0.00	0.93	0.00
LUMO+2	–2.704	0.16	0.00	0.81	0.03
LUMO+3	–2.637	0.08	0.01	0.92	0.00
LUMO+4	–2.478	0.09	0.01	0.90	0.01
LUMO+5	–2.005	0.03	0.01	0.95	0.00

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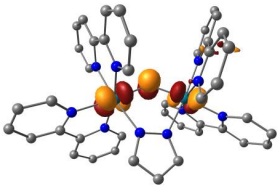
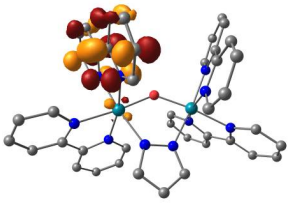
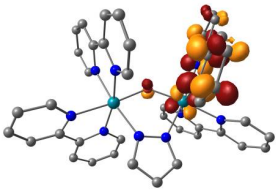
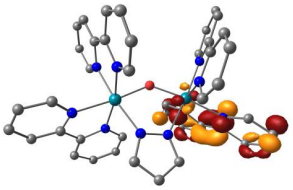
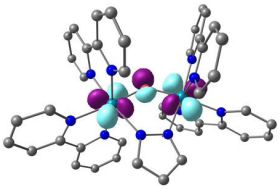
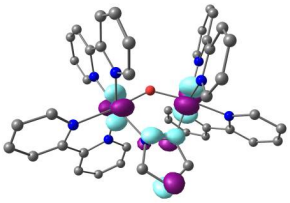
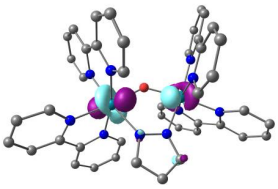
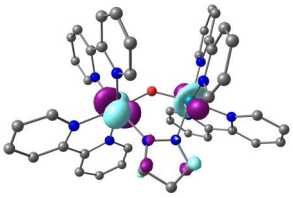
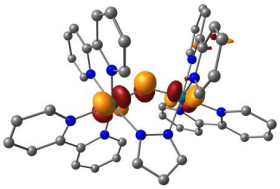
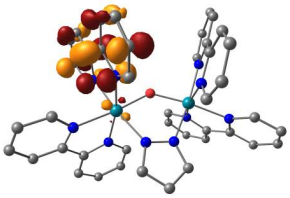
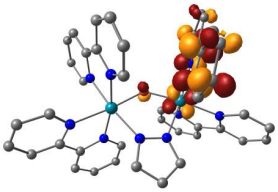
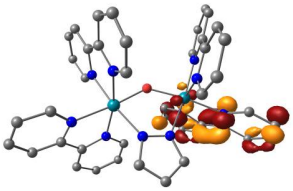
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S4. Composition and Energies of Selected Molecular Orbitals of 1^{3+} (BS (1,1) *S*=0) (*rac*, Molecule A)

MO	energy(eV)	composition			
		Os	pz	bpy	O
		α-spin			
HOMO–5	-13.936	0.08	0.19	0.73	0.00
HOMO–4	-13.073	0.70	0.11	0.18	0.01
HOMO–3	-12.925	0.74	0.02	0.22	0.02
HOMO–2	-12.529	0.63	0.15	0.22	0.01
HOMO–1	-12.451	0.57	0.27	0.16	0.01
SOMO	-12.092	0.63	0.03	0.19	0.14
LUMO	-10.456	0.42	0.01	0.38	0.19
LUMO+1	-9.574	0.08	0.00	0.91	0.01
LUMO+2	-9.348	0.10	0.01	0.89	0.01
LUMO+3	-9.292	0.17	0.00	0.79	0.04
LUMO+4	-9.066	0.09	0.01	0.90	0.00
LUMO+5	-8.073	0.04	0.00	0.95	0.00
		β-spin			
HOMO–5	-13.936	0.08	0.19	0.73	0.00
HOMO–4	-13.037	0.70	0.11	0.18	0.01
HOMO–3	-12.925	0.74	0.02	0.22	0.02
HOMO–2	-12.529	0.63	0.15	0.22	0.01
HOMO–1	-12.451	0.57	0.27	0.16	0.01
HOMO	-12.092	0.63	0.03	0.19	0.14
LUMO	-10.456	0.42	0.01	0.38	0.19
LUMO+1	-9.574	0.08	0.00	0.91	0.01
LUMO+2	-9.348	0.10	0.01	0.89	0.01
LUMO+3	-9.292	0.17	0.00	0.79	0.04
LUMO+4	-9.066	0.09	0.01	0.90	0.00
LUMO+5	-8.703	0.04	0.00	0.95	0.00

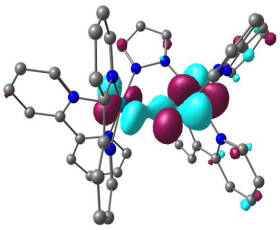
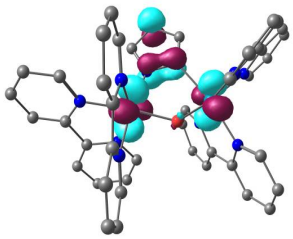
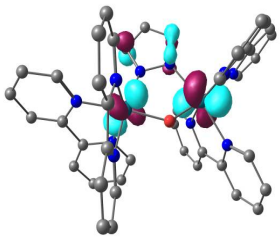
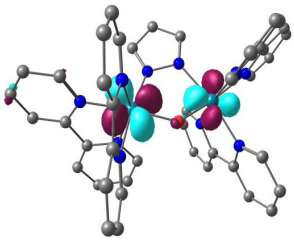
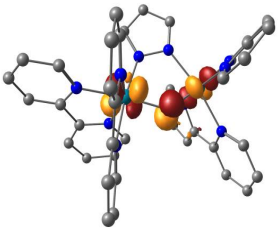
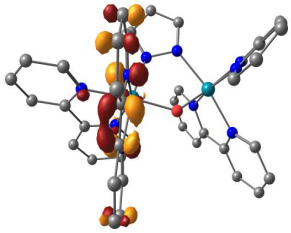
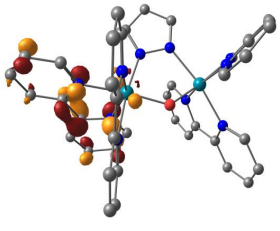
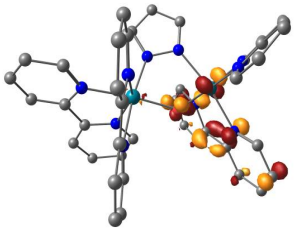
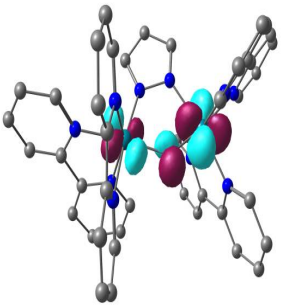
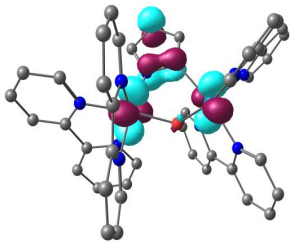
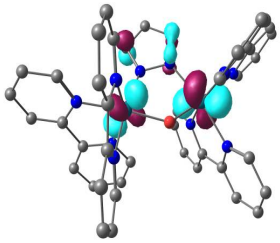
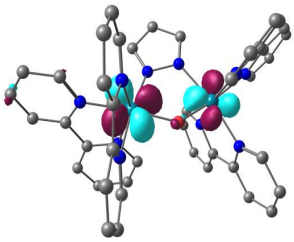
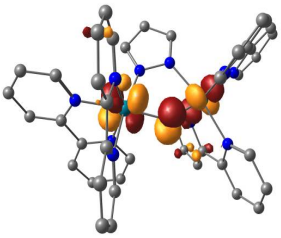
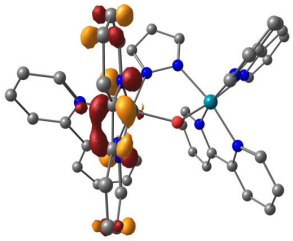
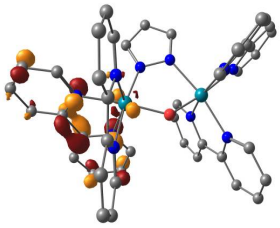
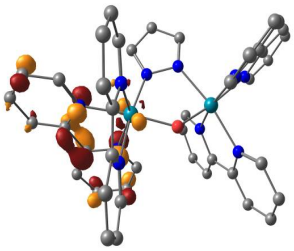
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S5. Composition and Energies of Selected Molecular Orbitals of 1^{4+} (S=1/2) (*meso*, Molecule A) ($E_{S=3/2}-E_{S=1/2}$= 1044.501712 cm^{-1})

MO	energy(eV)	composition			
		Os	pz	bpy	O
		α-spin			
HOMO–5	–16.612	0.43	0.02	0.55	0.01
HOMO–4	–16.505	0.09	0.02	0.89	0.00
HOMO–3	–16.394	0.69	0.02	0.28	0.01
HOMO–2	–16.009	0.52	0.34	0.14	0.00
HOMO–1	–15.915	0.64	0.06	0.17	0.14
SOMO	–15.827	0.45	0.40	0.13	0.02
LUMO	–13.944	0.55	0.01	0.21	0.23
LUMO+1	–12.004	0.06	0.00	0.93	0.01
LUMO+2	–11.986	0.07	0.00	0.92	0.01
LUMO+3	–11.919	0.06	0.01	0.93	0.00
LUMO+4	–11.790	0.07	0.01	0.92	0.00
LUMO+5	–11.112	0.03	0.00	0.97	0.00
		β-spin			
HOMO–5	–16.640	0.03	0.01	0.96	0.00
HOMO–4	–16.495	0.01	0.01	0.98	0.00
HOMO–3	–16.389	0.72	0.03	0.23	0.02
HOMO–2	–15.925	0.54	0.33	0.12	0.01
HOMO–1	–15.853	0.75	0.02	0.19	0.04
HOMO	–15.718	0.50	0.34	0.14	0.03
LUMO	–13.805	0.63	0.03	0.19	0.14
LUMO+1	–13.751	0.61	0.01	0.20	0.18
LUMO+2	–12.002	0.06	0.00	0.94	0.01
LUMO+3	–11.967	0.07	0.00	0.92	0.01
LUMO+4	–11.874	0.09	0.00	0.90	0.01
LUMO+5	–11.746	0.08	0.01	0.90	0.01

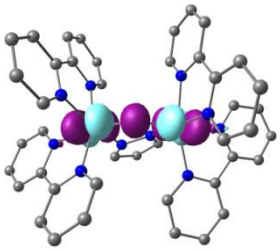
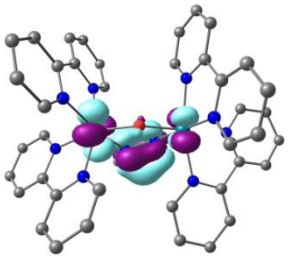
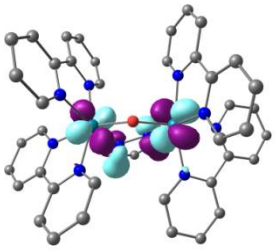
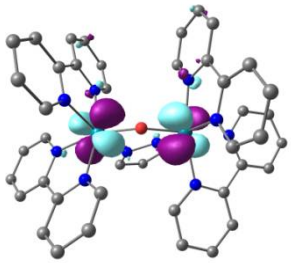
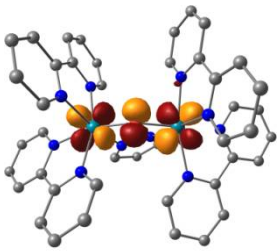
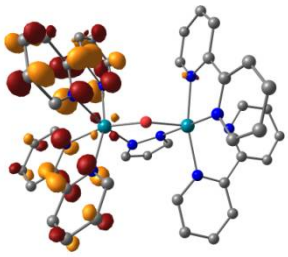
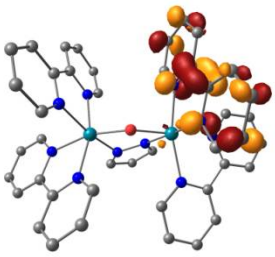
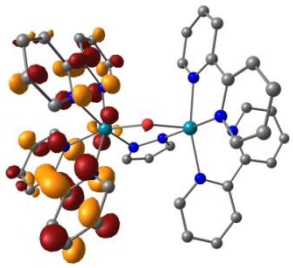
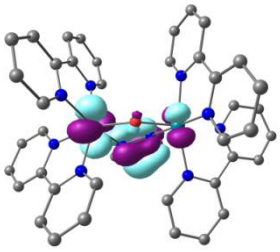
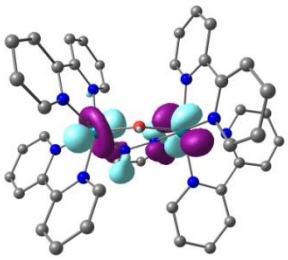
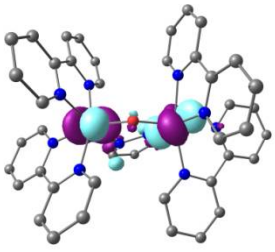
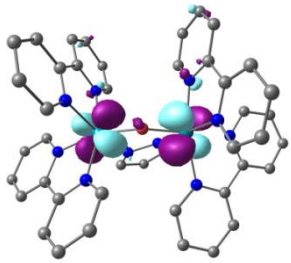
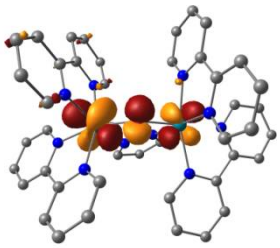
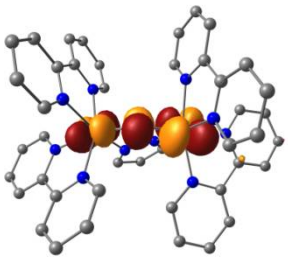
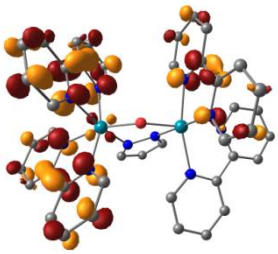
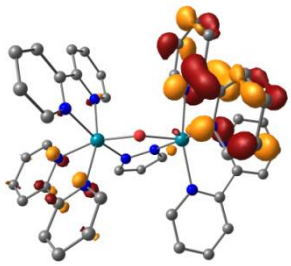
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S6. Composition and Energies of Selected Molecular Orbitals of 1^{4+} (*S*=1/2) (*rac*, Molecule A) ($E_{S=3/2}-E_{S=1/2}$= 402.8895783 cm^{-1})

MO	energy(eV)	composition			
		Os	pz	bpy	O
		α-spin			
HOMO–5	–16.617	0.07	0.00	0.93	0.00
HOMO–4	–16.598	0.21	0.00	0.78	0.00
HOMO–3	–16.525	0.59	0.06	0.33	0.02
HOMO–2	–16.083	0.61	0.14	0.18	0.08
HOMO–1	–15.835	0.59	0.19	0.17	0.05
SOMO	–15.809	0.42	0.47	0.10	0.01
LUMO	–14.029	0.56	0.01	0.22	0.22
LUMO+1	–12.041	0.06	0.00	0.93	0.01
LUMO+2	–11.993	0.08	0.00	0.90	0.01
LUMO+3	–11.919	0.06	0.01	0.93	0.00
LUMO+4	–11.896	0.07	0.00	0.93	0.00
LUMO+5	–11.116	0.04	0.01	0.95	0.00
		β-spin			
HOMO–5	–16.630	0.02	0.02	0.96	0.00
HOMO–4	–16.610	0.03	0.01	0.96	0.00
HOMO–3	–16.315	0.73	0.02	0.23	0.02
HOMO–2	–15.877	0.55	0.29	0.15	0.00
HOMO–1	–15.865	0.70	0.06	0.20	0.03
HOMO	–15.704	0.50	0.38	0.12	0.00
LUMO	–13.955	0.67	0.02	0.16	0.15
LUMO+1	–13.824	0.60	0.00	0.20	0.19
LUMO+2	–12.039	0.06	0.00	0.93	0.01
LUMO+3	–11.995	0.09	0.00	0.90	0.01
LUMO+4	–11.874	0.08	0.01	0.91	0.00
LUMO+5	–11.873	0.08	0.01	0.91	0.00

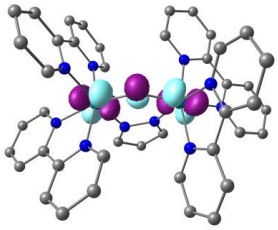
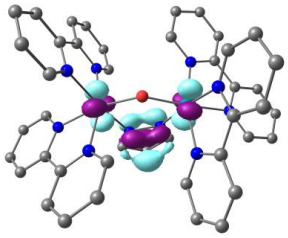
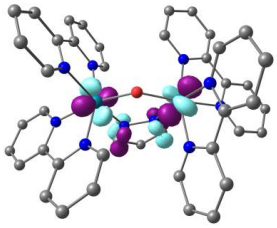
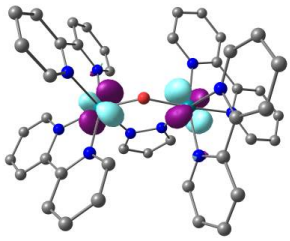
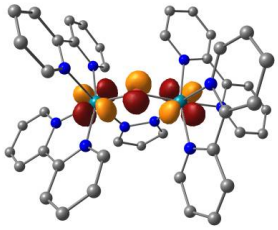
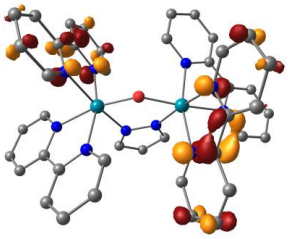
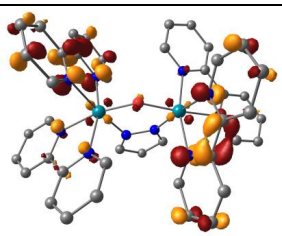
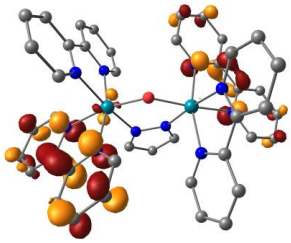
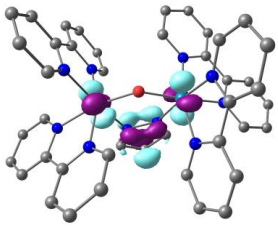
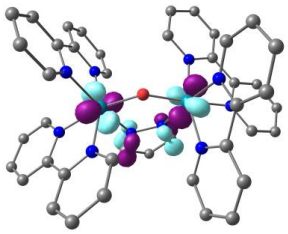
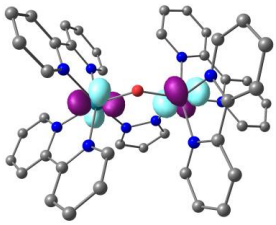
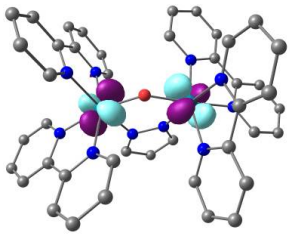
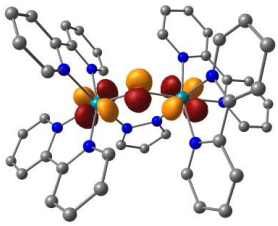
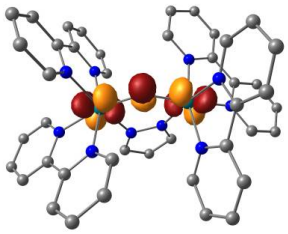
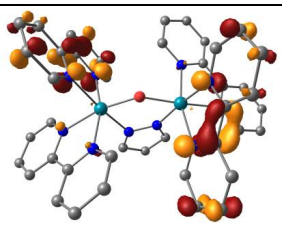
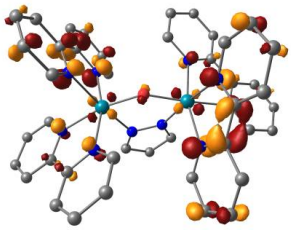
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7. Composition and Energies of Selected Molecular Orbitals of 1^{5+} (*S*=0) (*meso*, Molecule A) ($E_{S=2}-E_{S=0}$= 2486.954822 cm^{-1})

MO	energy(eV)	composition			
		Os	pz	bpy	O
HOMO–5	–19.638	0.35	0.04	0.61	0.00
HOMO–4	–19.549	0.14	0.09	0.76	0.00
HOMO–3	–19.454	0.33	0.10	0.58	0.00
HOMO–2	–19.420	0.39	0.12	0.48	0.01
HOMO–1	–19.387	0.23	0.01	0.75	0.01
HOMO	–19.175	0.41	0.44	0.12	0.03
LUMO	–18.071	0.64	0.06	0.18	0.13
LUMO+1	–17.558	0.57	0.02	0.22	0.20
LUMO+2	–15.128	0.07	0.00	0.92	0.01
LUMO+3	–15.110	0.07	0.00	0.93	0.01
LUMO+4	–14.786	0.06	0.01	0.93	0.00
LUMO+5	–14.568	0.07	0.01	0.91	0.00

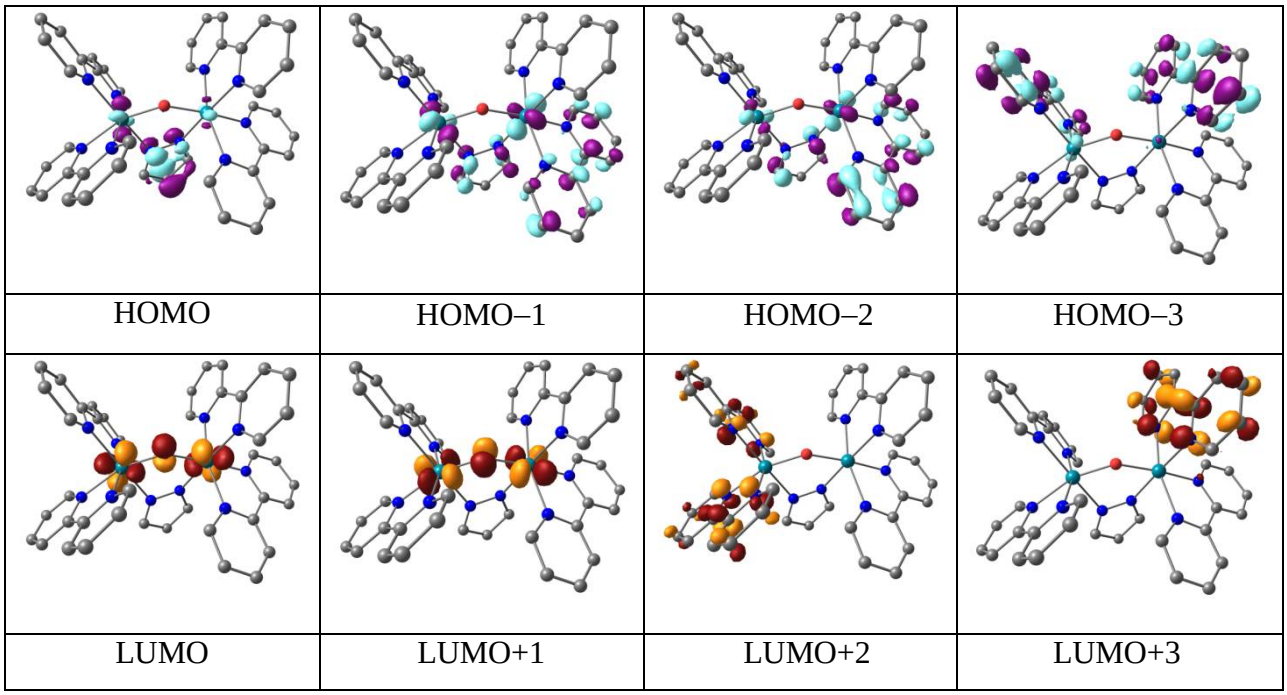


Table S8. Composition and Energies of Selected Molecular Orbitals of 1^{5+} (*S*=0) (*rac*, Molecule A) ($E_{S=2}$–$E_{S=0}$= 1857.786901 cm^{-1})

MO	energy(eV)	composition			
		Os	pz	bpy	O
HOMO–5	–19.358	0.06	0.00	0.94	0.00
HOMO–4	–19.321	0.05	0.01	0.94	0.00
HOMO–3	–19.233	0.10	0.10	0.80	0.00
HOMO–2	–19.223	0.07	0.04	0.89	0.00
HOMO–1	–19.096	0.41	0.27	0.31	0.00
HOMO	–18.915	0.34	0.55	0.09	0.02
LUMO	–17.563	0.64	0.03	0.16	0.18
LUMO+1	–17.309	0.58	0.02	0.20	0.20
LUMO+2	–14.693	0.06	0.00	0.93	0.01
LUMO+3	–14.667	0.07	0.00	0.92	0.01
LUMO+4	–14.570	0.07	0.01	0.91	0.00
LUMO+5	–14.562	0.06	0.01	0.93	0.00

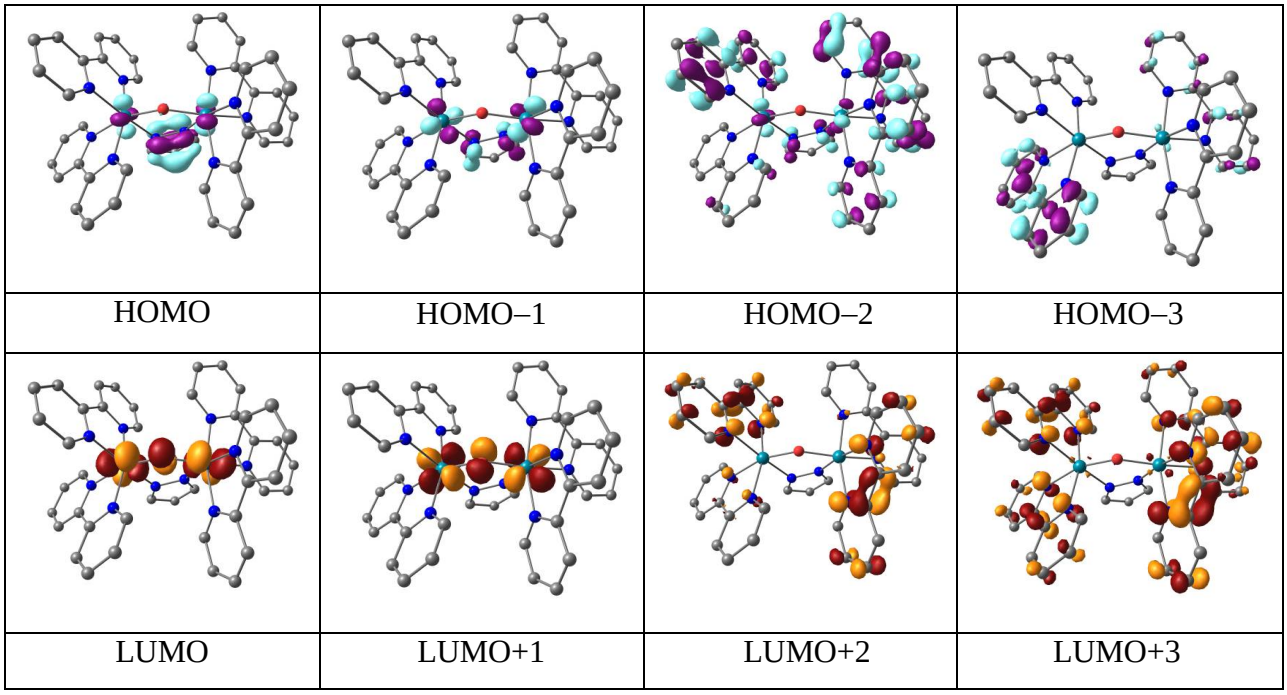


Table S9. Composition and Energies of Selected Molecular Orbitals of 1^{2+} (*S*=1/2) (*meso*, Molecule A)

MO	energy(eV)	composition			
		Os	pz	bpy	O
		α-spin			
HOMO–5	–10.119	0.79	0.00	0.20	0.01
HOMO–4	–9.833	0.78	0.02	0.19	0.01
HOMO–3	–9.708	0.66	0.21	0.13	0.00
HOMO–2	–9.541	0.63	0.20	0.16	0.01
HOMO–1	–8.872	0.62	0.01	0.19	0.18
SOMO	–8.710	0.51	0.02	0.28	0.19
LUMO	–6.641	0.06	0.00	0.93	0.00
LUMO+1	–6.564	0.08	0.01	0.90	0.01
LUMO+2	–6.456	0.10	0.00	0.89	0.00
LUMO+3	–6.361	0.14	0.01	0.83	0.02
LUMO+4	–5.784	0.05	0.01	0.95	0.00
LUMO+5	–5.727	0.04	0.00	0.95	0.00
		β-spin			
HOMO–5	–11.099	0.20	0.65	0.12	0.03
HOMO–4	–9.754	0.74	0.03	0.22	0.00
HOMO–3	–9.607	0.70	0.17	0.13	0.00
HOMO–2	–9.458	0.65	0.19	0.16	0.01
HOMO–1	–9.309	0.78	0.02	0.19	0.01
HOMO	–8.603	0.55	0.02	0.25	0.18
LUMO	–6.892	0.17	0.00	0.71	0.12
LUMO+1	–6.598	0.07	0.00	0.92	0.01
LUMO+2	–6.475	0.13	0.01	0.85	0.02
LUMO+3	–6.402	0.13	0.01	0.85	0.02
LUMO+4	–6.128	0.22	0.00	0.67	0.10
LUMO+5	–5.751	0.05	0.01	0.94	0.00

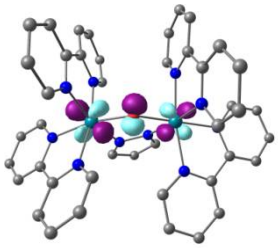
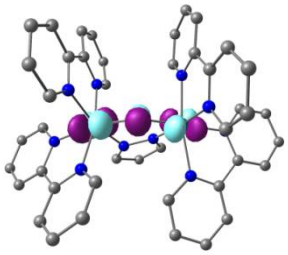
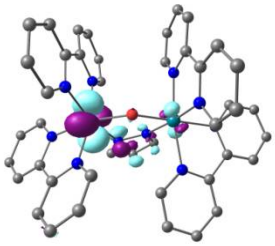
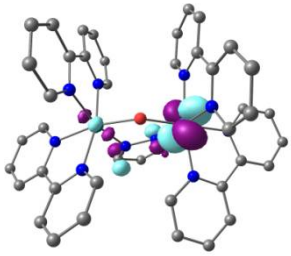
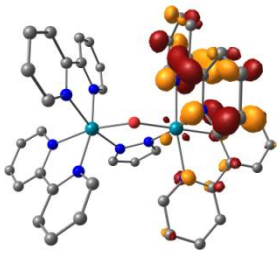
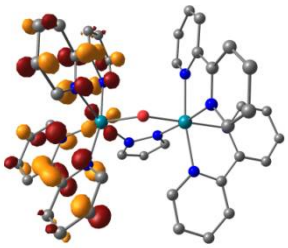
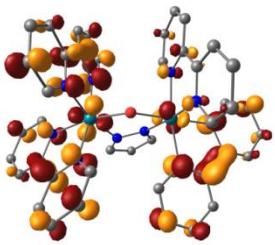
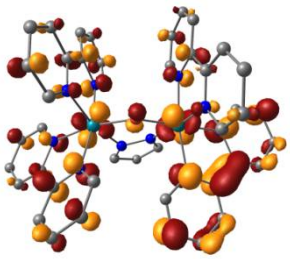
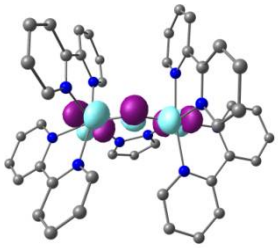
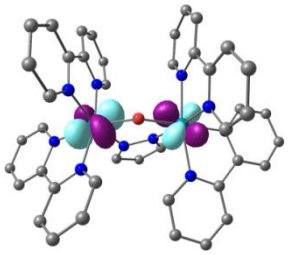
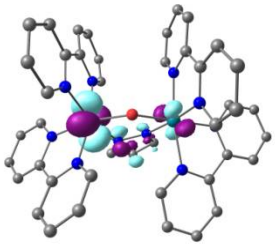
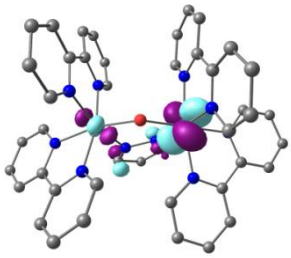
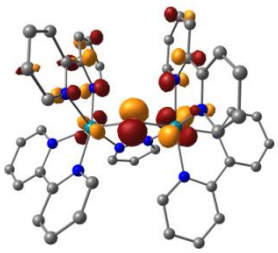
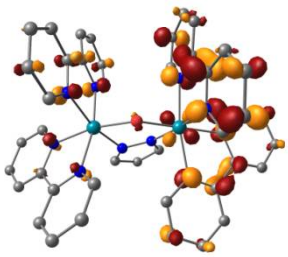
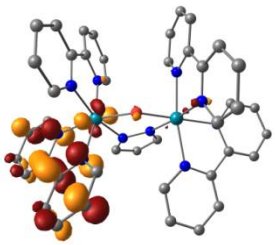
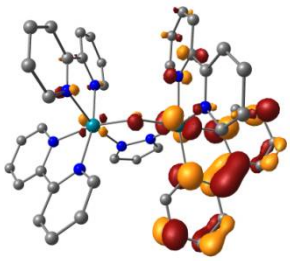
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10. Composition and Energies of Selected Molecular Orbitals of 1^{2+} (*S*=1/2) (*rac*, Molecule A)

MO	energy(eV)	composition			
		Os	pz	bpy	O
		α-spin			
HOMO–5	–10.217	0.79	0.00	0.20	0.00
HOMO–4	–9.993	0.79	0.02	0.19	0.00
HOMO–3	–9.746	0.64	0.20	0.16	0.00
HOMO–2	–9.600	0.64	0.22	0.13	0.00
HOMO–1	–8.605	0.51	0.00	0.29	0.20
SOMO	–8.527	0.54	0.02	0.24	0.19
LUMO	–6.644	0.07	0.00	0.93	0.00
LUMO+1	–6.588	0.09	0.01	0.89	0.01
LUMO+2	–6.431	0.13	0.00	0.86	0.01
LUMO+3	–6.391	0.14	0.01	0.83	0.03
LUMO+4	–5.778	0.07	0.01	0.92	0.01
LUMO+5	–5.720	0.04	0.00	0.96	0.00
		β-spin			
HOMO–5	–11.179	0.20	0.64	0.15	0.01
HOMO–4	–9.847	0.78	0.02	0.20	0.00
HOMO–3	–9.722	0.68	0.16	0.16	0.00
HOMO–2	–9.510	0.65	0.21	0.13	0.00
HOMO–1	–9.435	0.76	0.04	0.19	0.00
HOMO	–8.325	0.50	0.02	0.28	0.19
LUMO	–6.954	0.15	0.00	0.75	0.10
LUMO+1	–6.597	0.07	0.00	0.93	0.00
LUMO+2	–6.502	0.11	0.01	0.88	0.01
LUMO+3	–6.331	0.16	0.00	0.80	0.03
LUMO+4	–6.123	0.21	0.00	0.69	0.09
LUMO+5	–5.681	0.04	0.00	0.96	0.00

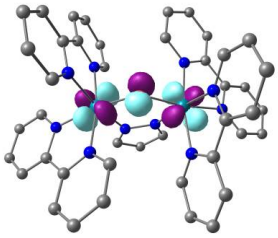
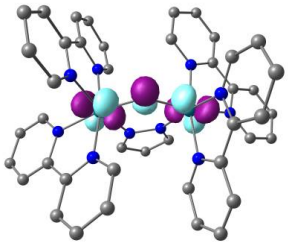
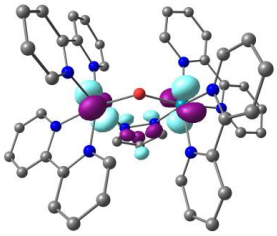
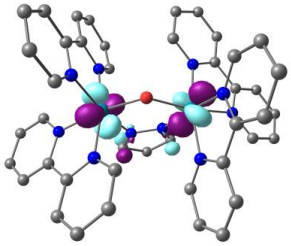
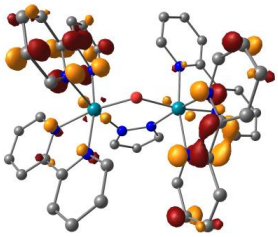
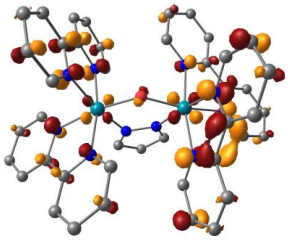
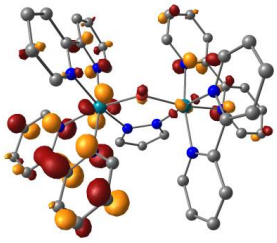
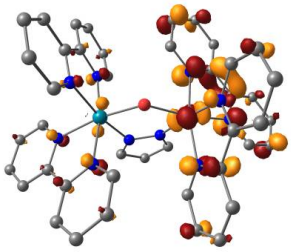
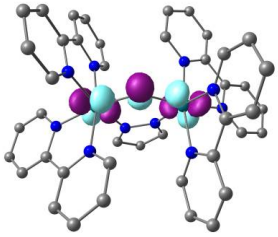
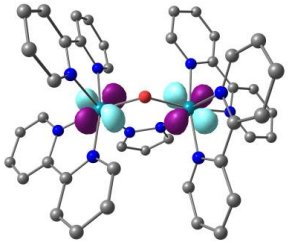
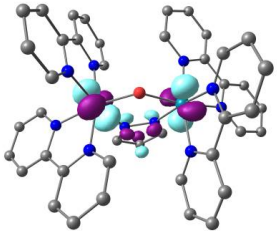
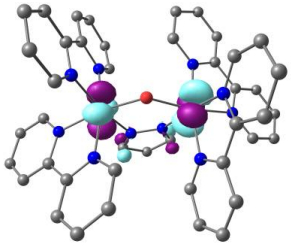
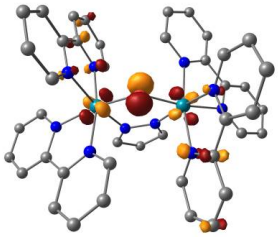
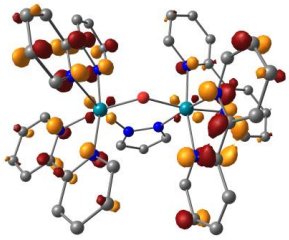
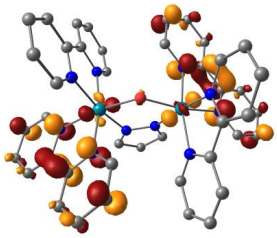
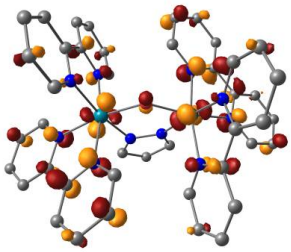
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11. Composition and Energies of Selected Molecular Orbitals of 1^+ (*S*=0) (*meso*, Molecule A) ($E_{S=1}-E_{S=0}$= 4276.046164 cm^{-1})

MO	energy(eV)	composition			
		Os	pz	bpy	O
HOMO–5	–7.021	0.71	0.06	0.24	0.00
HOMO–4	–6.803	0.68	0.11	0.21	0.00
HOMO–3	–6.758	0.71	0.10	0.18	0.01
HOMO–2	–6.747	0.73	0.09	0.18	0.01
HOMO–1	–5.923	0.51	0.02	0.29	0.18
HOMO	–5.274	0.37	0.00	0.40	0.23
LUMO	–4.010	0.10	0.01	0.89	0.00
LUMO+1	–3.935	0.11	0.01	0.86	0.02
LUMO+2	–3.737	0.12	0.00	0.88	0.00
LUMO+3	–3.566	0.18	0.00	0.76	0.06
LUMO+4	–3.190	0.05	0.01	0.94	0.00
LUMO+5	–3.116	0.04	0.01	0.95	0.00

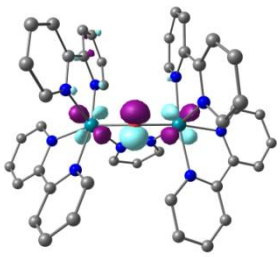
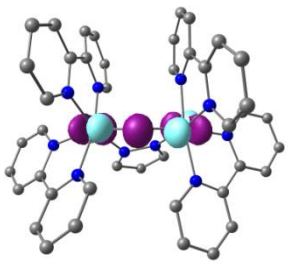
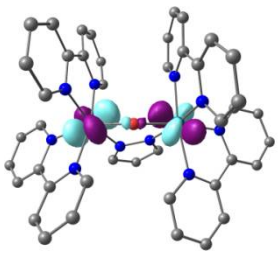
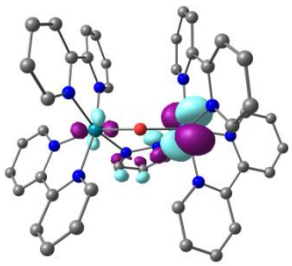
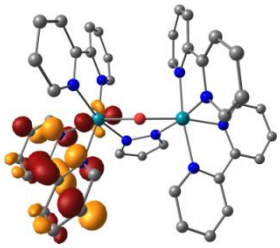
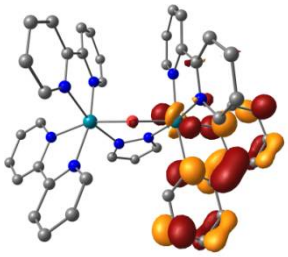
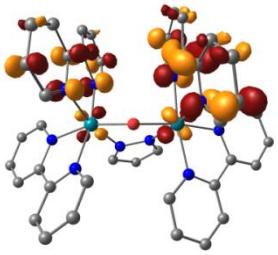
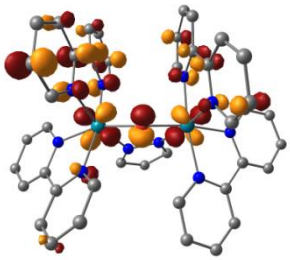
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12. Composition and Energies of Selected Molecular Orbitals of 1^+ (S=0) (*rac*, Molecule A) ($E_{S=1}$–$E_{S=0}$= 4251.377215 cm^{-1})

MO	energy(eV)	composition			
		Os	pz	bpy	O
HOMO–5	–7.003	0.72	0.08	0.20	0.00
HOMO–4	–6.911	0.69	0.05	0.24	0.01
HOMO–3	–6.822	0.69	0.09	0.22	0.00
HOMO–2	–6.700	0.72	0.13	0.15	0.00
HOMO–1	–5.963	0.52	0.02	0.27	0.18
HOMO	–5.372	0.36	0.00	0.42	0.22
LUMO	–3.976	0.10	0.01	0.89	0.00
LUMO+1	–3.943	0.12	0.01	0.87	0.01
LUMO+2	–3.763	0.14	0.00	0.84	0.02
LUMO+3	–3.647	0.18	0.00	0.77	0.05
LUMO+4	–3.145	0.06	0.01	0.93	0.00
LUMO+5	–3.112	0.03	0.01	0.96	0.00

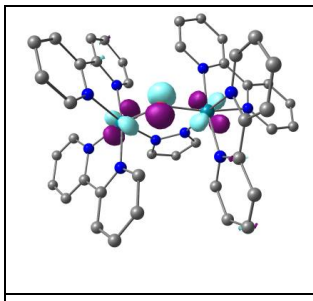
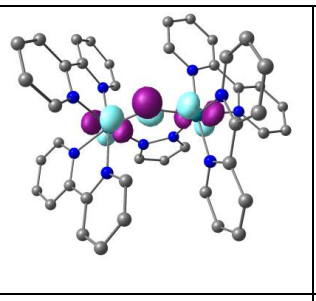
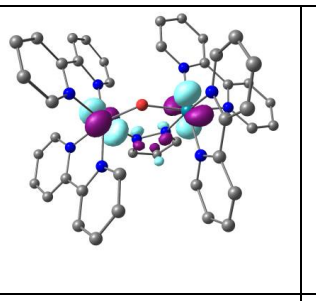
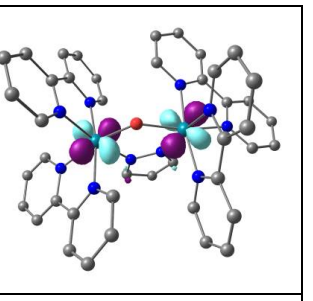
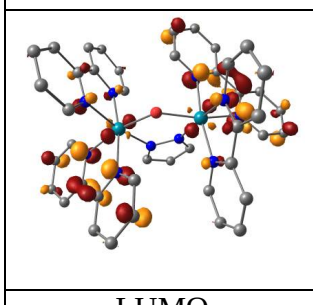
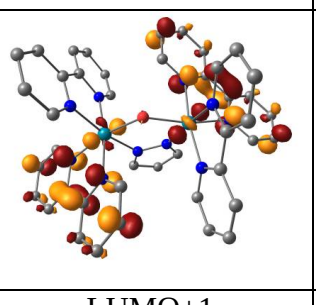
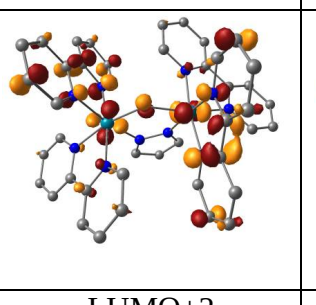
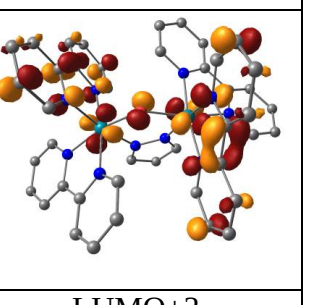
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13. TD-DFT ((U)B3LYP/CPCM/CH_3CN) Calculated Electronic Transitions for 1^n and 2^n.

λ /nm expt(DFT)	ε /$M^{-1}cm^{-1}$ (*f*)	transitions	character
		1^{4+} (*S*=1/2) (*meso*)	
1160 (1208)	1190 (0.014)	HOMO-1(β)→LUMO(β)(0.62)	Os(dπ)/bpy(π)→Os(dπ)/bpy(π*)
		HOMO-2(α)→LUMO+1(α)(0.21)	Os(dπ)/pz(π)→Os(dπ)/O(π*)
(1290)	(0.001)	HOMO(β)→LUMO+1(β)(0.68)	Os(dπ)/pz(π)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
(1000)	(0.001)	HOMO-2(β)→LUMO(β)(0.85)	Os(dπ)/pz(π)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
480 (506)	23930 (0.072)	HOMO-7(α)→LUMO(α)(0.44)	bpy(π)→Os(dπ)/O(π*)
		HOMO-4(β)→LUMO(β)(0.33)	bpy(π)→Os(dπ)/bpy(π*)
290 (281)	49490 (0.110)	HOMO-1(β)→LUMO+9(β)(0.29)	Os(dπ)/bpy(π)→bpy(π*)
		HOMO-1(β)→LUMO+10(β)(0.21)	Os(dπ)/bpy(π)→bpy(π*)
270 (278)	48040 (0.050)	HOMO-9(α)→LUMO+1(α)(0.33)	Os(dπ)/pz(π)/bpy(π)→bpy(π*)
		HOMO-8(β)→LUMO+2(β)(0.31)	Os(dπ)/pz(π)/bpy(π)→bpy(π*)
250 (275)	56680 (0.070)	HOMO(β)→LUMO+13(β)(0.28)	Os(dπ)/pz(π)/bpy(π)→bpy(π*)
		HOMO-3(β)→LUMO+9(β)(0.24)	Os(dπ)/bpy(π)→bpy(π*)
(275)	(0.012)	HOMO-6(β)→LUMO+5(β)(0.45)	bpy(π)→bpy(π*)
		HOMO-5(β)→LUMO+4(β)(0.19)	bpy(π)→bpy(π*)
		1^{3+} (BS (1,1) *S*=0) (*meso*)	
1310 (1218)	2340(0.0004)	HOMO-1(α)→LUMO(α)(0.69)	Os(dπ)/pz(π)→Os(dπ)/bpy(π*)/O(π*)
(966)	(0.006)	HOMO-2(α)→LUMO(α)(0.48)	Os(dπ)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
		HOMO-2(β)→LUMO(β)(0.48)	Os(dπ)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
630 (626)	20280 (0.048)	SOMO(α)→LUMO+1(α)(0.68)	Os(dπ)/bpy(π)→bpy(π*)

550 (562)	11410 (0.005)	SOMO(α)→LUMO+3(α)(0.67)	Os(dπ)/bpy(π)→bpy(π*)
(502)	(0.029)	SOMO(α)→LUMO+4(α)(0.66)	Os(dπ)/bpy(π)→bpy(π*)
440 (460)	10080 (0.012)	HOMO-3(α)→LUMO+1(α)(0.51)	Os(dπ)/bpy(π)→bpy(π*)
360 (352)	12770 (0.034)	HOMO-2(α)→LUMO+5(α)(0.45)	Os(dπ)/bpy(π)→bpy(π*)
		HOMO-2(β)→LUMO+5(β)(0.45)	Os(dπ)/bpy(π)→bpy(π*)
(347)	(0.037)	HOMO-2(α)→LUMO+5(α)(0.34)	Os(dπ)/bpy(π)→bpy(π*)
		HOMO-2(β)→LUMO+5(β) (0.34)	Os(dπ)/bpy(π)→bpy(π*)
290 (281)	69200 (0.113)	HOMO-6(α)→LUMO+3(α)(0.40)	bpy(π)→bpy(π*)
		HOMO-6(β)→LUMO+3(β)(0.40)	bpy(π)→bpy(π*)
240 (276)	49380 (0.086)	HOMO-6(α)→LUMO+3(α)(0.21)	bpy(π)→bpy(π*)
		HOMO-6(β)→LUMO+3(β)(0.21)	bpy(π)→bpy(π*)
(277)	(0.047)	HOMO-7(α)→LUMO+4(α)(0.25)	bpy(π)/pz(π)→bpy(π*)
		HOMO-7(β)→LUMO+4(β)(0.25)	bpy(π)/pz(π)→bpy(π*)
1^{2+} (*S*=1/2) (*meso*)			
1190 (935)	7380 (0.002)	HOMO(β)→LUMO+2(β)(0.78)	Os(dπ)/bpy(π)/O(π)→bpy(π*)/Os(dπ)
780 (772)	10460(0.023)	HOMO-2(β)→LUMO(β)(0.54)	Os(dπ)/pz(π)bpy(π)→bpy(π*)/Os(dπ)
(752)	(0.014)	HOMO-1(α)→LUMO+3(α)(0.52)	Os(dπ)/bpy(π)/O(π)→bpy(π*)/Os(dπ)
510(529)	17130(0.024)	HOMO(β)→LUMO+7(β)(0.47)	Os(dπ)/bpy(π)/O(π)→bpy(π*)
		HOMO-4(α)→LUMO(α)(0.15)	Os(dπ)/bpy(π)→bpy(π*)
(480)	(0.020)	HOMO-4(α)→LUMO(α)(0.64)	Os(dπ)/bpy(π)→bpy(π*)
450(440)	17130(0.028)	HOMO-1(α)→LUMO+11(α)(0.43)	Os(dπ)/bpy(π)→bpy(π*)
		HOMO-5(α)→LUMO(α)(0.34)	Os(dπ)/bpy(π)→bpy(π*)
290(292)	71590(0.031)	HOMO-7(β)→LUMO+1(β)(0.39)	bpy(π)→bpy(π*)

		HOMO-8(α)→LUMO(α)(0.30)	bpy(π)→bpy(π*)
240(285)	53190(0.030)	HOMO-9(β)→LUMO+1(β)(0.53)	bpy(π)→bpy(π*)
		1^{4+} (*S*=1/2) (*rac*)	
1160 (1106)	1190 (0.013)	HOMO-2(α)→LUMO(α)(0.46)	Os(dπ)/bpy(π)→Os(dπ)/ O(π*)/ bpy(π*)
		HOMO-2(β)→LUMO+1(β)(0.44)	Os(dπ)/pz(π)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
(1011)	(0.005)	HOMO-3(β)→LUMO+1(β)(0.80)	Os(dπ)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
480 (490)	23930 (0.038)	HOMO-8(β)→LUMO+1(β)(0.64)	Os(dπ)/pz(π)/bpy(π)→Os(dπ)/bpy(π*)/O(π*)
(474)	(0.266)	HOMO-10(α)→LUMO(α)(0.62)	pz(π)/bpy(π) /Os(dπ) →Os(dπ)/bpy(π*)/O(π*)
(467)	(0.239)	HOMO-10(α)→LUMO(α)(0.66)	pz(π)/bpy(π) /Os(dπ) →Os(dπ)/bpy(π*)/O(π*)
290 (294)	49490 (0.056)	HOMO-2(β)→LUMO+7(β)(0.28)	Os(dπ)/pz(π)→bpy(π*)
		HOMO-4(β)→LUMO+4(β)(0.25)	bpy(π)→bpy(π*)
270 (298)	48040 (0.054)	HOMO-2(α)→LUMO+6(α)(0.66)	Os(dπ)/bpy(π)→bpy(π*)
250 (279)	56680 (0.084)	HOMO-1(α)→LUMO+10(α)(0.35)	Os(dπ)/pz(π)→bpy(π*)
		HOMO-8(β)→LUMO+2(β)(0.25)	Os(dπ)/pz(π)/bpy(π)→bpy(π*)
(279)	(0.049)	HOMO-2(β)→LUMO+9(β)(0.40)	Os(dπ)/pz(π)→bpy(π*)
		HOMO-8(α)→LUMO+4(α)(0.24)	bpy(π) /Os(dπ) →bpy(π*)
		1^{3+} (BS (1,1) *S*=0) (*rac*)	
1310 (1101)	2340(0.003)	HOMO-2(β)→LUMO(β)(0.65)	Os(dπ)/bpy(π) /pz(π)→Os(dπ)/bpy(π*)/O(π*)
630 (598)	20280 (0.040)	SOMO→LUMO+2(α)(0.64)	Os(dπ)/bpy(π) →bpy(π*)
550 (577)	11410(0.547)	HOMO-4(β)→LUMO(β)(0.53)	Os(dπ)/bpy(π) /pz(π)→Os(dπ)/bpy(π*)
		SOMO→LUMO+4(α)(0.29)	Os(dπ)/bpy(π) →bpy(π*)
440 (451)	10080 (0.064)	HOMO-1(β)→LUMO+3(β)(0.54)	Os(dπ) pz(π)→ bpy(π*)/ Os(dπ)
360 (371)	12770 (0.067)	SOMO→LUMO+10(α)(0.24)	Os(dπ)/bpy(π) →bpy(π*)

		HOMO (β)→LUMO+10(β)(0.67)	Os(dπ)/bpy(π) →bpy(π*)
(359)	(0.069)	SOMO→LUMO+11(α)(0.56)	Os(dπ)/bpy(π) →bpy(π*)
		HOMO (β)→LUMO+11(β)(0.56)	Os(dπ)/bpy(π) →bpy(π*)
290 (300)	69200 (0.047)	HOMO-6(α)→LUMO+1(α)(0.37)	bpy(π)/pz(π)→bpy(π*)
		HOMO-5(β)→LUMO+2(β)(0.33)	bpy(π)/pz(π)→bpy(π*)
240 (283)	49380 (0.123)	HOMO-7(α)→LUMO+2(α)(0.27)	bpy(π)/pz(π)→bpy(π*)
		HOMO-7(β)→LUMO+2(β)(0.27)	bpy(π)/pz(π)→bpy(π*)
		1^{2+} (S=1/2) (*rac*)	
1190 (925)	7380 (0.004)	HOMO-2(β)→LUMO(β)(0.90)	Os(dπ)/pz(π)→ bpy(π*)/Os(dπ)
780 (768)	10460(0.064)	HOMO-3(β)→LUMO(β)(0.51)	Os(dπ)/pz(π)/ bpy(π)→ bpy(π*)/Os(dπ)
		SOMO→LUMO(α)(0.40)	Os(dπ)/bpy(π)→ bpy(π*)
(753)	(0.023)	SOMO→LUMO(α)(0.55)	Os(dπ)/bpy(π)→ bpy(π*)
510(502)	17130(0.040)	HOMO-3(α)→LUMO(α)(0.44)	Os(dπ)/pz(π)→ bpy(π*)
		HOMO(β)→LUMO+5(β)(0.36)	Os(dπ)/bpy(π)→ bpy(π*)
(474)	(0.079)	HOMO-3(α)→LUMO+3(α)(0.32)	Os(dπ)/pz(π)→ bpy(π*)
		SOMO→LUMO+5(α)(0.47)	Os(dπ)/bpy(π)→ bpy(π*)
450(417)	17130(0.040)	HOMO-1(α)→LUMO+8(α)(0.77)	Os(dπ)/bpy(π)→ bpy(π*)
290(288)	71590(0.075)	HOMO-1(α)→LUMO+13(α)(0.42)	Os(dπ)/bpy(π)→ bpy(π*)
		HOMO-7(β)→LUMO+3(β)(0.19)	bpy(π)→ bpy(π*)
240(283)	53190(0.072)	HOMO-8(α)→LUMO+1(α)(0.44)	bpy(π)→ bpy(π*)
		HOMO-7(α)→LUMO+2(α)(0.32)	bpy(π)→ bpy(π*)
		2^{3+} (S=1/2) (*meso*)	
1360(1481)	490(0.012)	HOMO-2(β)→LUMO(β)(0.79)	Os(dπ)/bpy(π)→Os(dπ)/bpy(π*)

660(602)	2290(0.0002)	HOMO(β)→LUMO+1(β)(0.97)	Os(dπ)/bpy(π)→bpy(π*)
(594)	(0.003)	HOMO(β)→LUMO+3(β)(0.59)	Os(dπ)/bpy(π)→bpy(π*)
480(559)	11560(0.006)	HOMO-1(α)→LUMO+3(α)(0.52)	Os(dπ)/pz(π)→bpy(π*)
(484)	(0.012)	HOMO-3(β)→LUMO+2(β)(0.87)	Os(dπ)/pz(π)→bpy(π*)
440(409)	12560(0.007)	HOMO-1(α)→LUMO+4(α)(0.73)	Os(dπ)/pz(π)→bpy(π*)
(439)	(0.020)	HOMO-3(α)→LUMO(α)(0.91)	Os(dπ)/pz(π)→bpy(π*)
370(387)	12700(0.034)	HOMO-4(α)→LUMO+1(α)(0.62)	Os(dπ)/pz(π)→bpy(π*)
(367)	(0.019)	HOMO-1(α)→LUMO+11(α)(0.62)	Os(dπ)/pz(π)→bpy(π*)
(370)	(0.010)	HOMO-2(α)→LUMO+8(α)(0.54)	Os(dπ)/bpy(π)→bpy(π*)
290(311)	82250(0.023)	HOMO-7(β)→LUMO+2(β)(0.53)	bpy(π)/pz(π)→bpy(π*)
250(288)	50080(0.004)	HOMO-6(α)→LUMO+3(α)(0.34)	bpy(π)→bpy(π*)
		HOMO-7(α)→LUMO+4(α)(0.26)	bpy(π)→bpy(π*)
(281)	(0.069)	HOMO-7(β)→LUMO+3(β)(0.38)	bpy(π)/pz(π)→bpy(π*)
		HOMO-5(β)→LUMO+4(β)(0.32)	bpy(π)/pz(π)→bpy(π*)
		2^{2+} (S=0) (*meso*)	
740(661)	3790(0.004)	HOMO→LUMO+1(0.69)	Os(dπ)/pz(π)→bpy(π*)/pz(π*)
500(544)	15020(0.003)	HOMO→LUMO+2(0.67)	Os(dπ)/pz(π)→bpy(π*)
(530)	(0.009)	HOMO→LUMO+3(0.67)	Os(dπ)/pz(π)→bpy(π*)
430(479)	16390(0.053)	HOMO-4→LUMO+3(0.56)	Os(dπ)/pz(π)→bpy(π*)
(404)	(0.023)	HOMO→LUMO+7(0.55)	Os(dπ)/pz(π)→bpy(π*)
380(371)	16410(0.094)	HOMO-5→LUMO+4(0.46)	Os(dπ)/bpy(π)→bpy(π*)/pz(π*)
		HOMO-4→LUMO+4(0.43)	Os(dπ)/pz(π)→bpy(π*)/pz(π*)
(384)	(0.072)	HOMO-1→LUMO+6(0.37)	Os(dπ)/pz(π)→bpy(π*)

		HOMO→LUMO+7(0.21)	Os(dπ)/pz(π)→bpy(π*)
350(346)	15660(0.017)	HOMO-5→LUMO+7(0.47)	Os(dπ)/bpy(π)→bpy(π*)
		HOMO-4→LUMO+7(0.32)	Os(dπ)/bpy(π)→bpy(π*)
(319)	(0.025)	HOMO-5→LUMO+8(0.45)	Os(dπ)/bpy(π)→bpy(π*)
		HOMO-5→LUMO+9(0.25)	Os(dπ)/bpy(π)→bpy(π*)
300 (277)	95260(0.529)	HOMO-10→LUMO(0.39)	bpy(π)→bpy(π*)
		HOMO-9→LUMO+1(0.36)	bpy(π)→bpy(π*)/pz(π*)
250(241)	53400(0.077)	HOMO-11→LUMO+4(0.34)	bpy(π)→bpy(π*)/pz(π*)
		HOMO-9→LUMO+5(0.22)	bpy(π)→bpy(π*)/pz(π*)
(236)	(0.102)	HOMO-13→LUMO+5(0.45)	pz(π)/bpy(π)→bpy(π*)/pz(π*)
		HOMO-10→LUMO+6(0.19)	bpy(π)→bpy(π*)
		2^{3+} (*S*=1/2) (*rac*)	
1360(1321)	490(0.009)	HOMO-2(β)→LUMO(β)(0.96)	Os(dπ) / bpy(π) /pz(π)→Os(dπ)/ pz(π*)/ bpy(π*)
660(619)	2290(0.003)	HOMO(β)→LUMO+3(β)(0.56)	Os(dπ) / bpy(π) →bpy(π*)
		SOMO→LUMO+2(α)(0.49)	Os(dπ) /pz(π) / bpy(π)→ bpy(π*)
(554)	(0.012)	HOMO-1(α)→LUMO+3(α)(0.63)	Os(dπ) /pz(π) / bpy(π)→ bpy(π*)
		HOMO-1(β)→LUMO+4(β)(0.62)	Os(dπ) /pz(π) / bpy(π)→ bpy(π*)
480(477)	11560(0.090)	HOMO-2(β)→LUMO+3(β)(0.62)	Os(dπ) / bpy(π) /pz(π)→ bpy(π*)
		HOMO-2(α)→LUMO+2(α)(0.63)	Os(dπ) /pz(π)→ bpy(π*)
(475)	(0.0300)	HOMO-3(β)→LUMO+2(β)(0.89)	Os(dπ) / bpy(π) → bpy(π*)
440(452)	12560(0.093)	HOMO-11(β)→LUMO(β)(0.87)	pz(π) / bpy(π) /Os(dπ)→ Os(dπ)/ pz(π*)/ bpy(π*)
370(355)	12700(0.086)	HOMO-2(α)→LUMO+8(α)(0.46)	Os(dπ) /pz(π)→ bpy(π*)

		HOMO-2(β)→LUMO+9(β)(0.43)	Os(dπ) / bpy(π) /pz(π) → bpy(π*)
290(313)	82250(0.045)	HOMO-6(α)→LUMO(α)(0.70)	bpy(π) /pz(π) → bpy(π*)
(281)	(0.249)	HOMO-7(α)→LUMO+3(α)(0.56)	bpy(π) → bpy(π*)
250(280)	50080(0.281)	HOMO-6(α)→LUMO+3(α)(0.32)	bpy(π) → bpy(π*)
		HOMO-5(β)→LUMO+4(β)(0.34)	bpy(π) → bpy(π*)
		2^{2+} (*S*=0) (*rac*)	
740(664)	3790(0.002)	HOMO→LUMO+3(0.47)	Os(dπ)/bpy(π)→ bpy(π*)
		HOMO-1→LUMO+2(0.42)	Os(dπ)/bpy(π)→ bpy(π*)
500(571)	15020(0.033)	HOMO-2→LUMO+2(0.41)	Os(dπ)/pz(π) → bpy(π*)
		HOMO-3→LUMO+1(0.28)	Os(dπ)/bpy(π)→ bpy(π*)
(500)	(0.024)	HOMO-3→LUMO+3(0.42)	Os(dπ)/bpy(π)→ bpy(π*)
(492)	(0.137)	HOMO-4→LUMO(0.42)	Os(dπ)/bpy(π)→ bpy(π*)
		HOMO-3→LUMO+3(0.39)	Os(dπ)/bpy(π)→ bpy(π*)
430(465)	16390(0.083)	HOMO-4→LUMO+3(0.43)	Os(dπ)/bpy(π)→ bpy(π*)
		HOMO-4→LUMO(0.11)	Os(dπ) / bpy(π) /pz(π)→ bpy(π*)
(408)	(0.056)	HOMO→LUMO+7(0.40)	Os(dπ) /pz(π) / bpy(π) → bpy(π*)
		HOMO-3→LUMO+5(0.12)	Os(dπ) / bpy(π) /pz(π) → bpy(π*)
380(384)	16410(0.112)	HOMO-2→LUMO+9(0.43)	Os(dπ) /pz(π) / bpy(π) → bpy(π*)
		HOMO→LUMO+6(0.13)	Os(dπ) / bpy(π) /pz(π) → bpy(π*)
350(330)	15660(0.194)	HOMO-4→LUMO+8(0.44)	Os(dπ)/bpy(π)→ bpy(π*)
		HOMO-5→LUMO+9(0.31)	Os(dπ)/bpy(π)→ bpy(π*)
300 (281)	95260(0.254)	HOMO-9→LUMO+2(0.33)	bpy(π)→ bpy(π*)
		HOMO→LUMO+3(0.18)	Os(dπ)/bpy(π)→ bpy(π*)
250(275)	53400(0.181)	HOMO-9→LUMO+1(0.24)	bpy(π)→ bpy(π*)

HOMO-13→LUMO+3(0.21)	bpy(π)→ bpy(π*)
HOMO-12→LUMO+1(0.21)	bpy(π)→ bpy(π*)

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

MO	energy(eV)	composition		
		Os	pz	bpy
HOMO–5	–9.510	0.65	0.14	0.21
HOMO–4	–9.424	0.60	0.23	0.17
HOMO–3	–9.287	0.42	0.34	0.24
HOMO–2	–9.101	0.60	0.23	0.17
HOMO–1	–8.946	0.42	0.38	0.20
HOMO	–8.351	0.56	0.25	0.18
LUMO	–6.742	0.08	0.14	0.79
LUMO+1	–6.722	0.07	0.17	0.76
LUMO+2	–6.522	0.10	0.06	0.84
LUMO+3	–6.240	0.11	0.04	0.84
LUMO+4	–5.852	0.06	0.19	0.75
LUMO+5	–5.737	0.05	0.16	0.79

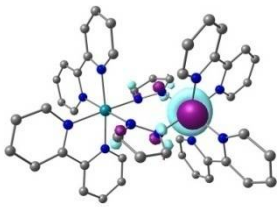
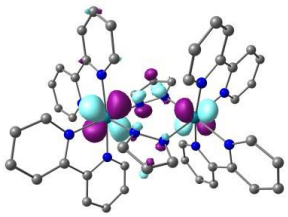
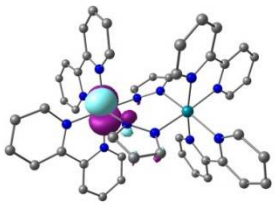
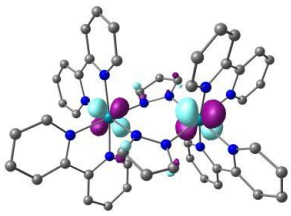
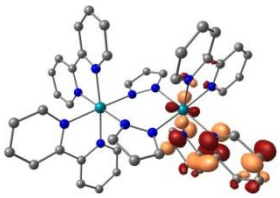
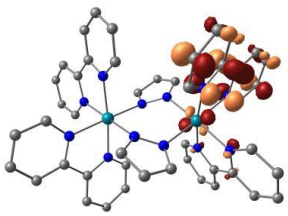
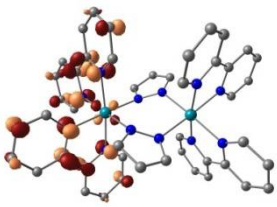
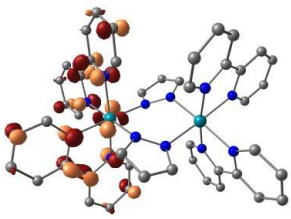
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15. Composition and Energies of Selected Molecular Orbitals of 2^{2+} (*rac*, *S*=0)

MO	energy(eV)	composition		
		Os	pz	bpy
HOMO–5	–9.754	0.71	0.05	0.24
HOMO–4	–9.587	0.73	0.05	0.22
HOMO–3	–9.234	0.64	0.14	0.22
HOMO–2	–9.215	0.70	0.16	0.14
HOMO–1	–9.059	0.68	0.18	0.14
HOMO	–8.767	0.60	0.14	0.26
LUMO	–6.660	0.06	0.01	0.93
LUMO+1	–6.410	0.12	0.01	0.87
LUMO+2	–6.337	0.10	0.01	0.89
LUMO+3	–6.332	0.10	0.01	0.89
LUMO+4	–5.771	0.05	0.02	0.93
LUMO+5	–5.561	0.05	0.02	0.93

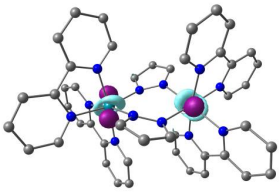
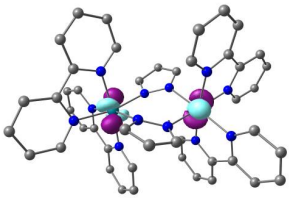
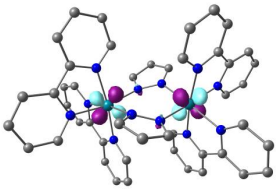
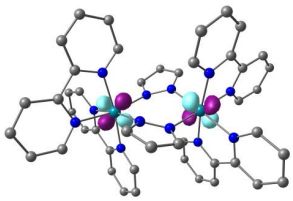
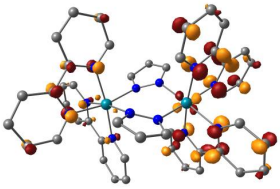
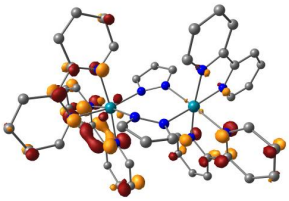
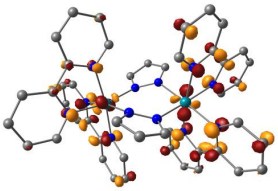
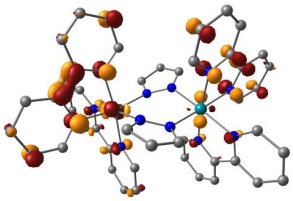
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16. Composition and Energies of Selected Molecular Orbitals of 2^{3+} (*meso*, *S*=1/2)

MO	energy(eV)	Composition		
		Os	pz	Bpy
		α-spin		
HOMO–5	–13.256	0.74	0.05	0.21
HOMO–4	–12.991	0.49	0.39	0.12
HOMO–3	–12.784	0.58	0.24	0.18
HOMO–2	–12.540	0.78	0.06	0.17
HOMO–1	–12.312	0.65	0.19	0.16
SOMO	–12.215	0.68	0.16	0.16
LUMO	–9.318	0.07	0.01	0.92
LUMO+1	–9.294	0.07	0.01	0.92
LUMO+2	–8.877	0.07	0.02	0.91
LUMO+3	–8.840	0.09	0.01	0.90
LUMO+4	–8.408	0.05	0.02	0.93
LUMO+5	–8.261	0.02	0.00	0.98
		β-spin		
HOMO–5	–13.655	0.06	0.30	0.64
HOMO–4	–12.975	0.70	0.10	0.20
HOMO–3	–12.582	0.59	0.22	0.18
HOMO–2	–12.275	0.71	0.11	0.18
HOMO–1	–12.108	0.68	0.15	0.16
HOMO	–11.685	0.72	0.13	0.15
LUMO	–10.960	0.74	0.12	0.14
LUMO+1	–9.301	0.08	0.01	0.91
LUMO+2	–9.281	0.08	0.01	0.91
LUMO+3	–8.872	0.07	0.02	0.91
LUMO+4	–8.829	0.10	0.01	0.89
LUMO+5	–8.403	0.05	0.02	0.93

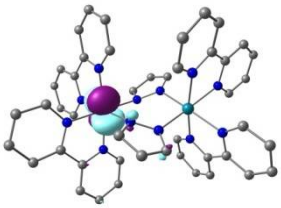
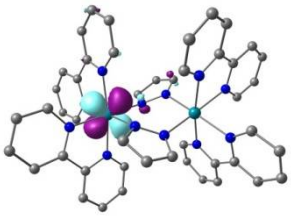
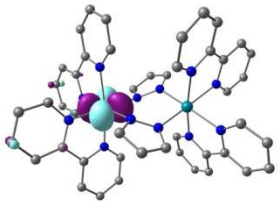
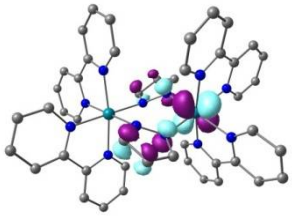
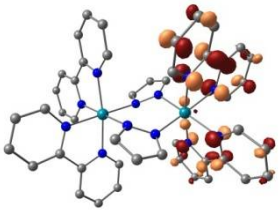
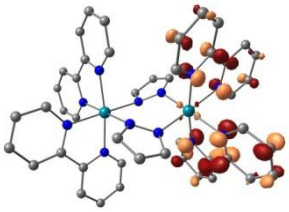
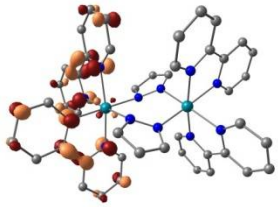
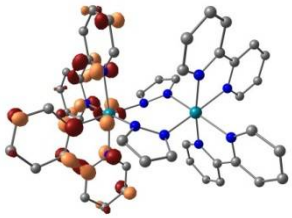
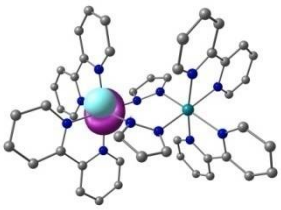
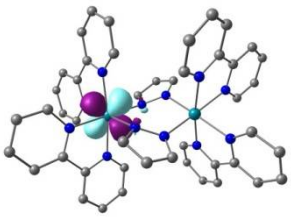
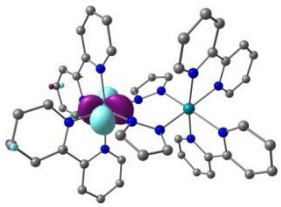
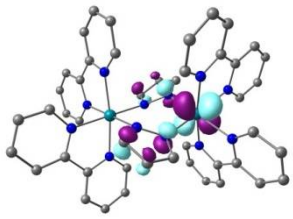
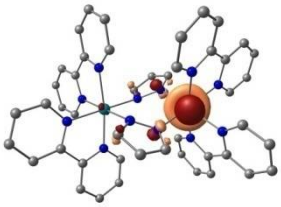
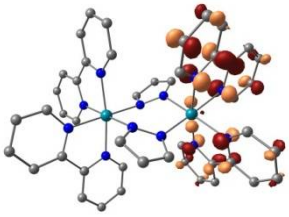
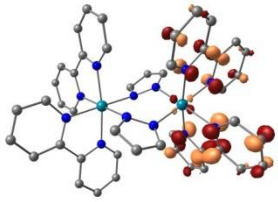
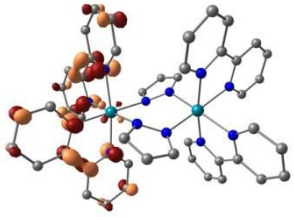
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17. Composition and Energies of Selected Molecular Orbitals of 2^{3+} (*rac*, *S*=1/2)

MO	energy(eV)	composition		
		Os	pz	bpy
		α-spin		
HOMO–5	–12.963	0.76	0.05	0.19
HOMO–4	–12.849	0.76	0.05	0.20
HOMO–3	–12.685	0.66	0.19	0.15
HOMO–2	–12.597	0.61	0.26	0.13
HOMO–1	–12.511	0.65	0.19	0.16
SOMO	–12.426	0.63	0.20	0.17
LUMO	–9.122	0.07	0.02	0.92
LUMO+1	–9.118	0.07	0.02	0.91
LUMO+2	–9.067	0.09	0.02	0.90
LUMO+3	–9.023	0.08	0.01	0.91
LUMO+4	–8.257	0.06	0.03	0.91
LUMO+5	–8.167	0.03	0.02	0.94
		β-spin		
HOMO–5	–13.737	0.06	0.47	0.47
HOMO–4	–12.698	0.72	0.08	0.20
HOMO–3	–12.678	0.74	0.06	0.20
HOMO–2	–12.382	0.65	0.17	0.18
HOMO–1	–12.298	0.65	0.18	0.17
HOMO	–11.673	0.77	0.10	0.14
LUMO	–10.907	0.67	0.18	0.15
LUMO+1	–9.113	0.07	0.02	0.91
LUMO+2	–9.109	0.08	0.02	0.90
LUMO+3	–9.052	0.09	0.02	0.89
LUMO+4	–9.010	0.08	0.01	0.91
LUMO+5	–8.253	0.06	0.03	0.91

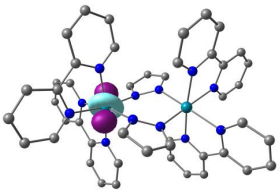
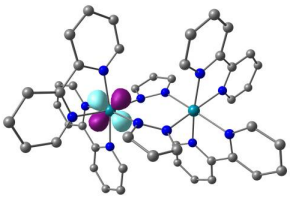
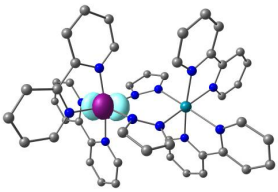
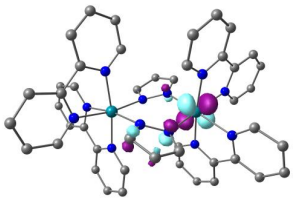
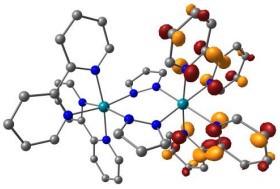
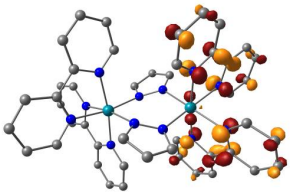
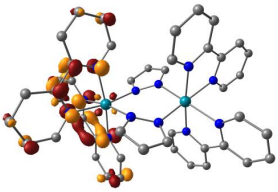
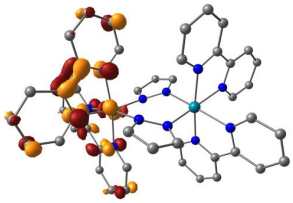
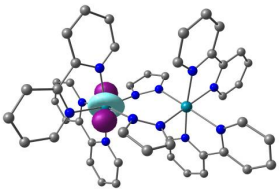
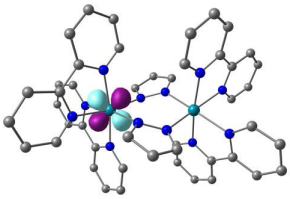
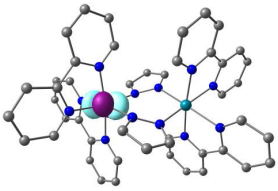
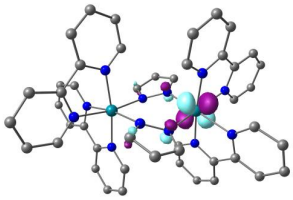
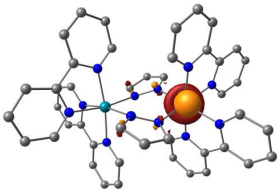
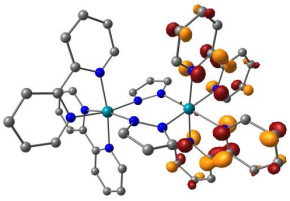
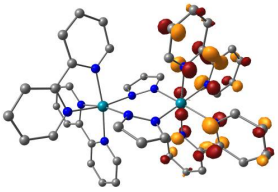
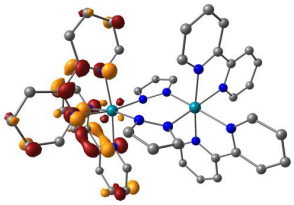
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18. Composition and Energies of Selected Molecular Orbitals of 2^+ (*meso*, *S*=1/2)

MO	energy(eV)	composition		
		Os	pz	bpy
		α-spin		
HOMO–5	–6.955	0.71	0.08	0.21
HOMO–4	–6.815	0.67	0.13	0.19
HOMO–3	–6.701	0.71	0.13	0.15
HOMO–2	–6.647	0.63	0.14	0.23
HOMO–1	–6.530	0.70	0.16	0.14
SOMO	–4.534	0.09	0.01	0.90
LUMO	–4.150	0.09	0.01	0.90
LUMO+1	–4.010	0.11	0.02	0.88
LUMO+2	–3.957	0.12	0.01	0.87
LUMO+3	–3.160	0.07	0.03	0.90
LUMO+4	–3.118	0.07	0.03	0.91
LUMO+5	–2.903	0.03	0.01	0.96
		β-spin		
HOMO–5	–7.052	0.73	0.05	0.22
HOMO–4	–6.922	0.71	0.07	0.21
HOMO–3	–6.778	0.67	0.13	0.20
HOMO–2	–6.701	0.72	0.13	0.15
HOMO–1	–6.633	0.65	0.14	0.20
HOMO	–6.515	0.70	0.16	0.14
LUMO	–3.840	0.08	0.02	0.90
LUMO+1	–3.756	0.09	0.01	0.89
LUMO+2	–3.745	0.10	0.02	0.88
LUMO+3	–3.718	0.10	0.01	0.89
LUMO+4	–3.134	0.07	0.03	0.90
LUMO+5	–3.097	0.07	0.03	0.91

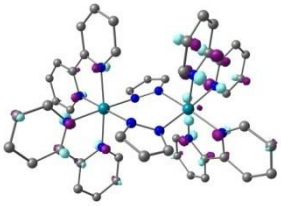
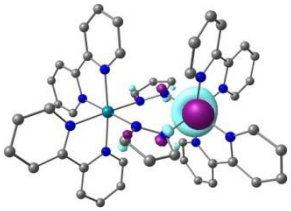
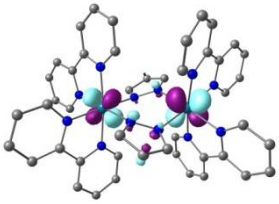
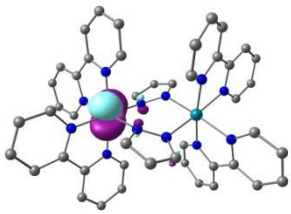
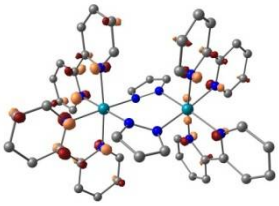
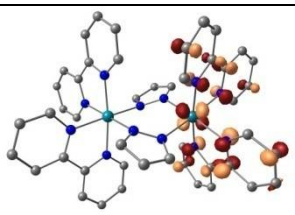
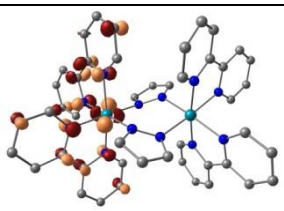
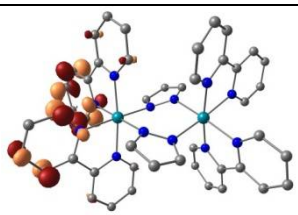
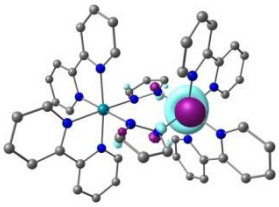
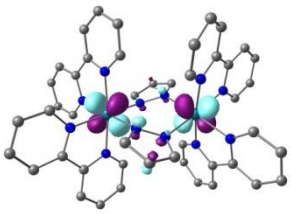
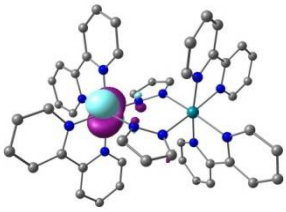
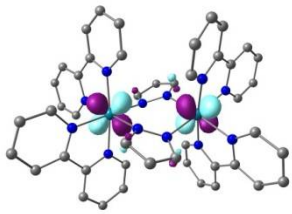
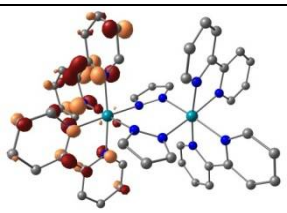
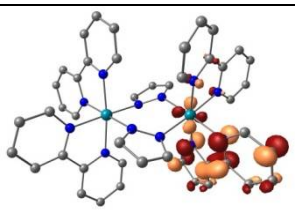
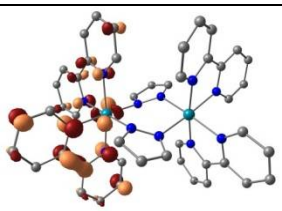
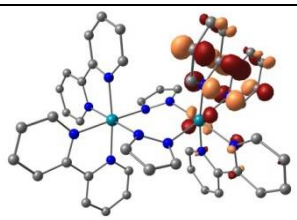
α-spin			
			
SOMO 1	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	energy(eV)	composition		
		Os	pz	bpy
		α-spin		
HOMO–5	–7.070	0.71	0.05	0.24
HOMO–4	–6.835	0.67	0.14	0.19
HOMO–3	–6.701	0.65	0.15	0.20
HOMO–2	–6.573	0.73	0.12	0.15
HOMO–1	–6.523	0.67	0.19	0.15
SOMO	–4.562	0.07	0.01	0.91
LUMO	–4.194	0.08	0.02	0.90
LUMO+1	–3.961	0.13	0.01	0.86
LUMO+2	–3.957	0.13	0.02	0.89
LUMO+3	–3.159	0.08	0.03	0.94
LUMO+4	–3.109	0.04	0.02	0.95
LUMO+5	–2.925	0.04	0.01	0.96
		β-spin		
HOMO–5	–7.130	0.73	0.06	0.21
HOMO–4	–7.086	0.73	0.06	0.22
HOMO–3	–6.775	0.67	0.14	0.19
HOMO–2	–6.656	0.66	0.14	0.20
HOMO–1	–6.575	0.74	0.12	0.15
HOMO	–6.520	0.67	0.19	0.15
LUMO	–3.844	0.08	0.02	0.90
LUMO+1	–3.813	0.07	0.01	0.91
LUMO+2	–3.718	0.11	0.02	0.87
LUMO+3	–3.708	0.11	0.01	0.88
LUMO+4	–3.130	0.08	0.03	0.88
LUMO+5	–3.078	0.04	0.02	0.94

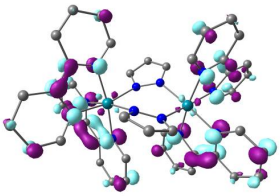
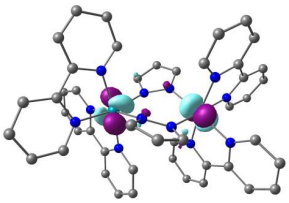
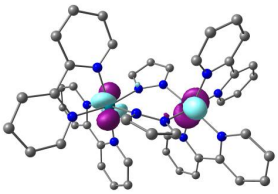
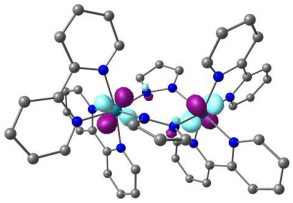
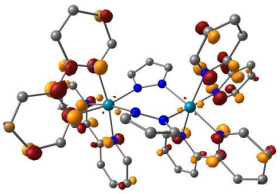
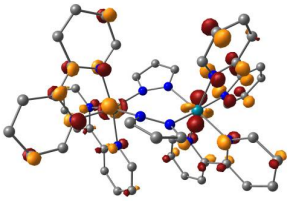
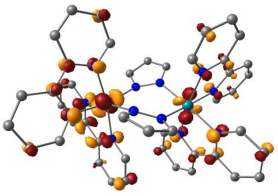
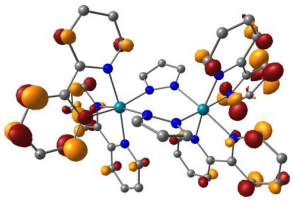
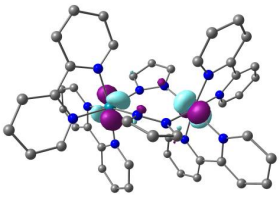
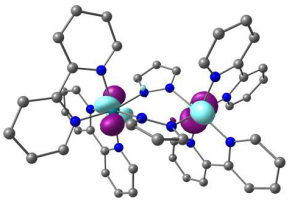
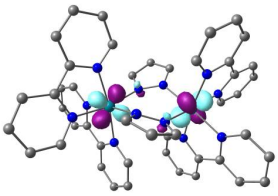
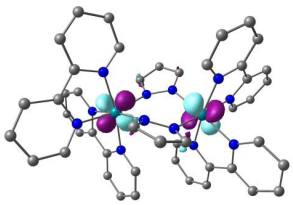
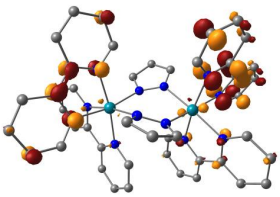
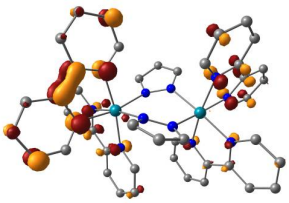
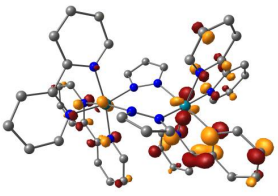
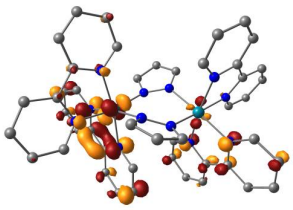
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20. Composition and Energies of Selected Molecular Orbitals of 2 (*meso*, S=1) ($E_{S=1}$–$E_{S=0}$= 3037.37524 cm^{-1})

MO	energy(eV)	composition		
		Os	pz	bpy
		α-spin		
HOMO–5	–4.258	0.63	0.12	0.26
HOMO–4	–4.111	0.66	0.13	0.21
HOMO–3	–4.051	0.69	0.14	0.18
HOMO–2	–4.020	0.73	0.13	0.14
SOMO2	–2.444	0.10	0.01	0.89
SOMO1	–2.315	0.07	0.01	0.92
LUMO	–1.667	0.15	0.02	0.84
LUMO+1	–1.462	0.16	0.02	0.82
LUMO+2	–0.666	0.08	0.02	0.89
LUMO+3	–0.527	0.08	0.03	0.89
LUMO+4	–0.422	0.04	0.01	0.95
LUMO+5	–0.365	0.08	0.01	0.90
		β-spin		
HOMO–5	–4.506	0.72	0.05	0.23
HOMO–4	–4.355	0.71	0.08	0.21
HOMO–3	–4.279	0.65	0.12	0.23
HOMO–2	–4.070	0.71	0.12	0.16
HOMO–1	–4.044	0.69	0.13	0.18
HOMO	–4.008	0.72	0.14	0.15
LUMO	–1.314	0.10	0.01	0.89
LUMO+1	–1.220	0.10	0.01	0.88
LUMO+2	–1.173	0.07	0.02	0.91
LUMO+3	–1.013	0.11	0.01	0.88
LUMO+4	–0.628	0.08	0.02	0.89
LUMO+5	–0.467	0.09	0.03	0.88

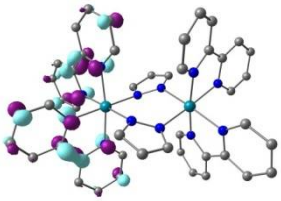
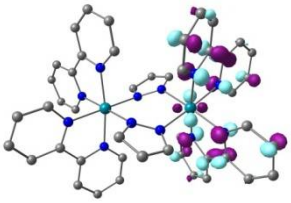
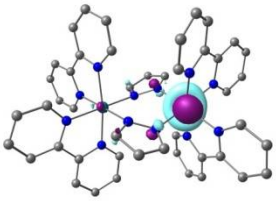
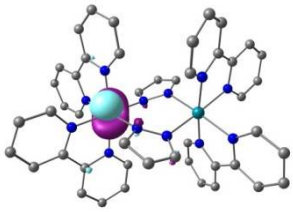
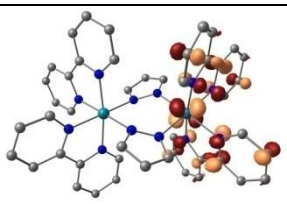
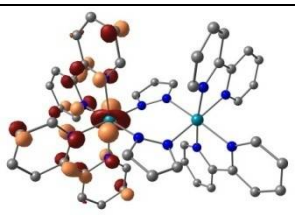
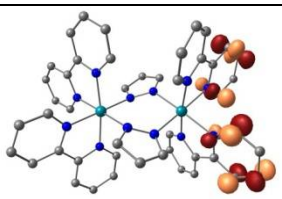
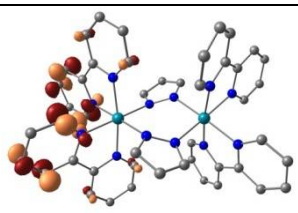
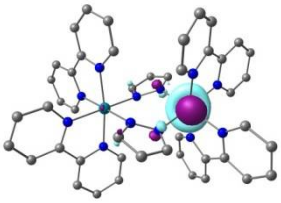
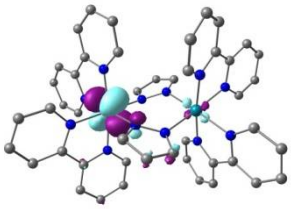
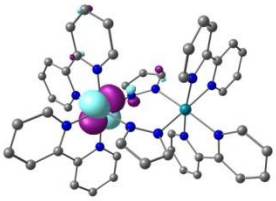
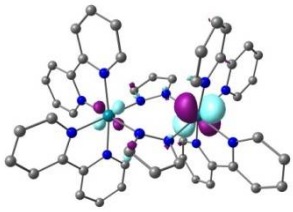
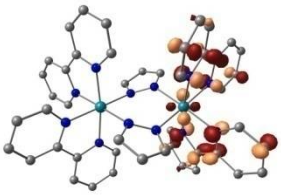
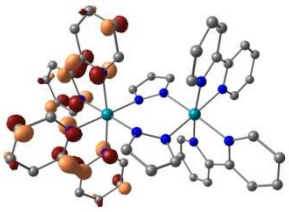
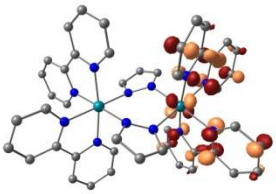
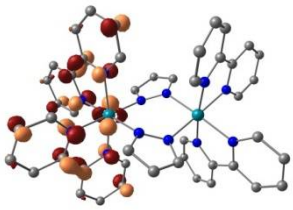
α-spin			
			
SOMO 1	SOMO 2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21. Composition and Energies of Selected Molecular Orbitals of 2 (*rac*, S=1) ($E_{S=1}$–$E_{S=0}$= 3141.384274 cm^{-1})

MO	energy(eV)	composition		
		Os	pz	bpy
		α-spin		
HOMO–5	–4.280	0.67	0.15	0.19
HOMO–4	–4.160	0.64	0.14	0.22
HOMO–3	–4.026	0.73	0.10	0.17
HOMO–2	–4.009	0.68	0.17	0.15
SOMO2	–2.424	0.06	0.01	0.93
SOMO1	–2.411	0.07	0.02	0.91
LUMO	–1.528	0.16	0.02	0.82
LUMO+1	–1.524	0.16	0.02	0.81
LUMO+2	–0.593	0.07	0.03	0.90
LUMO+3	–0.360	0.04	0.02	0.94
LUMO+4	–0.346	0.04	0.01	0.95
LUMO+5	–0.300	0.03	0.02	0.95
		β-spin		
HOMO–5	–4.565	0.71	0.06	0.23
HOMO–4	–4.539	0.71	0.06	0.23
HOMO–3	–4.203	0.68	0.13	0.19
HOMO–2	–4.119	0.67	0.14	0.19
HOMO–1	–4.043	0.74	0.10	0.16
HOMO	–4.000	0.68	0.16	0.16
LUMO	–1.280	0.07	0.02	0.92
LUMO+1	–1.269	0.07	0.02	0.90
LUMO+2	–1.089	0.12	0.02	0.86
LUMO+3	–1.081	0.11	0.02	0.87
LUMO+4	–0.533	0.08	0.03	0.89
LUMO+5	–0.484	0.05	0.03	0.93

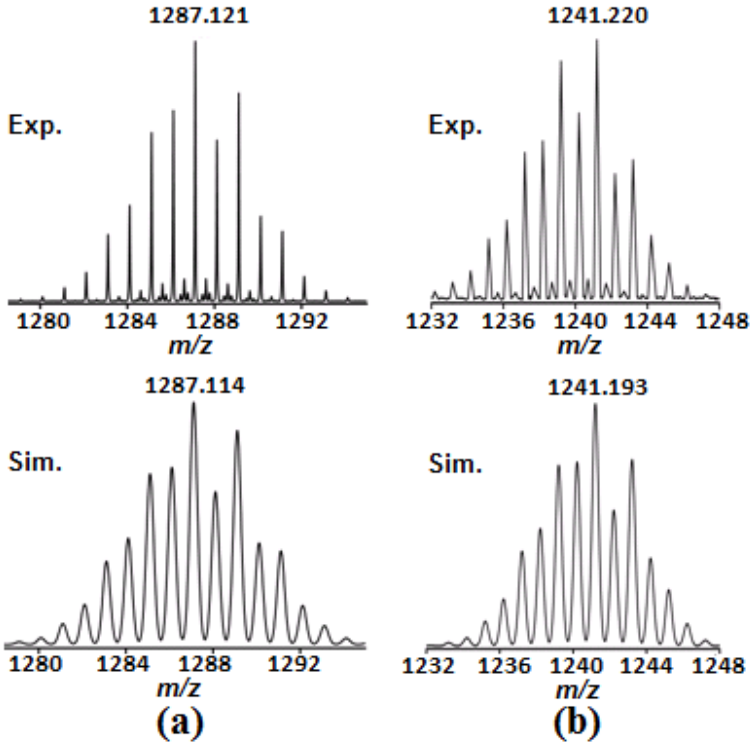


Figure S1. ESI-MS of (a) [**1**]$(ClO_4)_3$ and (b) [**2**]$(ClO_4)_2$ in CH_3CN.

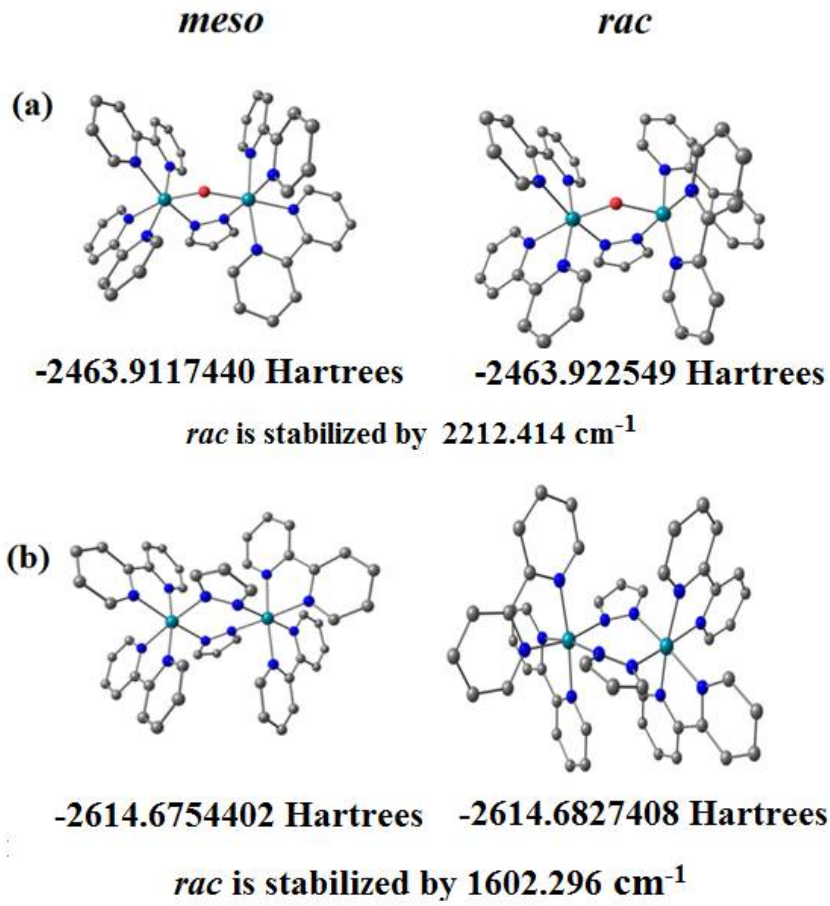


Figure S2. DFT optimized structures and energies of (a) $\mathbf{1}^{3+}$ (molecule A) and (b) $\mathbf{2}^{2+}$.

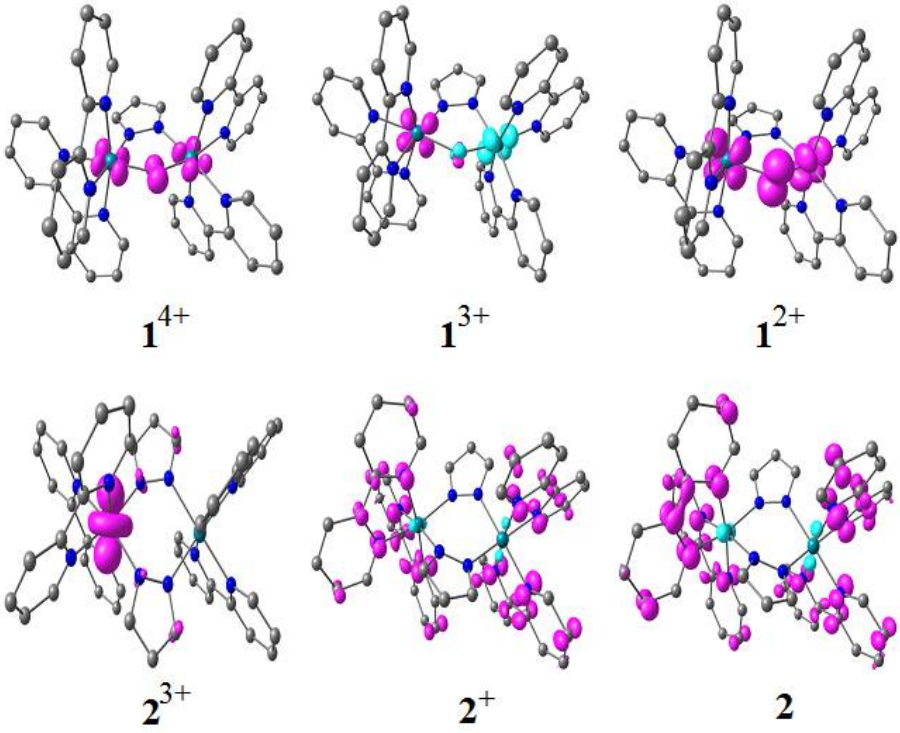


Figure S3. DFT calculated Mulliken spin density plots for paramagnetic $\mathbf{1}^n$ (*rac*) and $\mathbf{2}^n$ (*rac*).