Supplementary Information

Impact of {Os(pap)$_2$} in fine-tuning the binding modes and non-innocent potential of deprotonated 2,2′-bipyridine-3,3′-diol†

Prabir Ghosh[a] and Goutam Kumar Lahiri[*a]

[a]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India E-mail: lahiri@chem.iitb.ac.in*

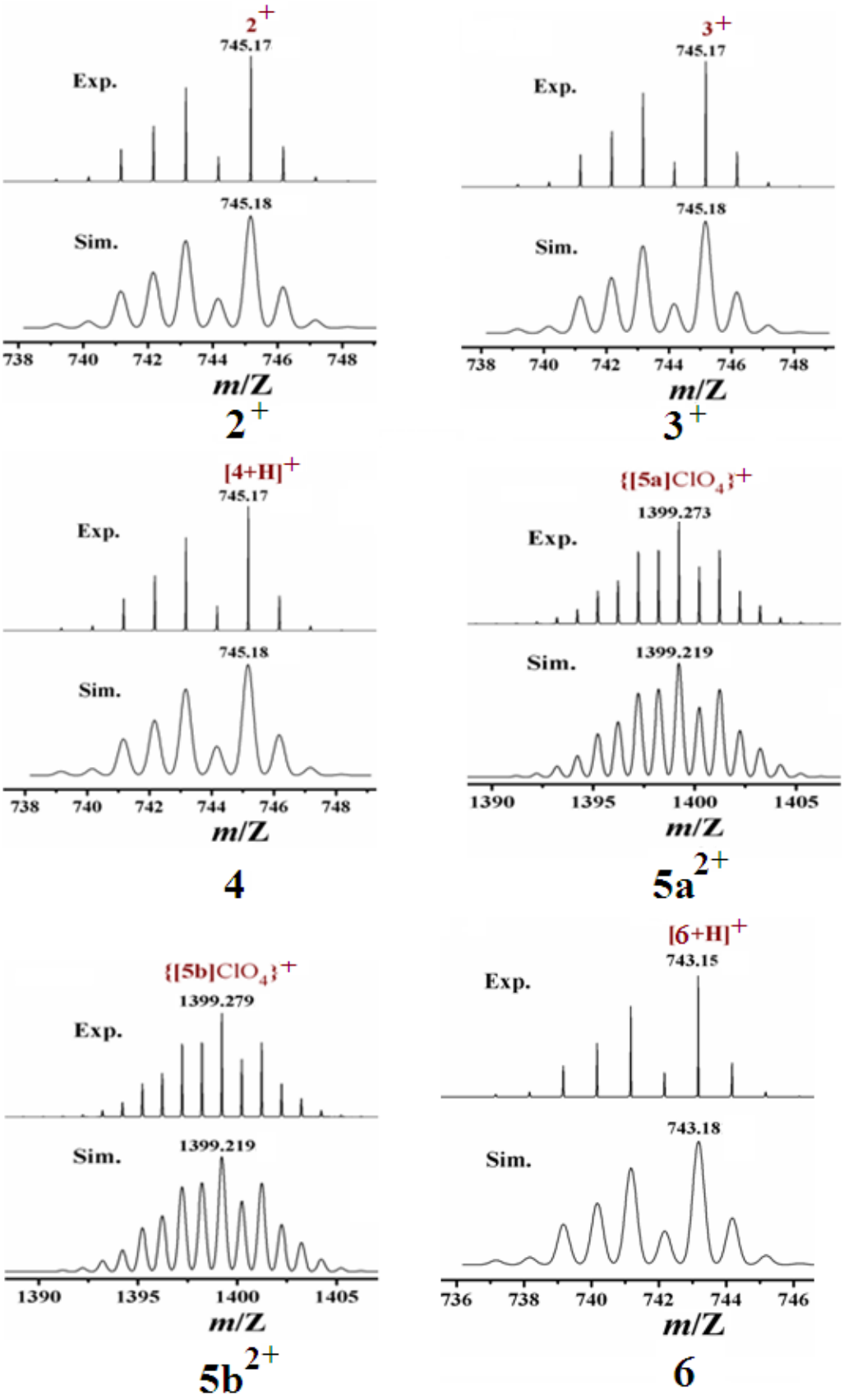


Fig. S1 Experimental and simulated ESI-MS(+) spectra of $\mathbf{2}^{+}$, $\mathbf{3}^{+}$, **4**, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$ and **6** in CH_3CN.

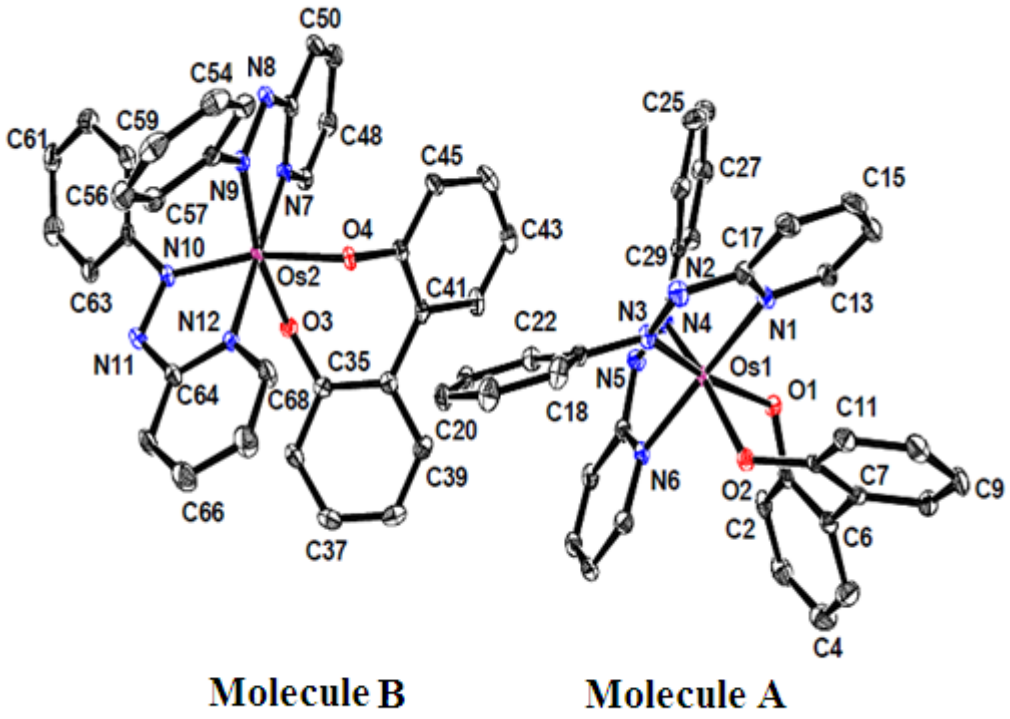


Fig. S2 ORTEP diagram of 2[**6**] showing two independent molecules (**A** and **B**) in the asymmetric unit. Ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

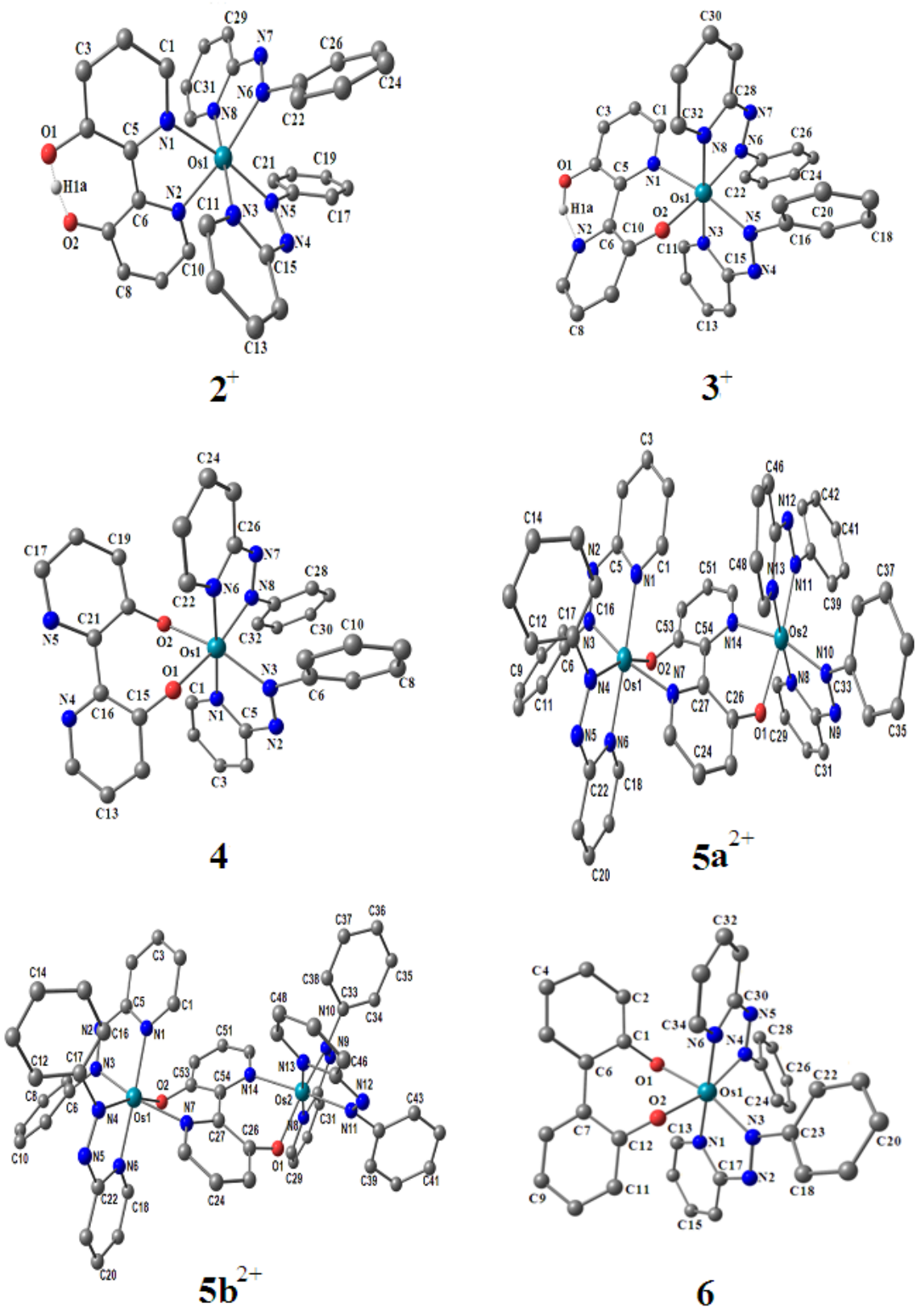


Fig. S3 DFT optimised (uB3LYP/6-31G*/LANL2DZ) structures of $\mathbf{2}^{+}$, $\mathbf{3}^{+}$, **4**, $\mathbf{5a}^{2+}$ $\mathbf{5b}^{2+}$ and **6**.

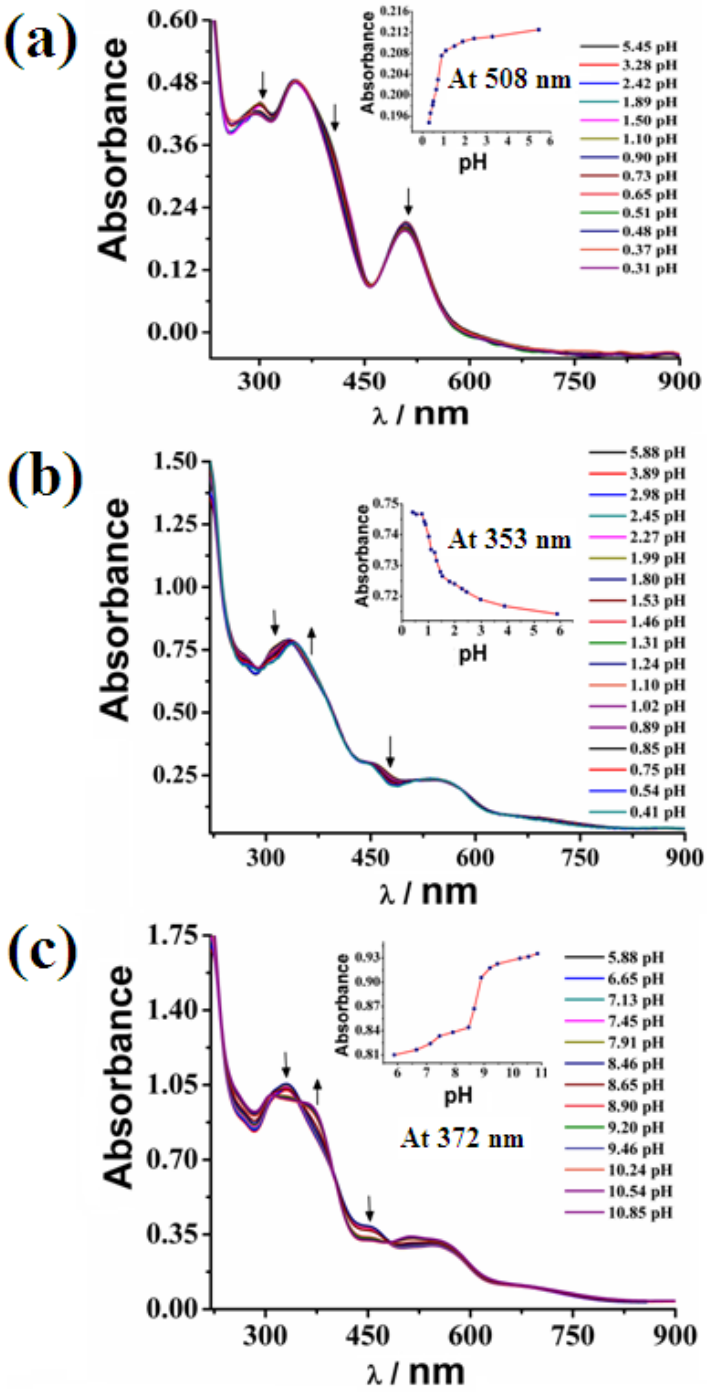
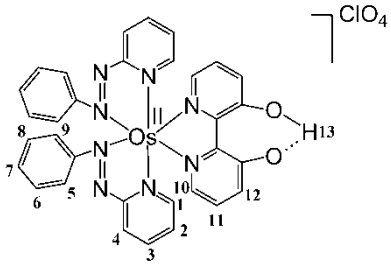


Fig. S4 Electronic spectra of (a) $\mathbf{2}^{+}$, (b) $\mathbf{3}^{+}$ and (c) $\mathbf{3}^{+}$ as a function of pH in 7:3 CH_3CN-H_2O. Insets show the change in absorbance at 508 nm for $\mathbf{2}^{+}$ (a), 353 nm for $\mathbf{3}^{+}$ (b) and 372 nm for $\mathbf{3}^{+}$ (c) with the pH.



[**2**]ClO4

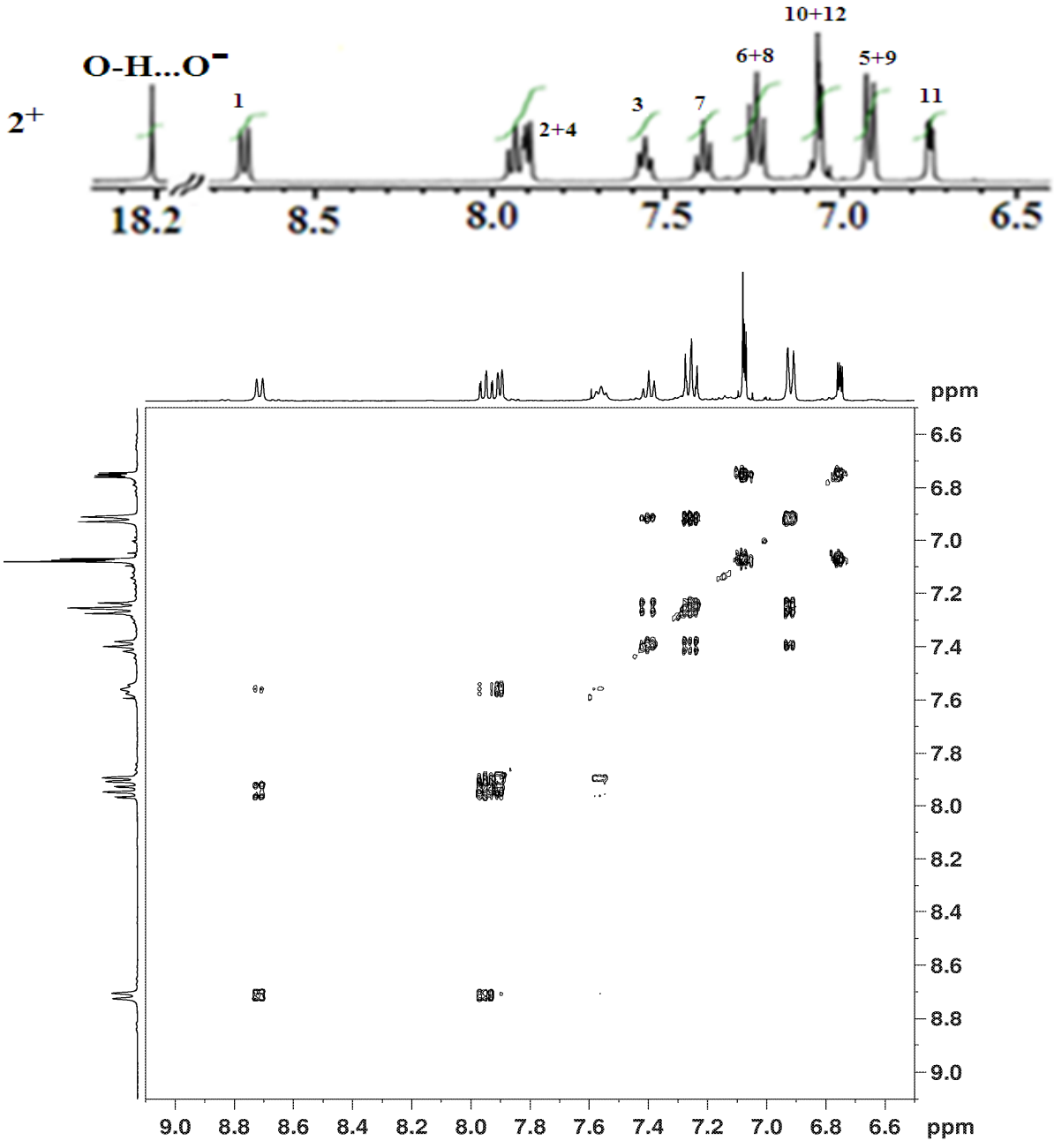


Fig. S5 ^{1}H-NMR and ^{1}H-^{1}H COSY NMR spectra of **2**$^{+}$ (in CD_3CN).

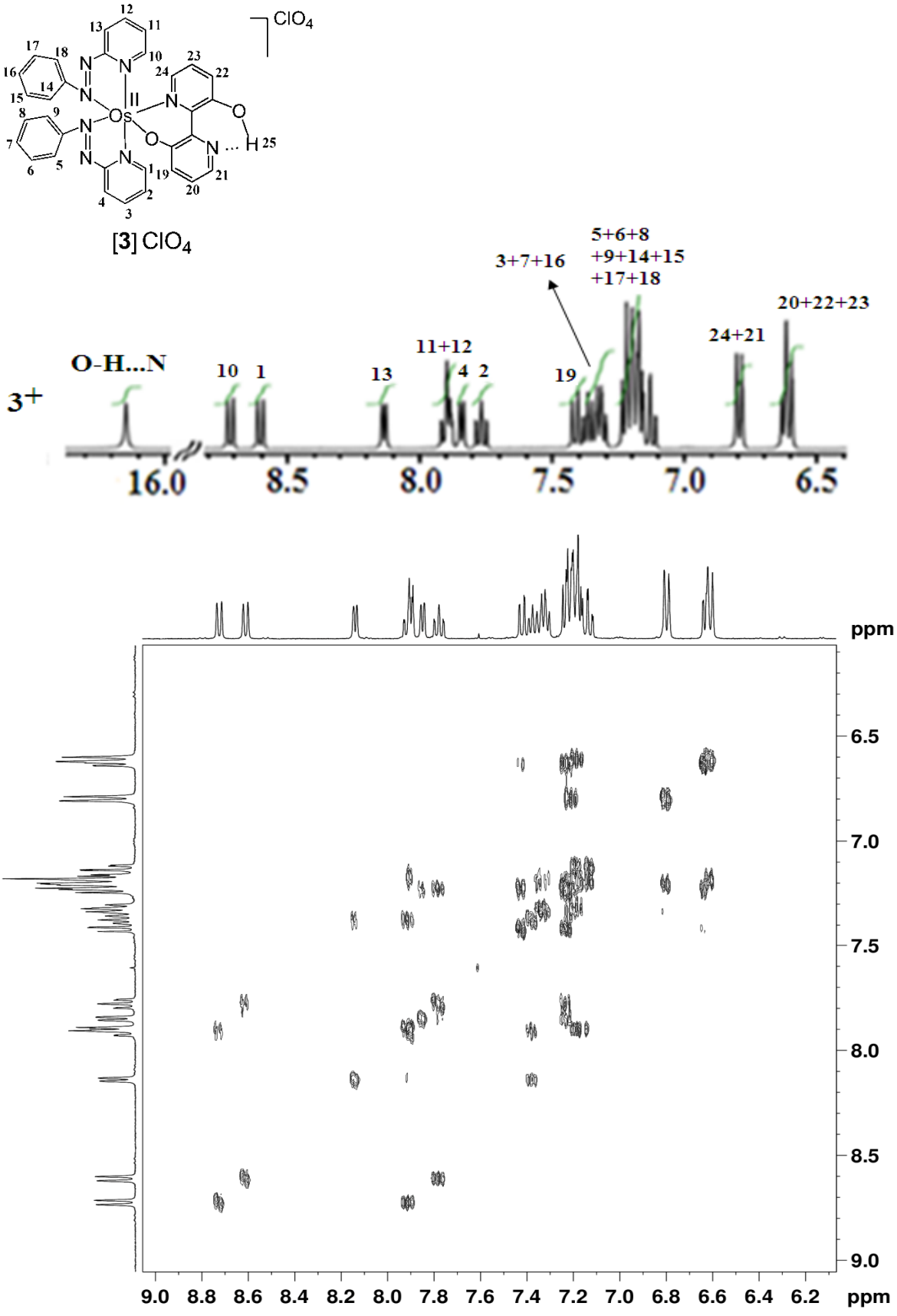


Fig. S6 ^{1}H-NMR and ^{1}H-^{1}H COSY NMR spectra of $\mathbf{3}^{+}$ (in CD_3CN).

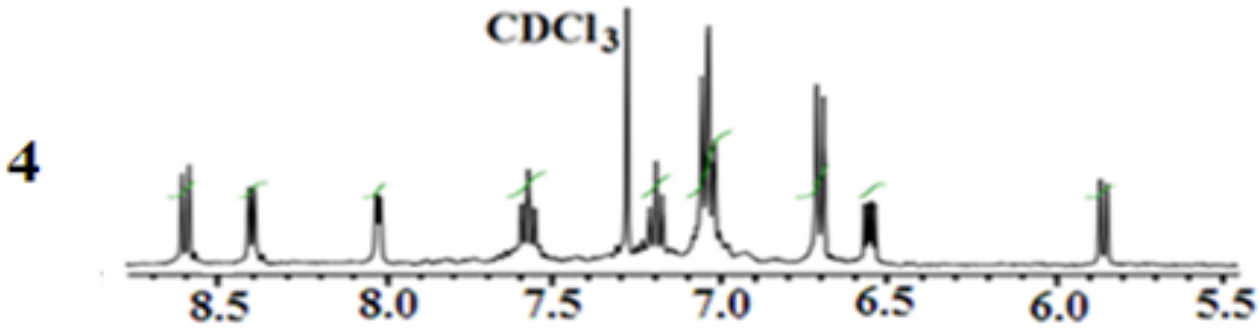
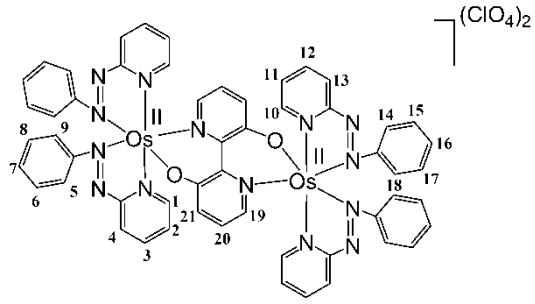


Fig. S7 ^{1}H-NMR spectra of **4** (in $CDCl_3$).



[**5a**](ClO$_4$)$_2$
ΛΔ (*meso*)

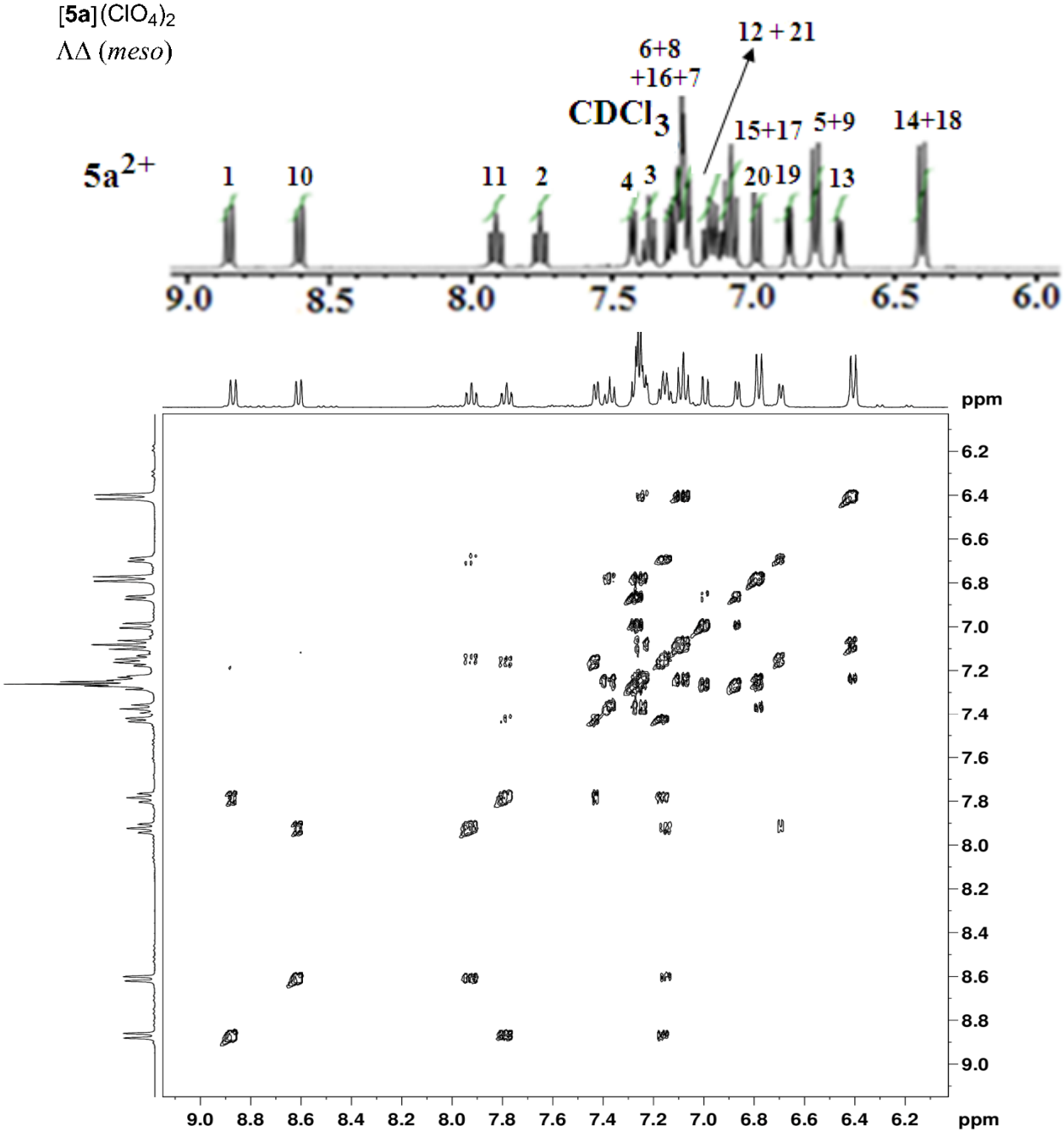


Fig.S8 ^{1}H-NMR and ^{1}H-^{1}H COSY NMR spectra of **5a**$^{2+}$ (in $CDCl_3$).

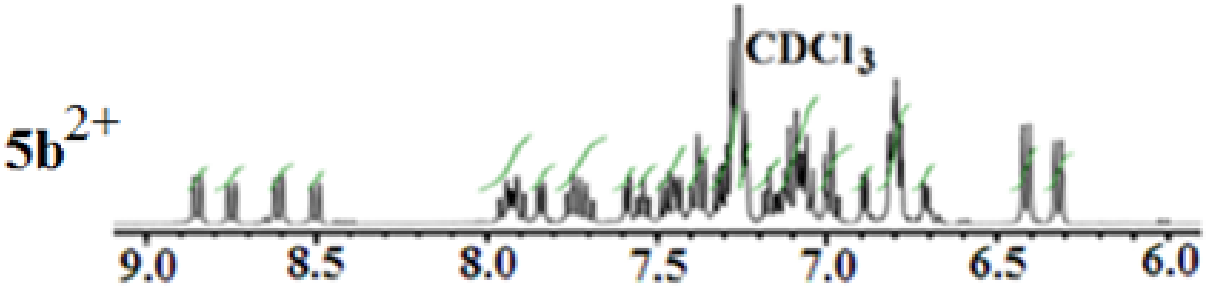
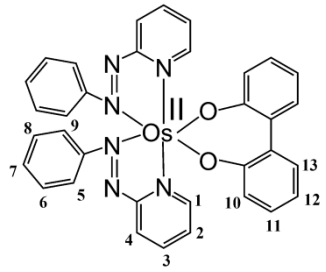
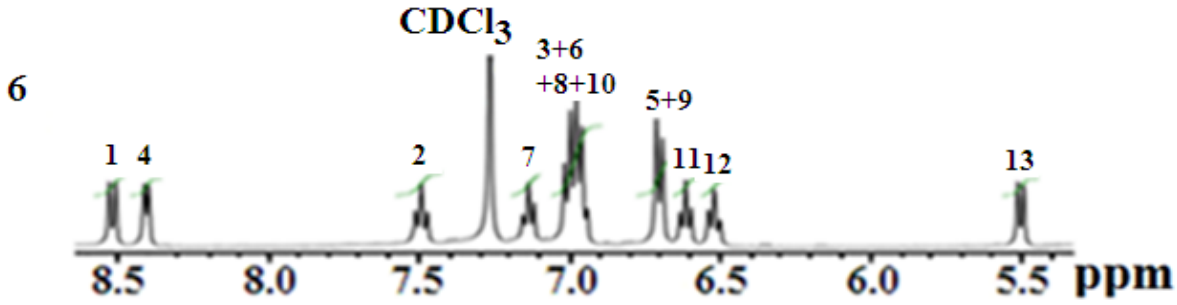


Fig. S9 ^{1}H-NMR spectra of **5b**$^{2+}$ (in $CDCl_3$).



6



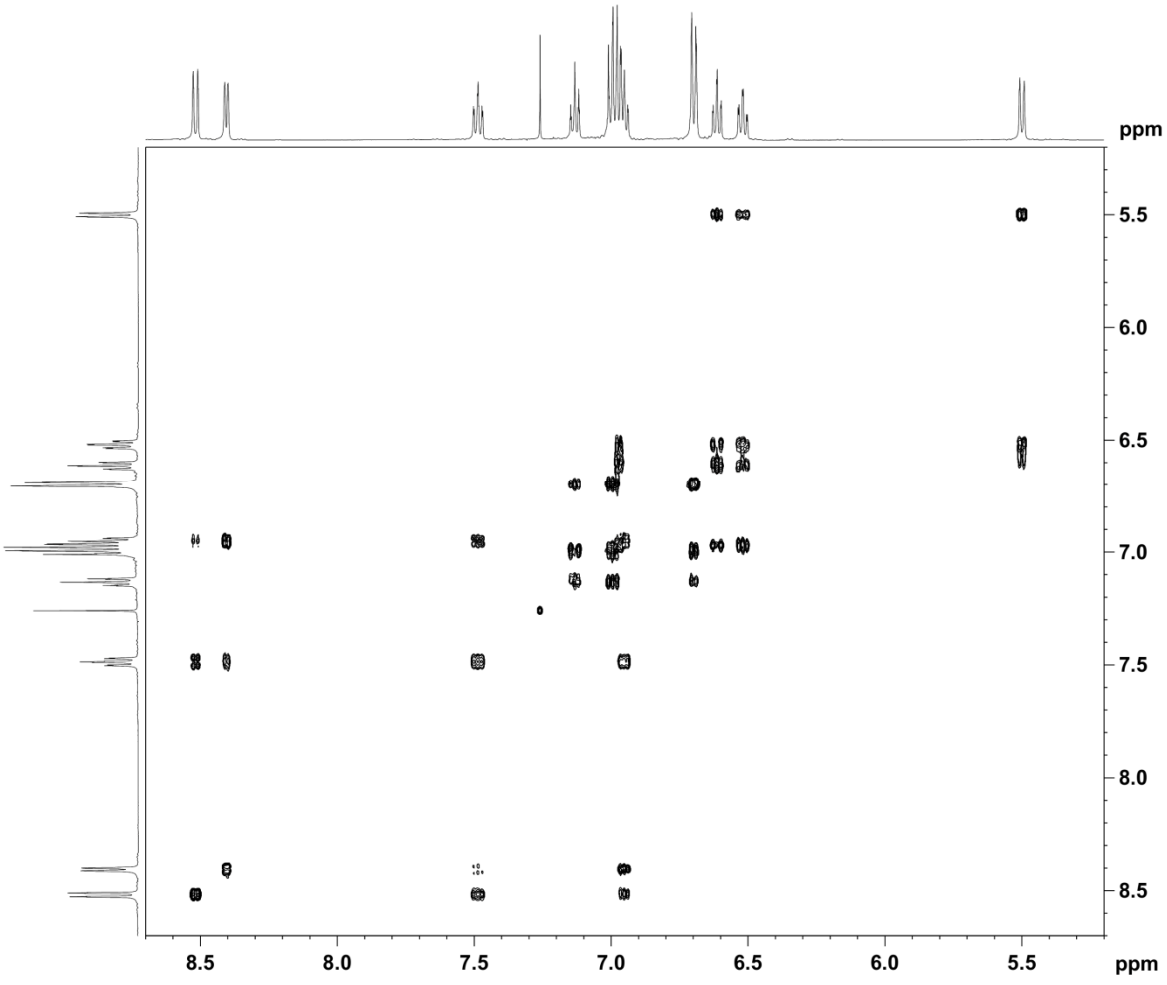


Fig. S10 ^{1}H-NMR and ^{1}H-^{1}H COSY NMR spectra of **6 (**in $CDCl_3$).

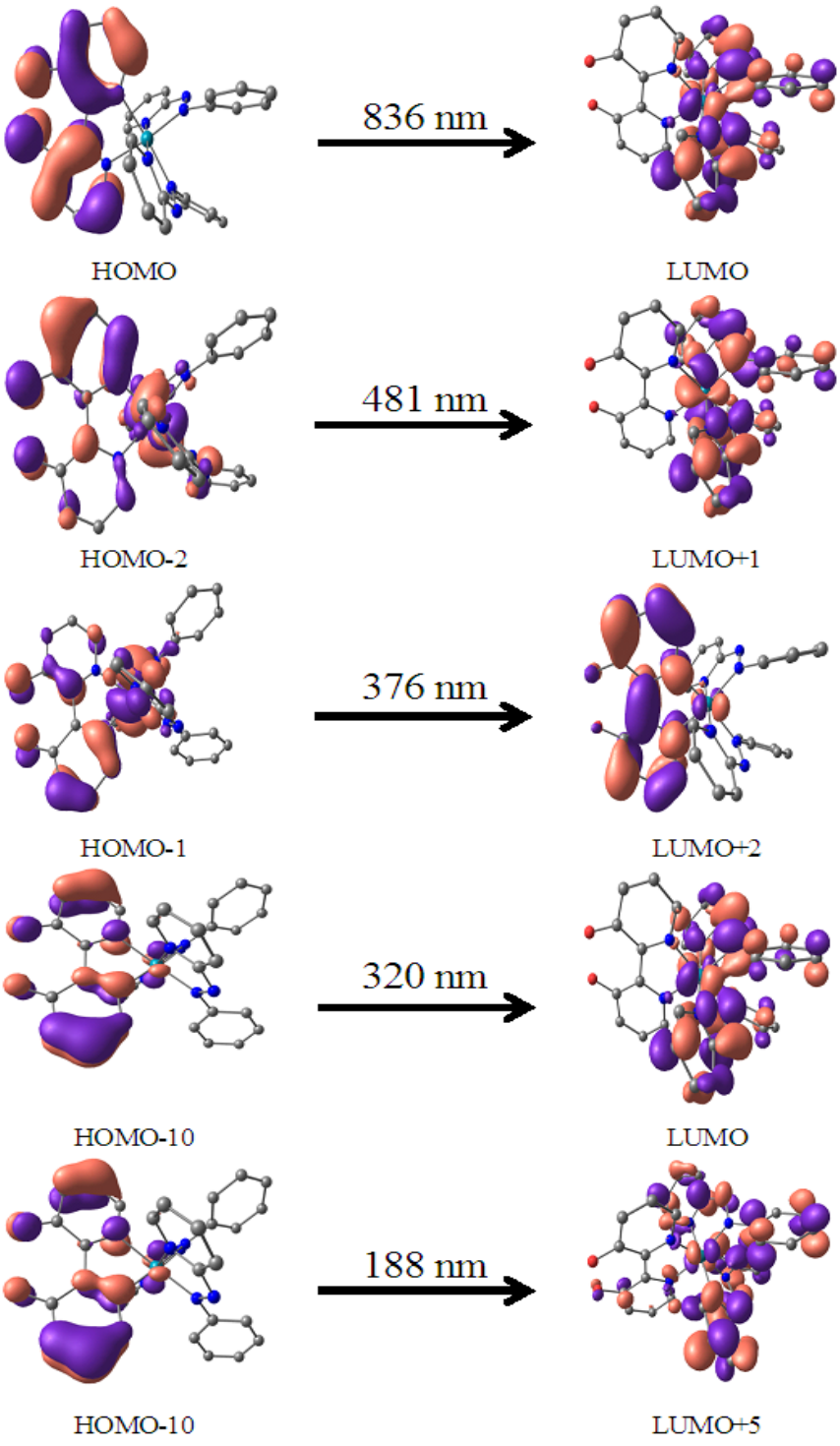


Fig. S11 TD-DFT computed molecular orbitals corresponding to electronic absorptions of $\mathbf{2}^{+}$.

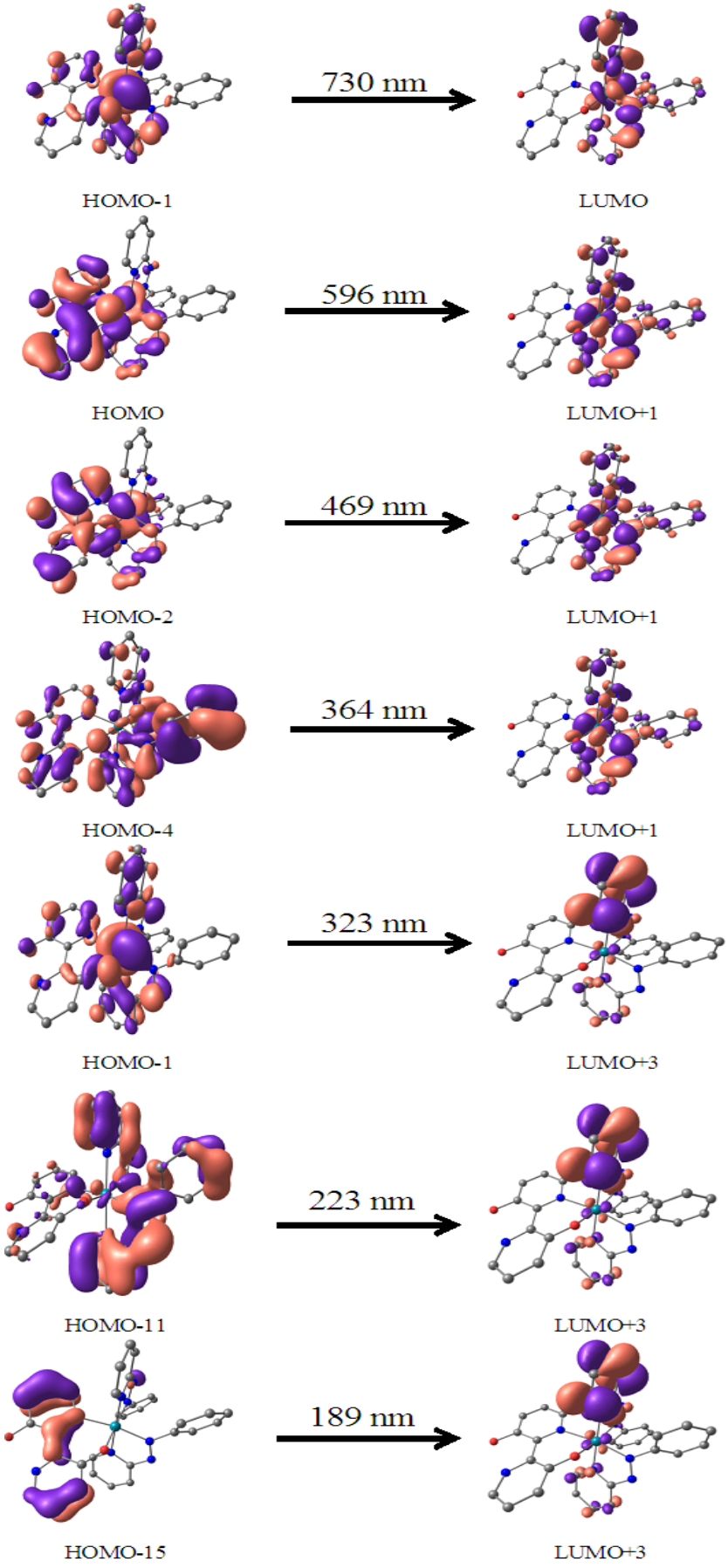


Fig. S12 TD-DFT computed molecular orbitals corresponding to electronic absorptions of $\mathbf{3}^{+}$.

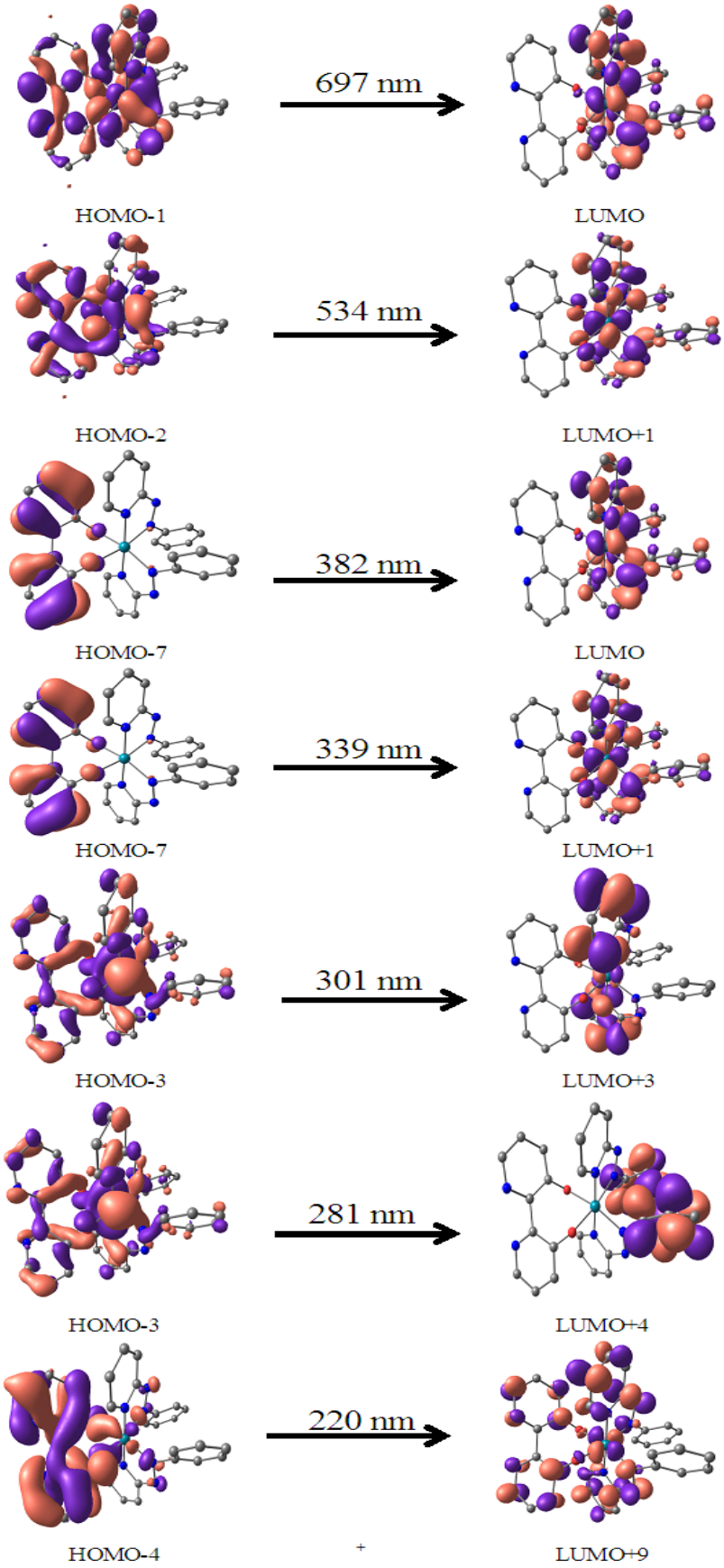


Fig. S13 TD-DFT computed molecular orbitals corresponding to electronic absorptions of **4**.

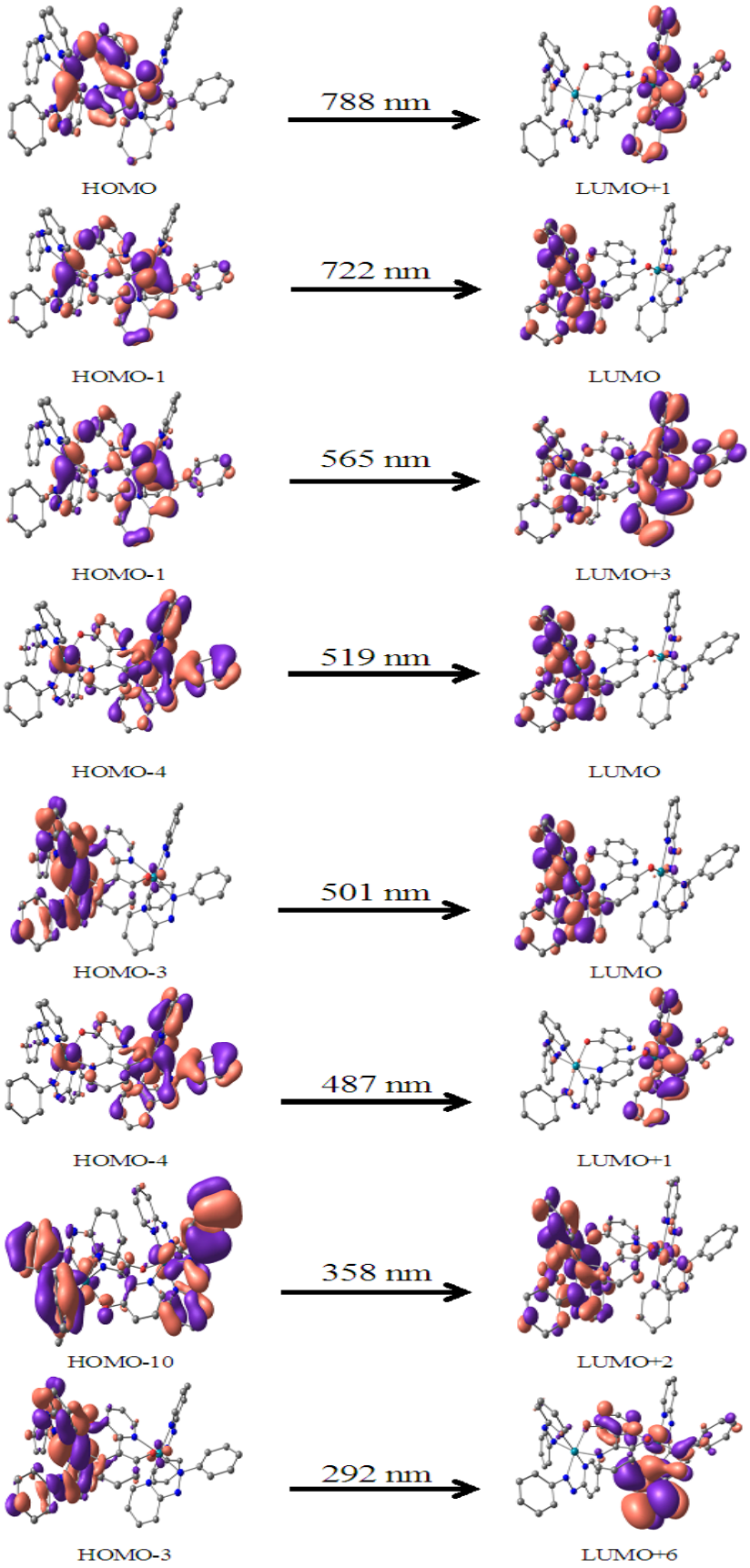


Fig. S14 TD-DFT computed molecular orbitals corresponding to electronic absorptions of **5a**$^{2+}$.

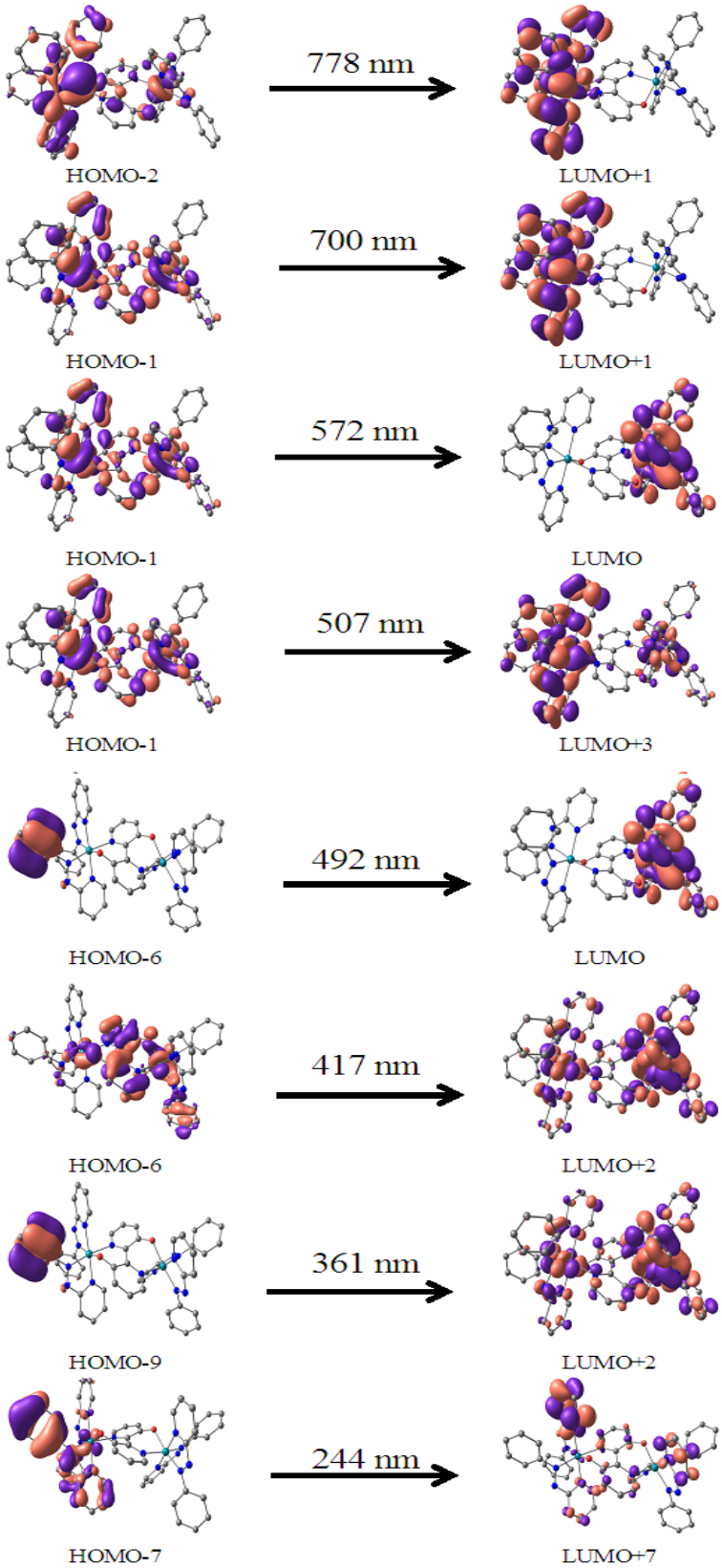


Fig. S15 TD-DFT computed molecular orbitals corresponding to electronic absorptions of **5b**$^{2+}$.

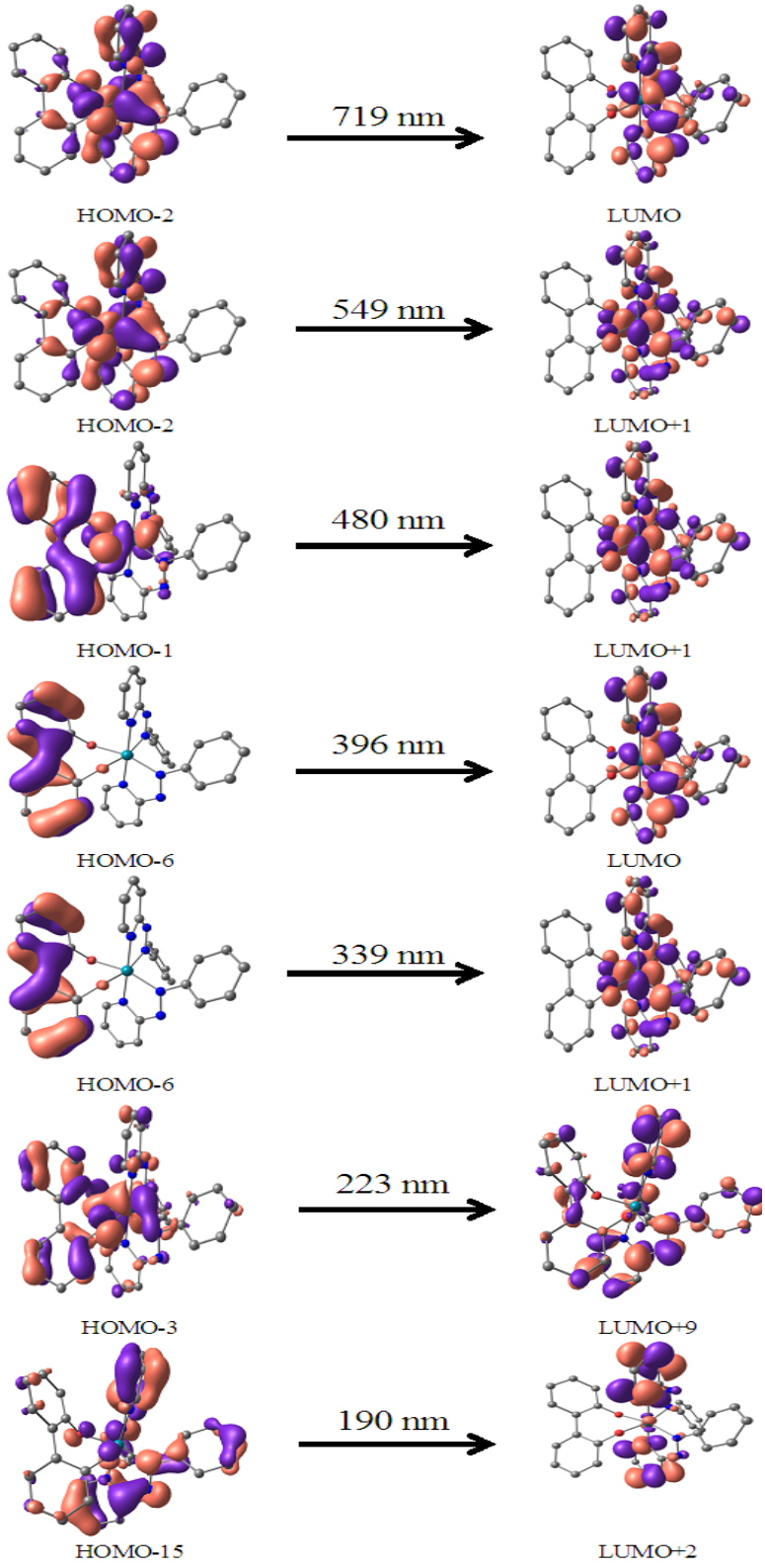


Fig. S16 TD-DFT computed Molecular orbitals corresponding to electronic absorptions of **6**.

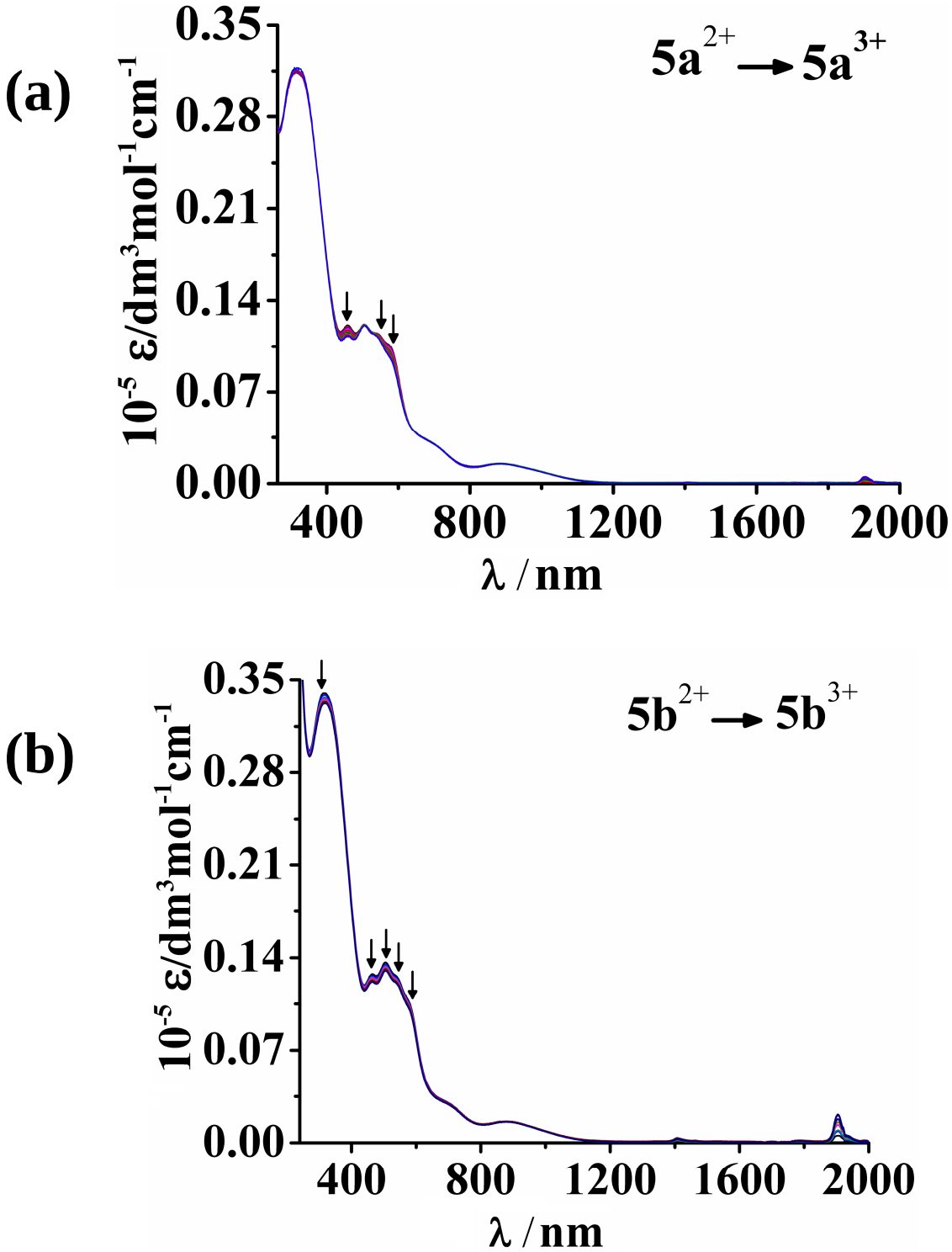


Fig. S17 UV-vis-NIR spectroelectrochemical plots for the conversions of (a) **5a**$^{2+}$→**5a**$^{3+}$ and (b) **5b**$^{2+}$→**5b**$^{3+}$ (10^{-5} M) on sequential additions of $(NH_4)_2Ce(NO_3)_6$ (CAN) (10^{-3} M) up to one equivalent in CH_3CN.

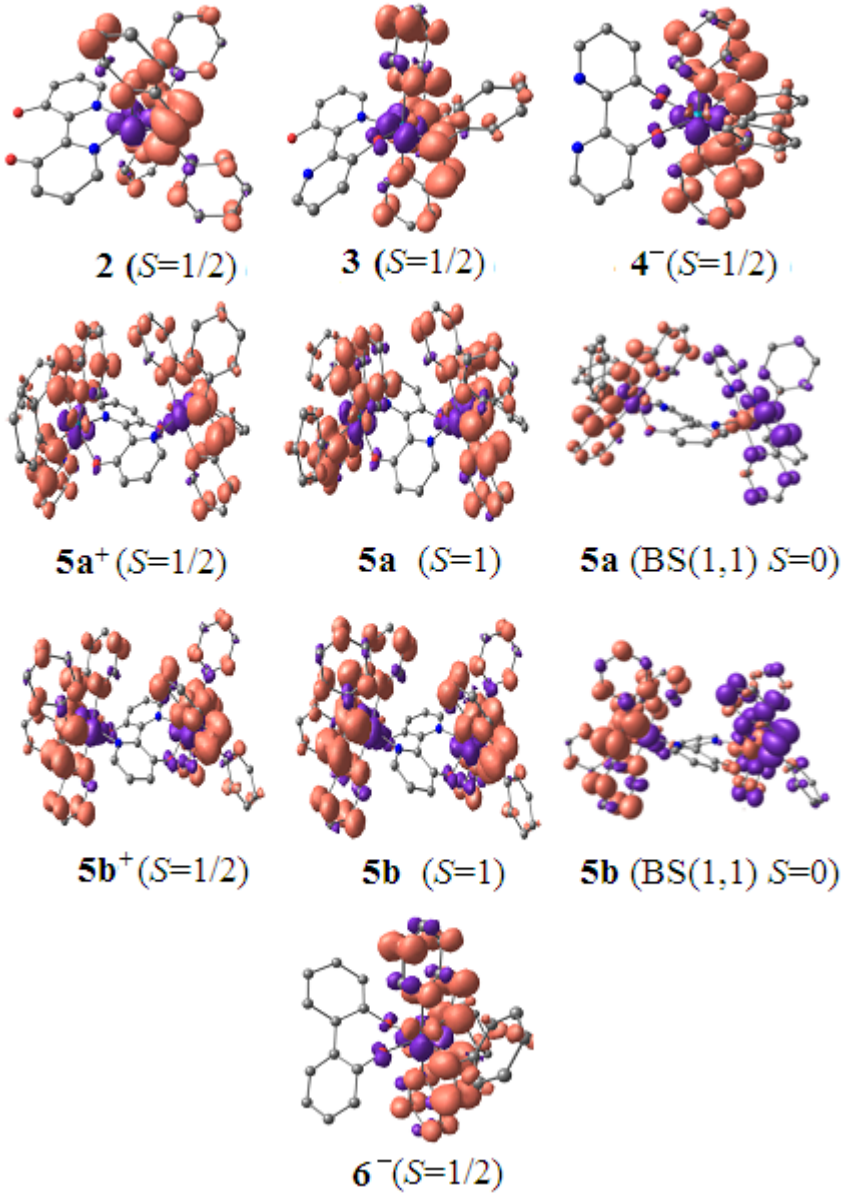


Fig. S18 Mulliken spin density plots (uB3LYP/6-31G*/LANL2DZ) of $\mathbf{2}^n$, $\mathbf{3}^n$, $\mathbf{4}^n$, $\mathbf{5a}^n$, $\mathbf{5b}^n$ and $\mathbf{6}^n$.

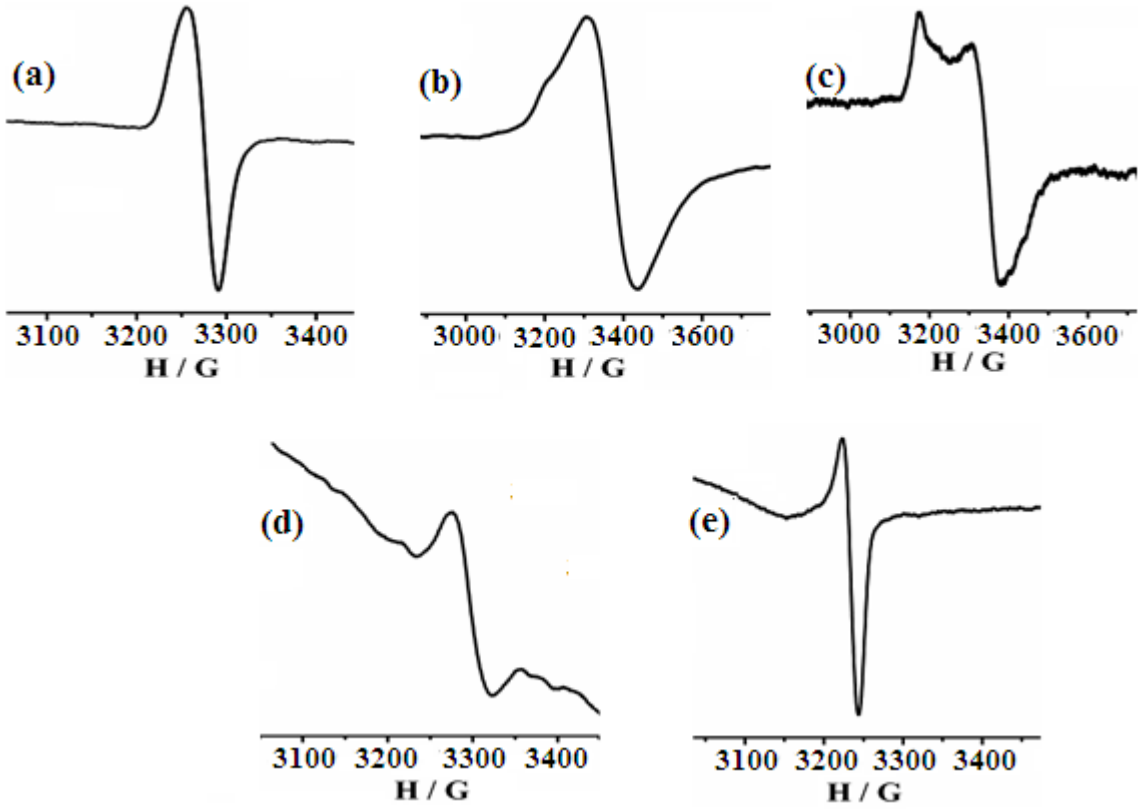


Fig. S19 EPR spectra of (a) **2**, (b) **3** (c) **5a**$^{+}$ (d) **5b**$^{+}$, (e) **6**$^{-}$.

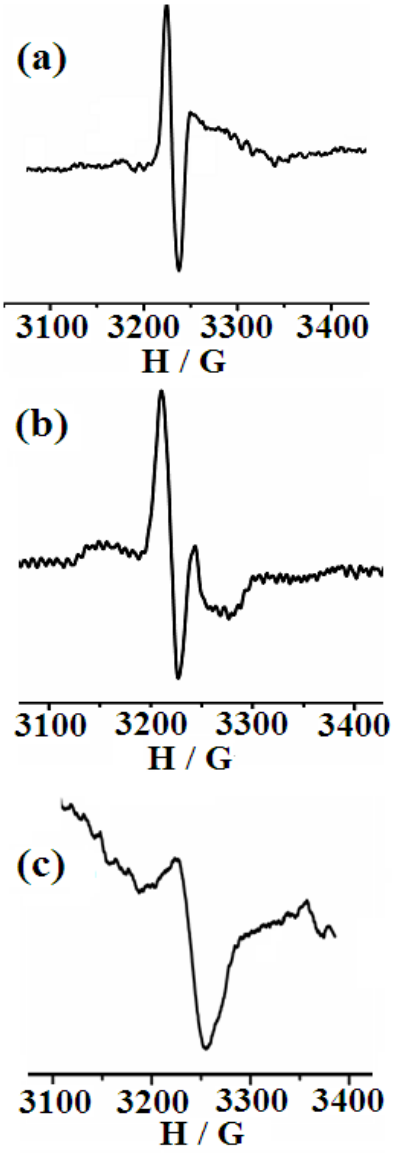


Fig. S20 EPR spectra of coulometrically generated (a) $\mathbf{2}^{2+}$, (b) $\mathbf{5a}^{3+}$ and (c) $\mathbf{6}^{+}$.

Table S1 Experimental and DFT calculated (B3LYP/6-31G*/LANL2DZ) selected bond angles (deg) for $\mathbf{2}^{+}$ and $\mathbf{3}^{+}$

$\mathbf{2}^{+}$			$\mathbf{3}^{+}$		
Bond angle (deg)	X-ray	DFT	Bond angle (deg)	X-ray	DFT
N1-Os1-N2	77.25(14)	76.967	N1-Os1-O2	85.52(9)	84.935
N1-Os1-N3	95.54(14)	94.037	N1-Os1-N3	96.46(10)	94.697
N1-Os1-N5	169.94(14)	168.920	N1-Os1-N5	171.81(10)	169.673
N1-Os1-N6	98.65(14)	98.364	N1-Os1-N6	94.59(10)	97.606
N1-Os1-N8	85.98(14)	85.066	N1-Os1-N8	89.72(10)	86.746
N2-Os1-N3	89.58(14)	85.350	O2-Os1-N3	86.48(9)	88.777
N2-Os1-N5	97.76(14)	98.807	O2-Os1-N5	91.74(9)	90.879
N2-Os1-N6	169.74(14)	168.383	O2-Os1-N6	166.97(10)	165.897
N2-Os1-N8	94.46(14)	93.650	O2-Os1-N8	90.71(10)	90.683
N3-Os1-N5	75.54(15)	75.304	N3-Os1-N5	75.64(11)	75.744
N3-Os1-N6	100.23(14)	105.721	N3-Os1-N6	106.43(10)	104.771
N3-Os1-N8	175.92(14)	178.789	N3-Os1-N8	172.98(9)	178.408
N5-Os1-N6	87.68(14)	87.624	N5-Os1-N6	89.81(10)	88.747
N5-Os1-N8	103.24(14)	105.547	N5-Os1-N8	98.04(11)	102.770
N6-Os1-N8	75.77(14)	75.235	N5-Os1-N1	171.81(10)	169.673
O1-H1···O2	157.4	171.488	O1-H1···N2	148.0	148.665
C4-O1-H1	109.5	110.914	C4-O1-H1	109.5	106.459

Table S2 Experimental and DFTcalculated (B3LYP/6-31G*/LANL2DZ) selected bond angles (deg) for [**5a**]$(ClO_4)_2 \cdot CH_2Cl_2$ and 2[**6**] .

5a^{2+}			2[**6**]		
Bond angle (deg)	X-ray	DFT	Bond angle (deg)	X-ray	DFT
N1-Os1-N3	76.0(3)	76.275	Molecule A		
N1-Os1-N4	103.9(3)	105.541	N1-Os1-N3	77.15(12)	76.326
N1-Os1-N6	172.5(3)	175.779	N1-Os1-N4	104.89(12)	104.327
N1-Os1-N7	100.2(3)	97.089	N1-Os1-N6	177.78(11)	179.189
N1-Os1-O2	85.6(2)	88.483	N1-Os1-O1	90.97(11)	89.057
N3-Os1-N4	96.5(3)	94.674	N1-Os1-O2	86.90(10)	90.365
N3-Os1-N6	96.5(3)	99.747	N3-Os1-N4	102.33(12)	100.242
N3-Os1-N7	166.2(2)	167.051	N3-Os1-N6	101.37(12)	104.068
N3-Os1-O2	85.4(2)	87.924	N3-Os1-O1	167.30(11)	164.212
N4-Os1-N6	76.3(3)	75.995	N3-Os1-O2	89.97(11)	89.679
N4-Os1-N7	97.2(3)	97.845	N4-Os1-N6	77.00(12)	76.325
N4-Os1-O2	170.5(3)	165.961	N4-Os1-O1	84.91(11)	89.015
N6-Os1-O2	94.2(3)	89.970	N4-Os1-O2	164.49(10)	163.81
N6-Os1-N7	87.1(3)	86.534	N6-Os1-O1	90.36(11)	90.475
N7-Os1-O2	81.1(2)	80.721	N6-Os1-O2	91.46(11)	88.930
N8-Os2-N10	76.4(3)	76.053	O1-Os1-O2	84.83(10)	84.403
N8-Os2-N11	101.9(3)	104.403	Molecule B		
N8-Os2-N13	174.8(3)	176.395	N7-Os2-N9	76.54(12)	-
N8-Os2-N14	97.2(2)	94.894	N7-Os2-N10	105.15(12)	-

N8-Os2-O1	82.3(2)	80.095	N7-Os2-N12	178.25(11)	-
N10-Os2-N11	102.3(3)	99.854	N7-Os2-O3	89.60(11)	-
N10-Os2-N13	99.1(3)	100.343	N7-Os2-O4	88.47(11)	-
N10-Os2-N14	166.6(3)	166.115	N9-Os2-N10	98.56(12)	-
N10-Os2-O1	85.1(3)	86.607	N9-Os2-N12	103.64(12)	-
N11-Os2-N13	76.2(3)	76.089	N9-Os2-O3	164.89(11)	-
N11-Os2-N14	90.4(2)	92.538	N9-Os2-O4	88.64(11)	-
N11-Os2-O1	172.1(2)	172.817	N10-Os2-N12	76.57(12)	-
N13-Os2-N14	87.8(2)	88.641	N10-Os2-O3	90.78(11)	-
N13-Os2-O1	100.1(3)	99.781	N10-Os2-O4	165.73(11)	-
N14-Os2-O1	82.4(2)	81.409	N12-Os2-O3	90.03(11)	-
			N12-Os2-O4	89.80(11)	-
			O3-Os2-O4	84.95(9)	-

Table S3 TD-DFT (B3LYP/6-31G*/LANL2DZ/CPCM/CH_3CN) calculated electronic transitions for $\mathbf{2}^+$, $\mathbf{3}^+$, **4**, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$ and **6**

λ /nm (expt.) (ε /$dm^3mol^{-1}cm^1$)	λ /nm (DFT) (*f*)	Transition	Character
		$\mathbf{2}^+(S = 0)$	
818 (220)	836 (0.0043)	HOMO→LUMO(0.70)	HL(π) →pap(π*)/ Os(dπ)
508(2620)	481(0.190)	HOMO-2→LUMO+1(0.61)	Os(dπ)/pap(π)→pap(π*)/ Os(dπ)
403(2420)	418(0.232)	HOMO-1→LUMO+2(0.68)	HL(π)→ HL(π*) /pap(π*)
345(5040)	376(0.329)	HOMO-5→LUMO+1(0.41)	HL(π)/ Os(dπ)→pap(π*)/ Os(dπ)
		HOMO-1→LUMO+2(0.13)	HL(π)→ HL(π*) /pap(π*)
303(4760)	320(0.105)	HOMO-10→LUMO (0.46)	HL(π) → pap(π*)
		HOMO-2→LUMO+4 (0.12)	Os(dπ)/pap(π)→pap(π*)
224(7080)	188(0.155)	HOMO-10→LUMO+5 (0.26)	HL(π) →pap(π*)
		HOMO-9→LUMO+10 (0.24)	pap(π)→pap(π*)/ HL(π*)
		$\mathbf{3}^+$ ($S = 0$)	
707(1330)	730(0.014)	HOMO-1→LUMO(0.59)	Os(dπ)/pap(π)→pap(π*)
561(5150)	596(0.045)	HOMO→LUMO+1(0.44)	HL(π)/ Os(dπ)→pap(π*)/ Os(dπ)
		HOMO→LUMO (0.23)	HL(π)/ Os(dπ)→pap(π*)
456(6740)	469(0.146)	HOMO-2→LUMO+1(0.55)	HL(π)/ Os(dπ)→pap(π*)/ Os(dπ)
384(13660)	364(0.164)	HOMO-4→LUMO+1(0.61)	pap(π)/ HL(π)→pap(π*)/ Os(dπ)
333(19620)	323(0.171)	HOMO-1→LUMO+3(0.64)	Os(dπ)/pap(π)→pap(π*)
268(15950)	223(0.116)	HOMO-11→LUMO+3(0.45)	pap(π)→ pap(π*)
		HOMO-9→LUMO+5(0.24)	pap(π)→ HL(π*)
223(30840)	189(0.130)	HOMO-15→LUMO+3(0.23)	HL(π)/ pap(π)→pap(π*)
		HOMO-6→LUMO+13(0.15)	pap(π)→ HL(π*)/ pap(π*)
		HOMO-10→LUMO+6(0.14)	HL(π)→pap(π*)
		4($S = 0$)	
622(4810)	697(0.038)	HOMO-1→LUMO(0.44)	L(π)/Os(dπ) /pap(π)→pap(π*)
		HOMO-2→LUMO+1(0.33)	Os(dπ)/L(π) /pap(π) →pap(π*)/Os(dπ)
516(8780)	534(0.127)	HOMO-2→LUMO+1(0.58)	Os(dπ) /L(π) /pap(π)→pap(π*)/Os(dπ)
388(13870)	382(0.141)	HOMO-7→LUMO(0.70)	L(π) →pap(π*)
340(22350)	339(0.117)	HOMO-7→LUMO+1(0.64)	L(π)→pap(π*)/Os(dπ)
306(26210)	301(0.165)	HOMO-3→LUMO+3(0.60)	Os(dπ) / pap(π)→pap(π*)
		HOMO-16→LUMO(0.24)	pap(π)→pap(π*)
284(24490)	281(0.081)	HOMO-3→LUMO+4(0.55)	Os(dπ) / pap(π)→pap(π*)
222(46320)	220(0.148)	HOMO-4→LUMO+9(0.40)	L(π) →pap(π*)/L(π*)
		HOMO-6→LUMO+7(0.17)	L(π) →pap(π*)
		$\mathbf{5a}^{2+}$($S = 0$)	
884(1860)	788(0.009)	HOMO→LUMO+1(0.52)	pap(π)/Os(dπ)/L(π)→pap(π*)/Os(dπ)
		HOMO→LUMO(0.31)	pap(π)/Os(dπ) /L(π)→pap(π*)
691(3640)	722(0.017)	HOMO-1→LUMO(0.46)	Os(dπ) /L(π) /pap(π)→pap(π*)

		HOMO→LUMO(0.19)	pap(π)/Os(dπ)→pap(π*)
574(12140)	565(0.046)	HOMO-1→LUMO+3(0.30)	Os(dπ) /L(π) /pap(π)→pap(π*)/Os(dπ)
		HOMO→LUMO+3(0.20)	pap(π)/Os(dπ)→pap(π*)/Os(dπ)
542(12910)	519(0.057)	HOMO-4→LUMO(0.31)	Os(dπ) /pap(π)→ pap(π*)
		HOMO→LUMO+3(0.30)	pap(π)/Os(dπ)→pap(π*)
506(12790)	501(0.079)	HOMO-3→LUMO(0.30)	Os(dπ) /pap(π)→ pap(π*)
		HOMO-5→LUMO+1(0.20)	Os(dπ) /pap(π)→ pap(π*)/Os(dπ)
458(12650)	487(0.089)	HOMO-4→LUMO+1(0.48)	Os(dπ) /pap(π)→ pap(π*)/Os(dπ)
		HOMO-6→LUMO+1(0.28)	pap(π)→ pap(π*)/Os(dπ)
318(35550)	358(0.344)	HOMO-10→LUMO+2(0.34)	pap(π)→ pap(π*)/Os(dπ)/L(π*)
		HOMO-8→LUMO+3(0.34)	pap(π)→ pap(π*)/Os(dπ)
220(57320)	292(0.065)	HOMO-3→LUMO+6(0.27)	Os(dπ) /pap(π)→ pap(π*)
		HOMO-18→LUMO(0.12)	pap(π)→ pap(π*)
		5b^{2+}(S = 0)	
884(1600)	778(0.002)	HOMO-2→LUMO+1(0.52)	Os(dπ) /pap(π)→ pap(π*)
694(3160)	700(0.018)	HOMO-1→LUMO+1(0.44)	Os(dπ) /L(π) /pap(π)→ pap(π*)
		HOMO→LUMO+1(0.31)	Os(dπ) /pap(π)→ pap(π*)
579(10420)	572(0.058)	HOMO-1→LUMO(0.32)	Os(dπ) /L(π) /pap(π)→ pap(π*)
		HOMO-2→LUMO(0.18)	Os(dπ) /pap(π)→ pap(π*)
544(12350)	507(0.049)	HOMO-1→LUMO+3(0.37)	Os(dπ) /L(π) /pap(π)→pap(π*)/Os(dπ)
		HOMO-4→LUMO+3(0.25)	Os(dπ) /pap(π) /L(π) →pap(π*)
509(13370)	492(0.068)	HOMO-6→LUMO(0.45)	Os(dπ) /L(π) /pap(π)→pap(π*)
		HOMO-5→LUMO(0.26)	Os(dπ) /pap(π)→pap(π*)
463(12460)	417(0.094)	HOMO-6→LUMO+2(0.67)	Os(dπ) /L(π) /pap(π)→ L(π*)
310(34200)	361(0.213)	HOMO-9→LUMO+2(0.43)	pap(π)→pap(π*)/Os(dπ)
		HOMO-9→LUMO+2(0.38)	pap(π)→pap(π*)/Os(dπ)
224(55820)	244(0.045)	HOMO-7→LUMO+7(0.27)	pap(π) → pap(π*)
		HOMO-10→LUMO+6(0.26)	pap(π) → pap(π*)
		6(S = 0)	
648(4100)	719(0.029)	HOMO-2→LUMO(0.56)	pap(π)/ L′(π)/ Os(dπ)→pap(π*)/Os(dπ)
525(5910)	549(0.15)	HOMO-2→LUMO+1(0.57)	pap(π)/ L′(π)/ Os(dπ)→pap(π*)/Os(dπ)
484(4780)	480(0.097)	HOMO-1→LUMO+1(0.59)	L′(π)→pap(π*)/Os(dπ)
382(8340)	396(0.190)	HOMO-6→LUMO(0.67)	L′(π)→pap(π*)/Os(dπ)
342(13230)	339(0.168)	HOMO-6→LUMO+1(0.53)	L′(π)→pap(π*)/Os(dπ)
296(19990)	223(0.404)	HOMO-3→LUMO+9(0.42)	L′(π)/Os(dπ)/pap(π)→pap(π*)
		HOMO-2→LUMO+9(0.14)	pap(π)/ L′(π)→pap(π*)
220(42510)	190(0.201)	HOMO-15→LUMO+2(0.31)	pap(π)→pap(π*)
		HOMO-6→LUMO+11(0.20)	L′(π)→ L′(π*)/pap(π*)

Table S4 TD-DFT calculated (CPCM/CH_3CN) electronic transitions for $\mathbf{2}^+$ by multiple methods and basis set

Expt.	TZVP+LANL2DZ				6-31G*+ LANL2DZ
	PBE	PBE0	BP86	B3LYP	B3LYP
818(220)	754(0.001)	785(0.009)	745(0.001)	869(0.007)	836(0.004)
508(2620)	505(0.073)	460(0.219)	505(0.0738)	476(0.197)	481(0.190)
403(2420)	404(0.194)	429(0.162)	404(0.154)	445(0.208)	418(0.232)
345(5040)	392(0.206)	389(0.186)	393(0.214)	364(0.162)	376(0.329)
303(4760)	299(0.052)	290(0.161)	359(0.068)	303(0.145)	320(0.105)
224(7080)	237(0.069)	222(0.176)	236(0.080)	191(0.217)	188(0.155)

Table S5 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{2}^{+}$ in *S* =0 state

MO	Energy (eV)	% Composition		
		Os	pap	HL
LUMO+5	-3.228	2	92	6
LUMO+4	-4.209	4	89	7
LUMO+3	-4.287	5	86	10
LUMO+2	-4.423	6	25	70
LUMO+1	-5.714	24	72	4
LUMO	-6.113	12	84	4
HOMO	-7.443	1	4	96
HOMO-1	-8.302	1	1	99
HOMO-2	-8.740	69	18	13
HOMO-3	-8.821	39	17	45
HOMO-4	-9.334	54	40	6
HOMO-5	-9.443	33	16	50

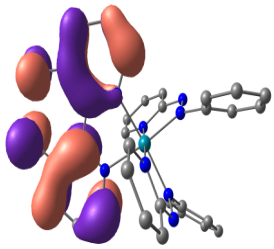
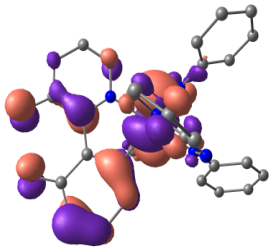
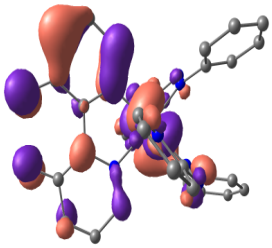
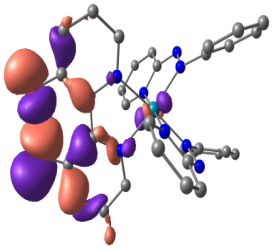
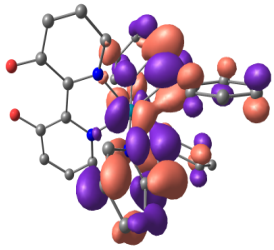
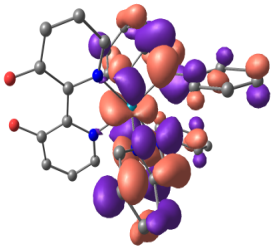
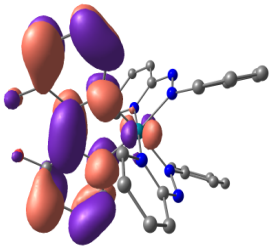
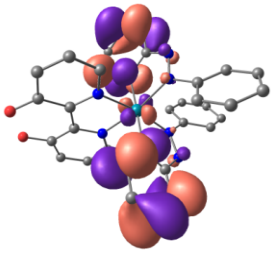
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S6 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{2}^{2+}$ in *S* =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	HL
α-MO				
LUMO+5	-6.738	4	94	2
LUMO+4	-6.902	1	42	56
LUMO+3	-7.011	1	66	92
LUMO+2	-8.124	12	13	76
LUMO+1	-8.426	19	77	3
LUMO	-8.712	7	77	16
SOMO	-11.491	65	29	6
HOMO-1	-11.807	50	38	12
HOMO-2	-11.973	13	84	3
HOMO-3	-12.015	58	36	6
HOMO-4	-12.079	8	88	3
HOMO-5	-12.086	19	78	3
β-MO				
LUMO+5	-6.745	4	92	4
LUMO+4	-6.807	2	86	12
LUMO+3	-7.946	9	7	84
LUMO+2	-8.428	19	77	3
LUMO+1	-8.674	9	82	9
LUMO	-10.416	1	2	97
HOMO	-11.479	65	28	6
HOMO-1	-11.735	53	29	18
HOMO-2	-11.964	7	90	2
HOMO-3	-12.015	58	37	5
HOMO-4	-12.073	5	93	2
HOMO-5	-12.082	18	80	2

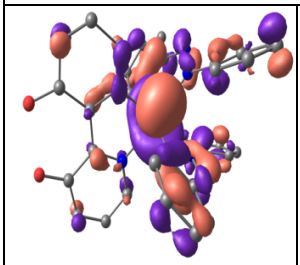
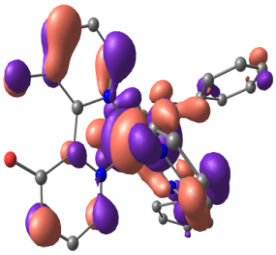
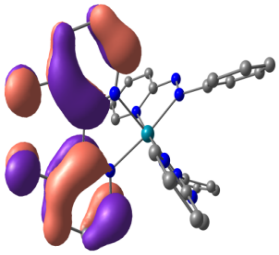
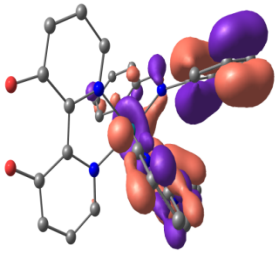
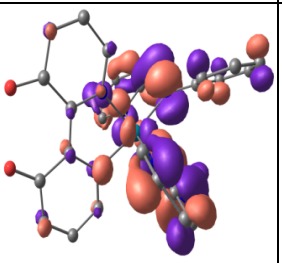
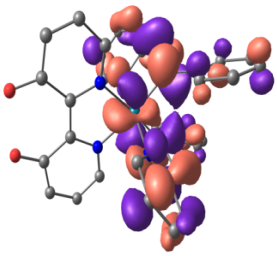
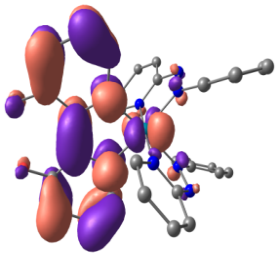
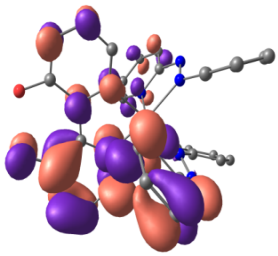
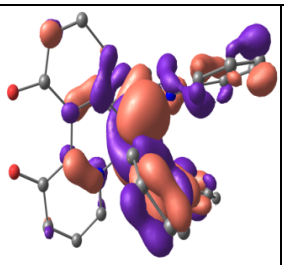
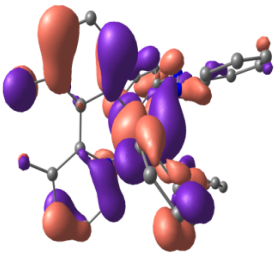
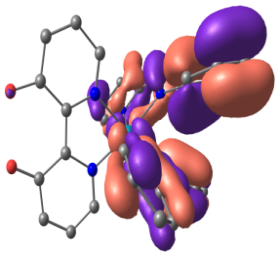
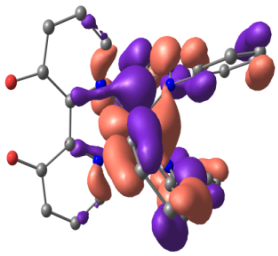
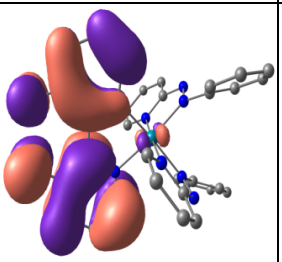
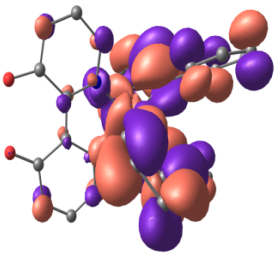
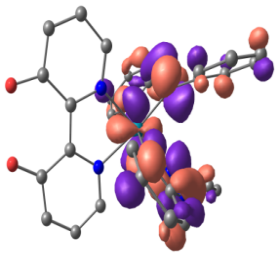
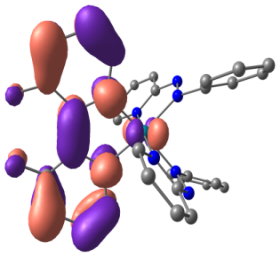
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **2** in *S* =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	HL
α-MO				
LUMO+5	-0.151	3	94	4
LUMO+4	-0.289	2	12	86
LUMO+3	-1.030	5	95	1
LUMO+2	-1.078	4	93	3
LUMO+1	-1.609	8	5	87
LUMO	-2.613	28	67	4
SOMO	-3.780	12	84	4
HOMO-1	-4.981	1	2	97
HOMO-2	-5.309	74	18	8
HOMO-3	-5.661	54	21	24
HOMO-4	-5.838	53	42	5
HOMO-5	-6.406	3	2	96
β-MO				
LUMO+5	-0.273	2	9	89
LUMO+4	-0.955	4	95	1
LUMO+3	-0.992	4	93	3
LUMO+2	-1.570	9	8	83
LUMO+1	-2.201	17	80	3
LUMO	-2.355	10	83	8
HOMO	-4.969	2	2	96
HOMO-1	-5.314	72	20	7
HOMO-2	-5.516	59	21	21
HOMO-3	-5.904	63	32	6
HOMO-4	-6.394	3	10	87
HOMO-5	-6.407	4	46	51

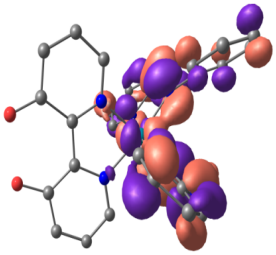
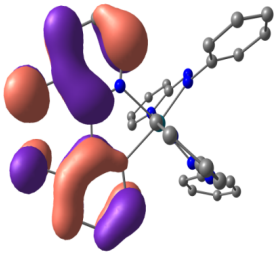
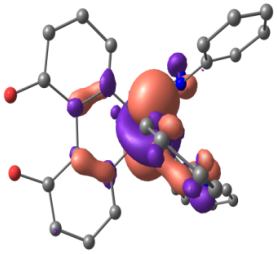
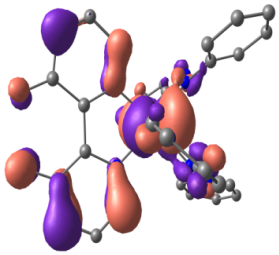
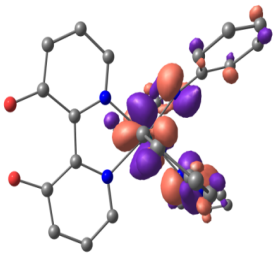
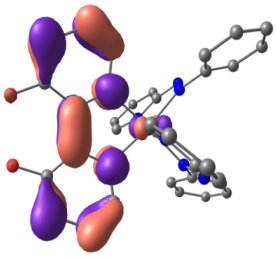
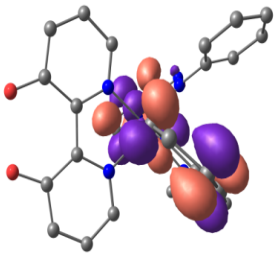
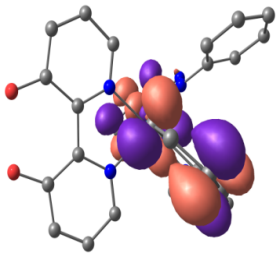
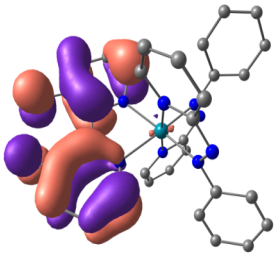
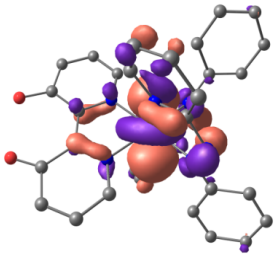
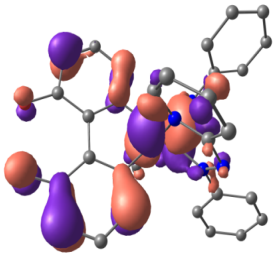
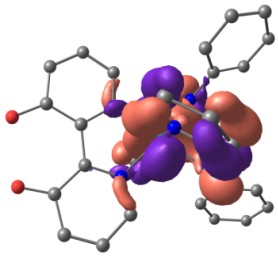
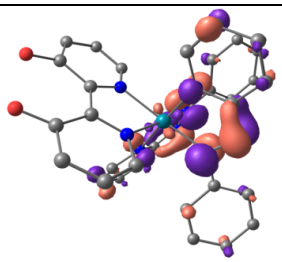
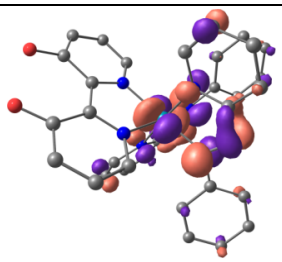
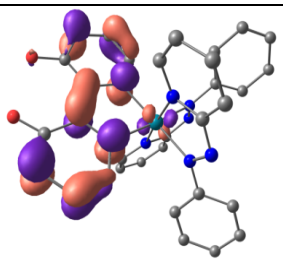
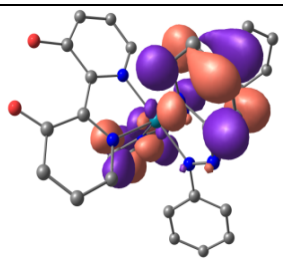
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{2}^{-}$ in S =0 state, ($E_{S=1}$-$E_{S=0}$=659 cm^{-1})

MO	Energy (eV)	% Composition		
		Os	pap	HL
LUMO+5	2.705	5	20	75
LUMO+4	2.432	3	13	84
LUMO+3	2.228	4	88	8
LUMO+2	2.111	4	87	9
LUMO+1	1.102	9	5	87
LUMO	0.831	25	71	4
HOMO	-0.547	8	88	4
HOMO-1	-2.090	72	22	6
HOMO-2	-2.359	23	6	71
HOMO-3	-2.470	50	12	38
HOMO-4	-2.661	53	42	5
HOMO-5	-3.288	0	99	1

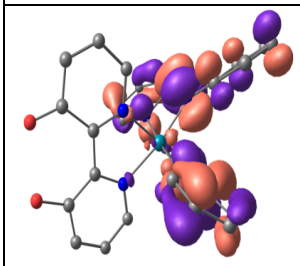
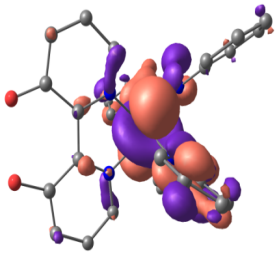
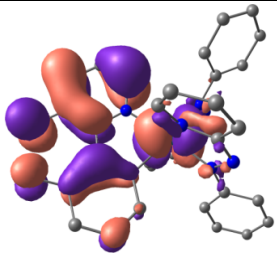
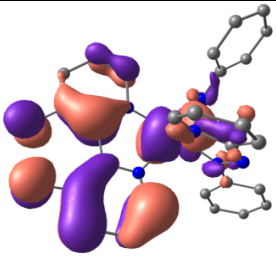
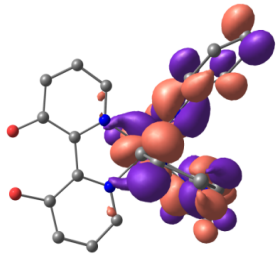
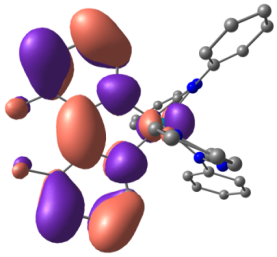
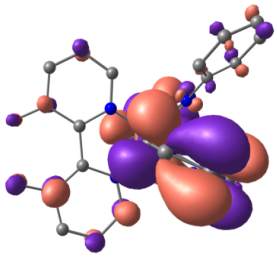
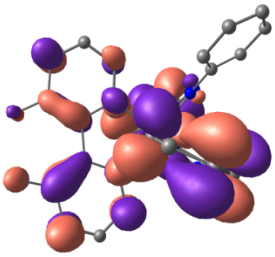
α-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{3}^{+}$ in $S = 0$ state

MO	Energy(eV)	% Composition		
		Os	pap	HL
LUMO+5	-3.319	5	12	83
LUMO+4	-3.880	3	88	8
LUMO+3	-4.013	4	89	7
LUMO+2	-4.307	3	14	83
LUMO+1	-5.205	26	64	9
LUMO	-5.804	14	82	3
HOMO	-8.057	22	21	58
HOMO-1	-8.443	61	24	15
HOMO-2	-8.842	38	18	43
HOMO-3	-8.947	53	33	15
HOMO-4	-9.437	1	52	47
HOMO-5	-9.456	1	96	3

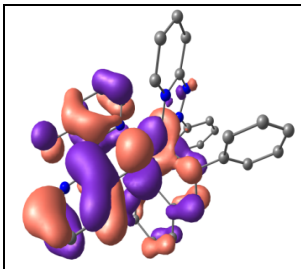
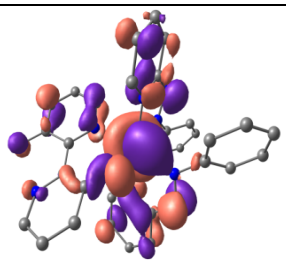
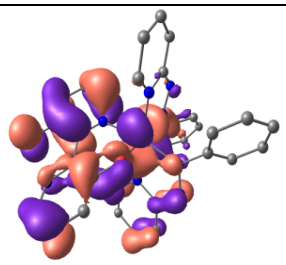
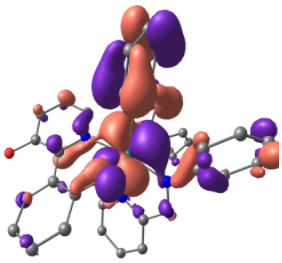
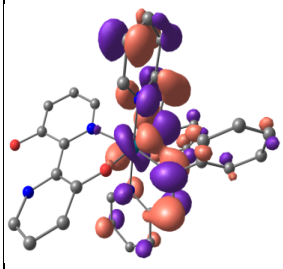
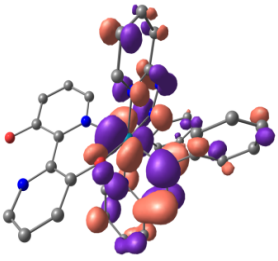
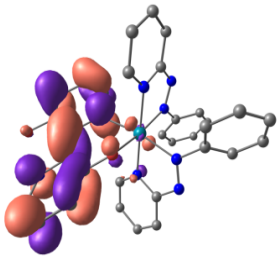
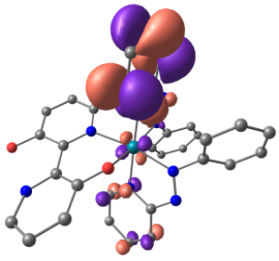
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{3}^{2+}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	HL
α-MO				
LUMO+5	-6.505	4	12	84
LUMO+4	-6.803	4	89	7
LUMO+3	-7.011	2	92	5
LUMO+2	-7.566	2	5	93
LUMO+1	-8.619	19	4	77
LUMO	-8.864	10	87	3
SOMO	-11.633	9	5	86
HOMO-1	-11.832	44	45	11
HOMO-2	-12.033	9	90	1
HOMO-3	-12.082	3	95	2
HOMO-4	-12.113	30	48	22
HOMO-5	-12.227	1	99	0
β-MO				
LUMO+5	-6.803	4	92	4
LUMO+4	-6.939	3	91	6
LUMO+3	-7.488	2	5	92
LUMO+2	-8.478	25	69	7
LUMO+1	-8.797	14	83	3
LUMO	-10.169	32	22	46
HOMO	-11.618	37	22	40
HOMO-1	-11.713	42	25	33
HOMO-2	-11.997	23	73	5
HOMO-3	-12.078	5	94	1
HOMO-4	-12.154	24	72	4
HOMO-5	-12.224	1	99	1

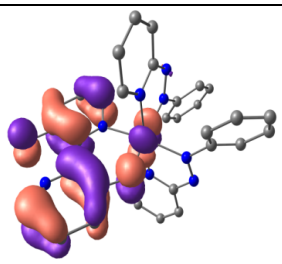
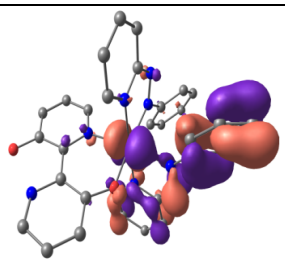
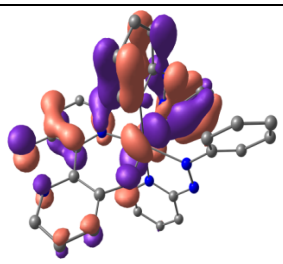
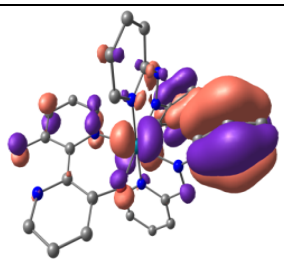
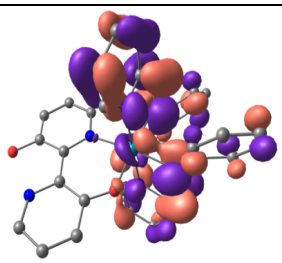
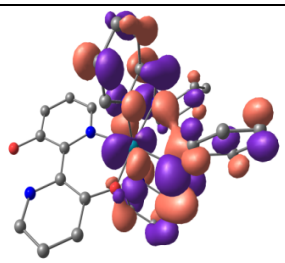
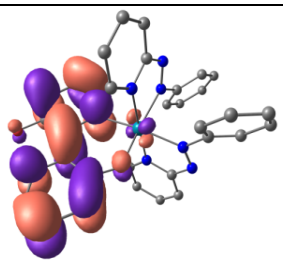
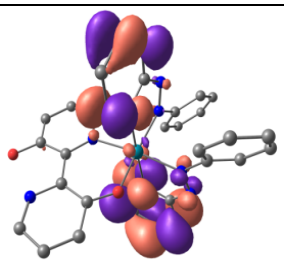
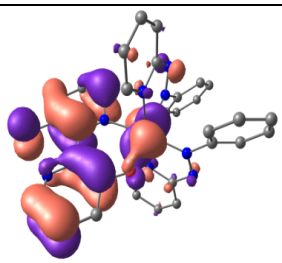
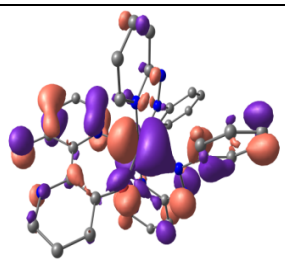
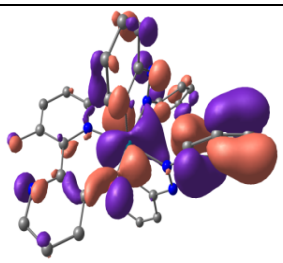
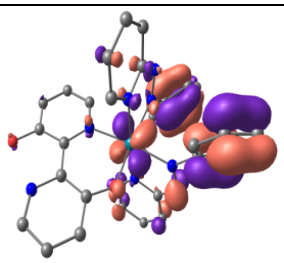
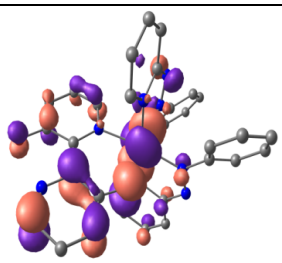
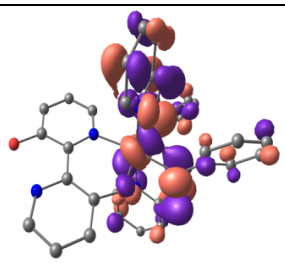
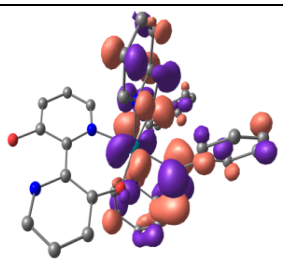
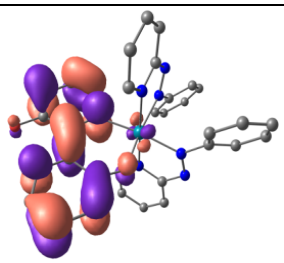
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **3** in S =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	HL
α-MO				
LUMO+5	-0.116	5	10	85
LUMO+4	-0.529	4	22	73
LUMO+3	-0.732	4	90	6
LUMO+2	-0.811	4	78	18
LUMO+1	-1.653	5	6	90
LUMO	-2.136	33	56	11
SOMO	-3.503	14	83	3
HOMO-1	-4.921	50	22	28
HOMO-2	-4.986	52	33	15
HOMO-3	-5.586	64	31	15
HOMO-4	-5.817	15	13	72
HOMO-5	-6.314	3	94	3
β-MO				
LUMO+5	-0.496	4	34	61
LUMO+4	-0.653	4	89	7
LUMO+3	-0.745	4	66	30
LUMO+2	-1.634	5	13	82
LUMO+1	-1.810	17	74	9
LUMO	-2.017	12	78	10
HOMO	-4.884	54	19	27
HOMO-1	-5.005	59	25	16
HOMO-2	-5.452	64	25	10
HOMO-3	-5.833	18	15	67
HOMO-4	-6.155	4	91	5
HOMO-5	-6.304	8	89	4

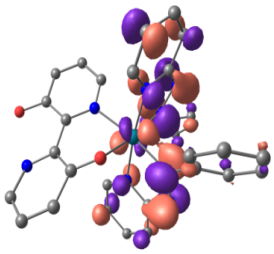
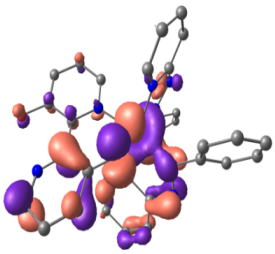
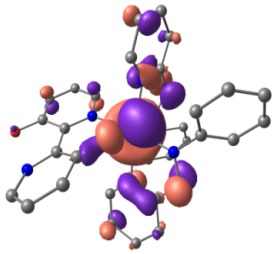
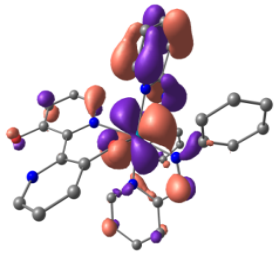
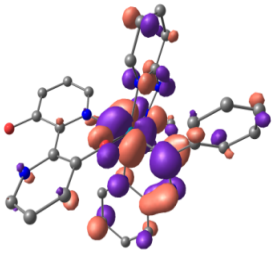
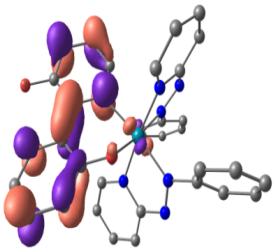
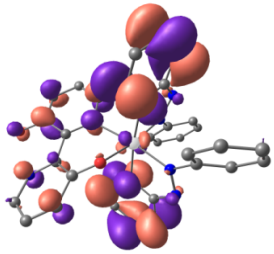
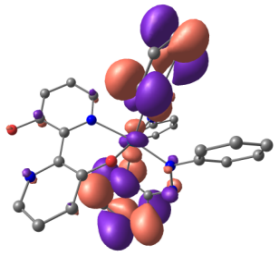
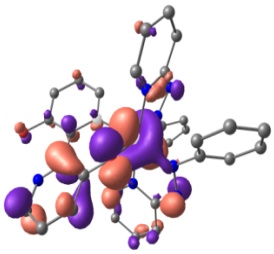
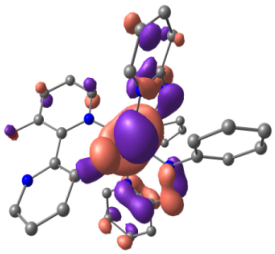
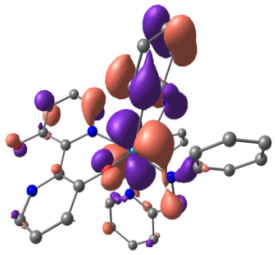
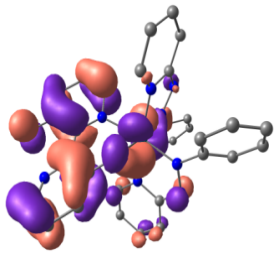
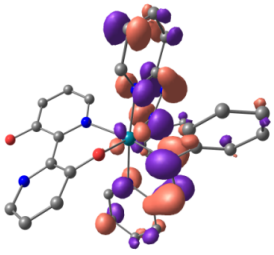
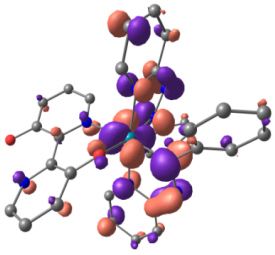
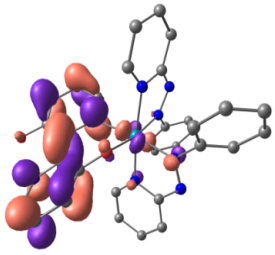
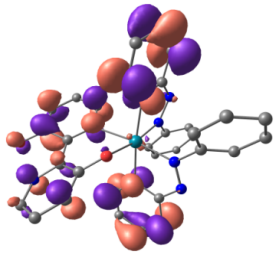
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{3}^{-}$ in S = 0 state, ($E_{S=1}$-$E_{S=0}$=1140 cm^{-1})

MO	Energy (eV)	% Composition		
		Os	pap	HL
LUMO+5	2.602	6	83	11
LUMO+4	2.545	4	48	48
LUMO+3	2.484	3	53	44
LUMO+2	2.044	4	10	86
LUMO+1	1.344	28	63	10
LUMO	0.973	4	6	90
HOMO	-0.238	8	88	4
HOMO-1	-1.692	64	27	9
HOMO-2	-1.792	59	21	19
HOMO-3	-2.274	61	32	6
HOMO-4	-3.004	2	91	7
HOMO-5	-3.034	7	18	74

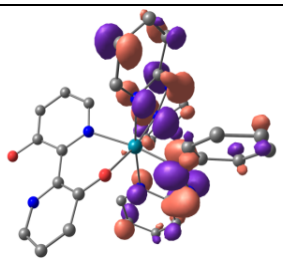
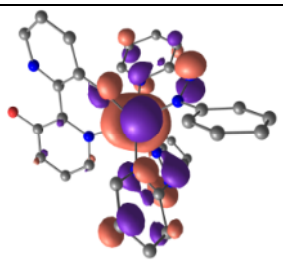
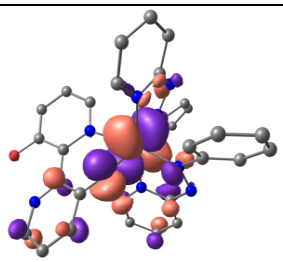
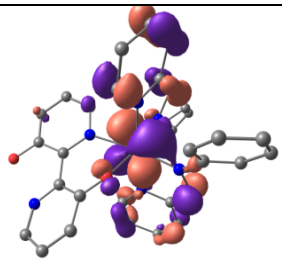
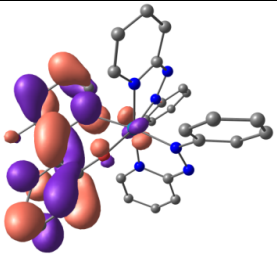
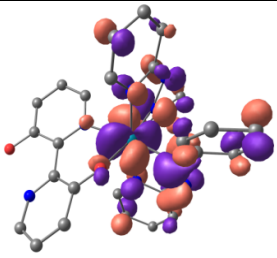
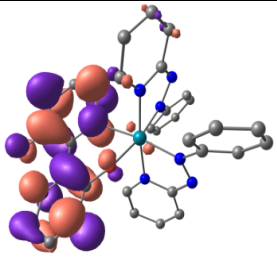
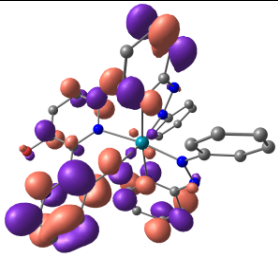
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for **4** in *S* = 0 state

MO	Energy(eV)	% Composition		
		Os	pap	L
LUMO+5	-0.374	10	82	7
LUMO+4	-0.454	2	97	1
LUMO+3	-1.106	4	95	1
LUMO+2	-1.143	3	95	2
LUMO+1	-2.394	31	61	8
LUMO	-2.977	13	85	2
HOMO	-5.023	9	13	78
HOMO-1	-5.110	31	27	42
HOMO-2	-5.324	43	18	39
HOMO-3	-5.554	63	19	17
HOMO-4	-5.669	6	11	83
HOMO-5	-5.994	12	06	82

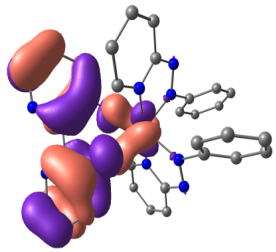
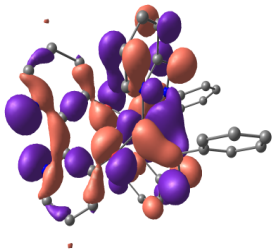
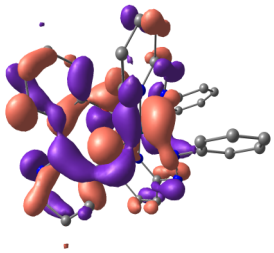
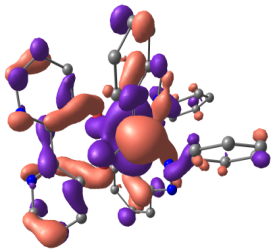
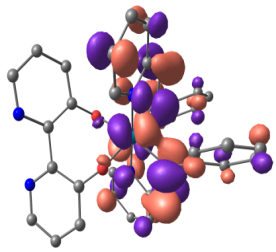
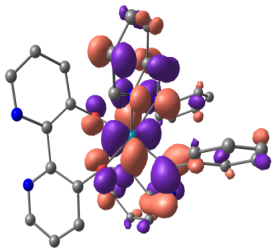
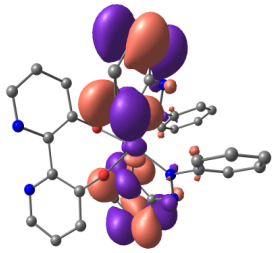
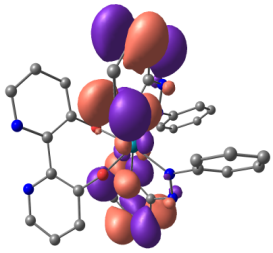
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{4}^{+}$ in *S* =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-3.248	25	33	42
LUMO+4	-3.622	7	83	10
LUMO+3	-4.122	2	2	96
LUMO+2	-4.123	3	3	94
LUMO+1	-5.724	25	70	5
LUMO	-6.081	14	84	3
SOMO	-8.597	14	14	72
HOMO-1	-8.706	18	16	65
HOMO-2	-8.981	33	15	52
HOMO-3	-9.178	7	7	86
HOMO-4	-9.252	45	45	11
HOMO-5	-9.286	16	24	61
β-MO				
LUMO+5	-3.515	6	9	85
LUMO+4	-4.097	3	95	2
LUMO+3	-4.113	3	95	3
LUMO+2	-5.594	30	63	7
LUMO+1	-6.062	16	81	3
LUMO	-7.355	33	18	49
HOMO	-8.353	26	25	49
HOMO-1	-8.721	42	21	37
HOMO-2	-8.806	30	13	57
HOMO-3	-8.898	18	18	65
HOMO-4	-9.217	13	12	76
HOMO-5	-9.288	16	11	74

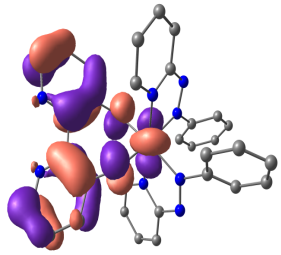
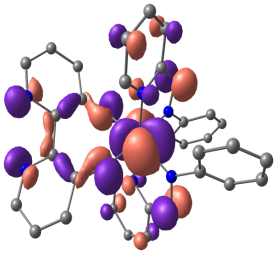
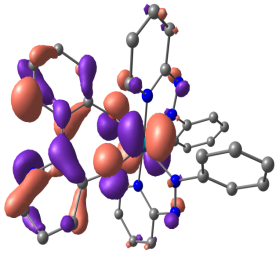
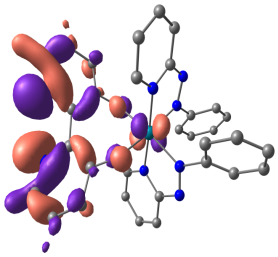
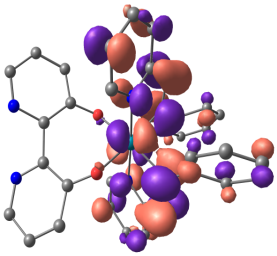
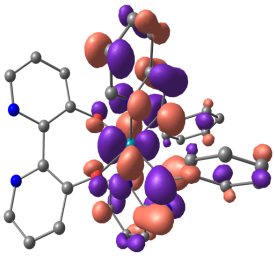
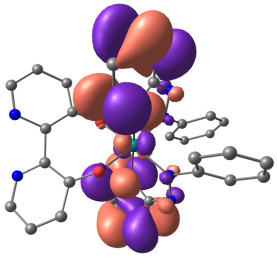
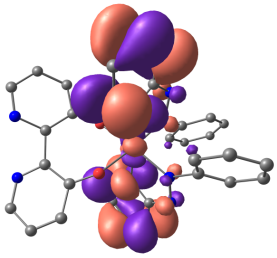
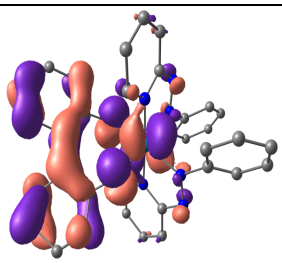
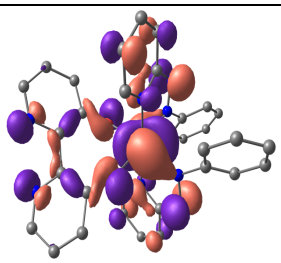
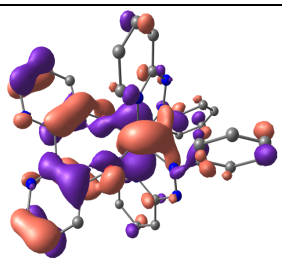
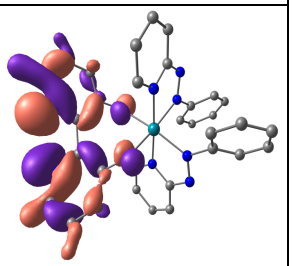
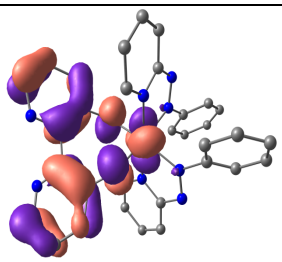
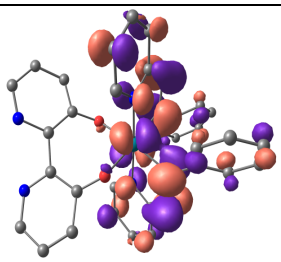
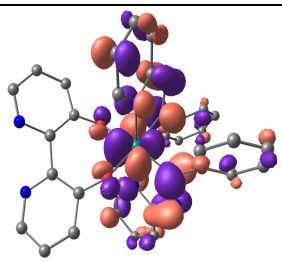
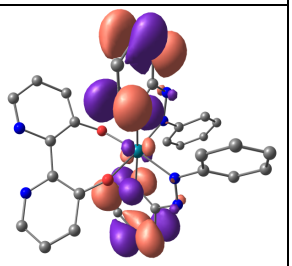
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{4}^{-}$ in *S* =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	2.611	6	92	2
LUMO+4	2.491	2	98	1
LUMO+3	2.287	2	4	94
LUMO+2	2.047	4	95	2
LUMO+1	2.041	4	93	3
LUMO	0.983	41	48	11
SOMO	-0.715	19	78	3
HOMO-1	-1.915	48	37	15
HOMO-2	-2.135	34	33	32
HOMO-3	-2.310	46	26	28
HOMO-4	-2.536	17	13	69
HOMO-5	-2.974	3	16	81
β-MO				
LUMO+5	2.527	2	98	1
LUMO+4	2.289	1	4	94
LUMO+3	2.122	5	92	4
LUMO+2	2.109	3	95	2
LUMO+1	1.081	23	71	6
LUMO	0.822	16	82	2
HOMO	-1.897	50	28	22
HOMO-1	-2.035	53	23	21
HOMO-2	-2.103	48	21	31
HOMO-3	-2.525	16	13	70
HOMO-4	-2.963	3	19	79
HOMO-5	-3.343	3	8	88

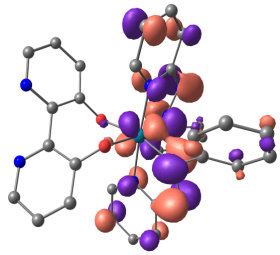
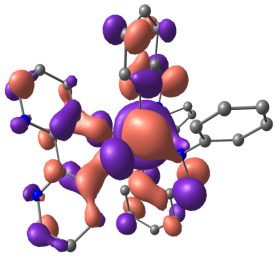
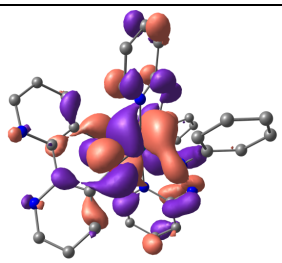
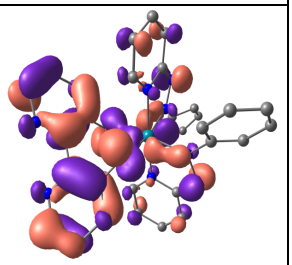
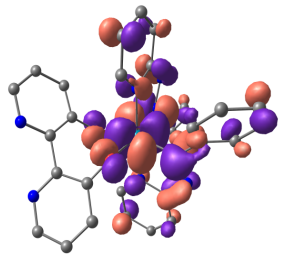
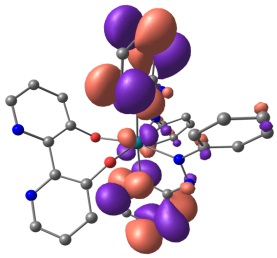
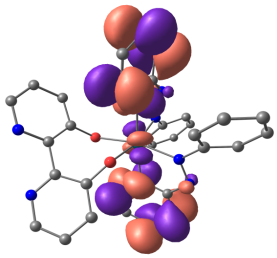
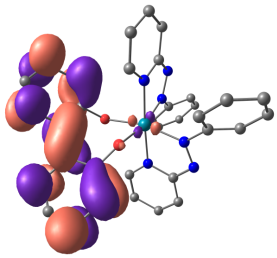
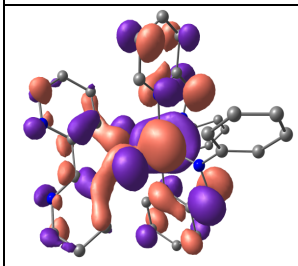
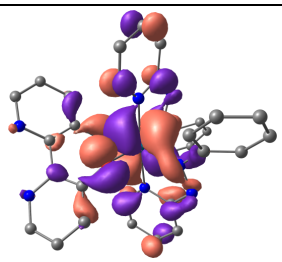
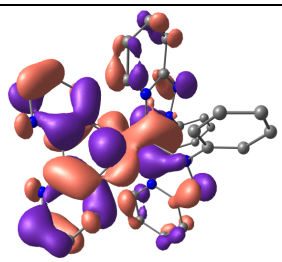
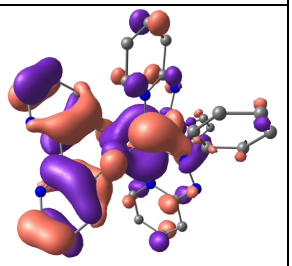
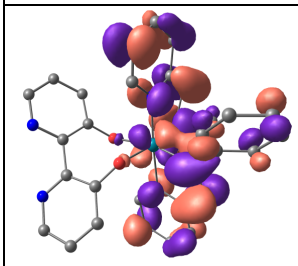
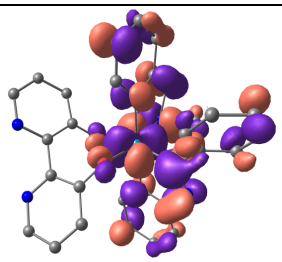
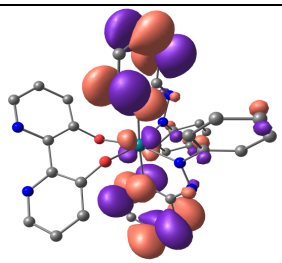
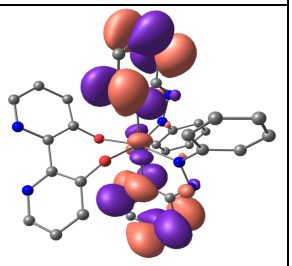
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{4}^{2-}$ in S = 0 state, ($E_{S=1}$-$E_{S=0}$=2396cm^{-1})

MO	Energy(eV)	% Composition		
		Os	pap	L
LUMO+5	5.472	5	94	1
LUMO+4	5.453	4	92	4
LUMO+3	5.330	4	94	1
LUMO+2	5.244	6	89	6
LUMO+1	4.820	1	3	96
LUMO	4.317	33	61	7
HOMO	2.491	10	88	2
HOMO-1	1.388	57	30	12
HOMO-2	1.204	62	20	18
HOMO-3	0.905	45	38	17
HOMO-4	0.251	5	12	83
HOMO-5	-0.161	2	23	75

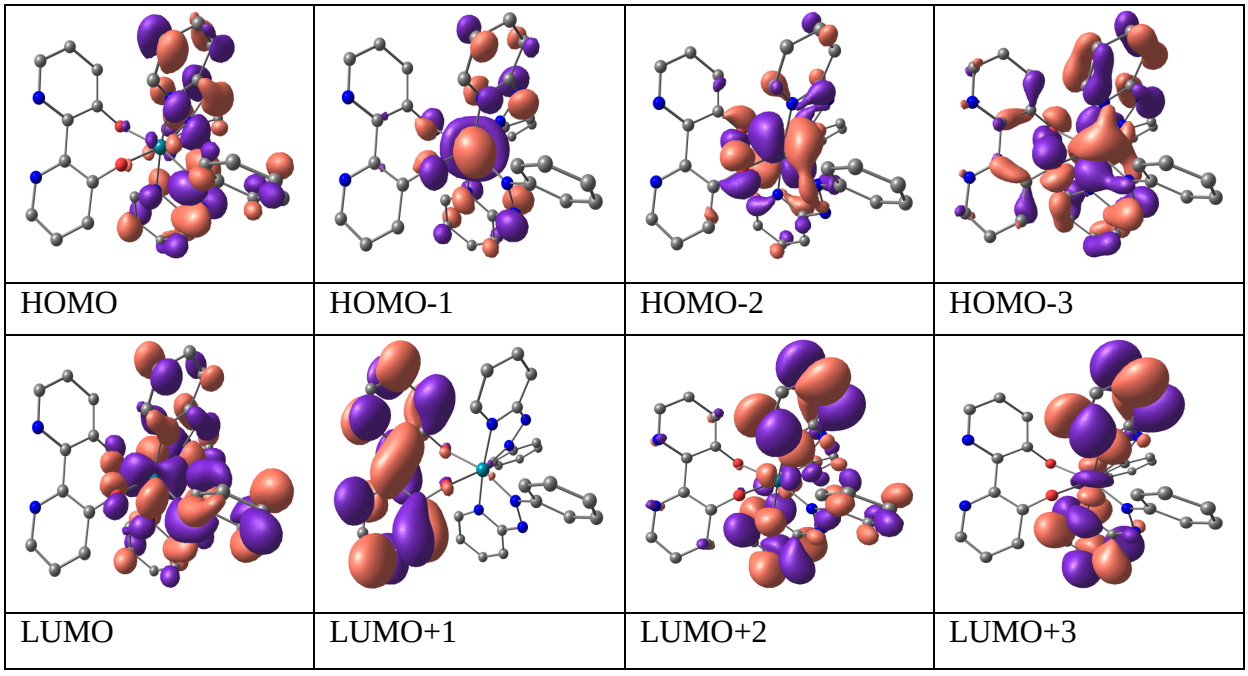


Table S17 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for **5a**$^{2+}$ in *S*=0 state

MO	Energy (eV)	% Composition		
		Os	pap	L
LUMO+5	-6.259	6	82	12
LUMO+4	-6.615	16	32	53
LUMO+3	-7.194	21	72	7
LUMO+2	-7.362	15	47	39
LUMO+1	-7.578	20	73	7
LUMO	-7.825	11	75	14
HOMO	-9.828	39	40	21
HOMO-1	-10.165	37	31	32
HOMO-2	-10.536	41	38	20
HOMO-3	-10.615	49	36	15
HOMO-4	-10.731	53	36	10
HOMO-5	-10.942	52	31	18

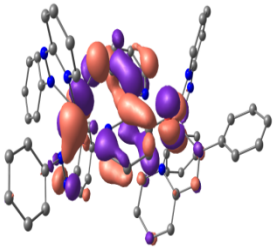
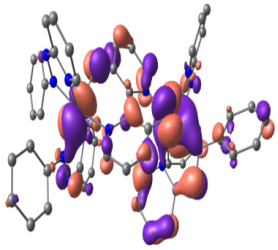
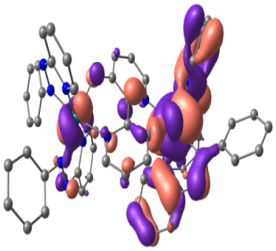
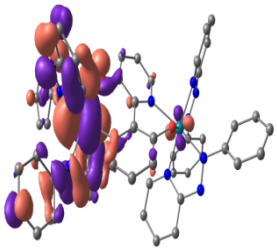
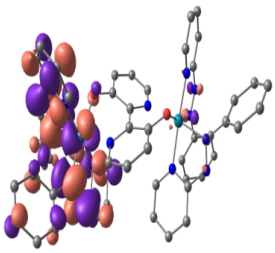
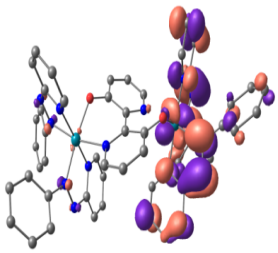
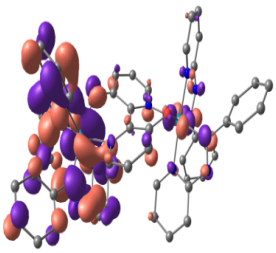
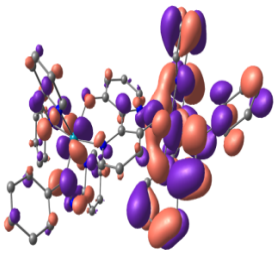
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **5a**$^{3+}$ in *S* =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-8.250	5	70	25
LUMO+4	-9.123	7	12	81
LUMO+3	-9.547	20	73	8
LUMO+2	-9.627	17	73	10
LUMO+1	-9.929	9	88	4
LUMO	-10.022	12	83	4
SOMO	-12.843	41	34	25
HOMO-1	-12.879	34	37	29
HOMO-2	-12.905	32	64	4
HOMO-3	-12.977	21	64	15
HOMO-4	-13.035	23	66	11
HOMO-5	-13.046	21	76	4
β-MO				
LUMO+5	-9.066	7	12	81
LUMO+4	-9.470	24	67	9
LUMO+3	-9.569	21	67	12
LUMO+2	-9.895	13	84	3
LUMO+1	-9.947	15	80	4
LUMO	-11.593	40	23	37
HOMO	-12.270	54	28	18
HOMO-1	-12.773	58	32	10
HOMO-2	-12.891	23	72	5
HOMO-3	-12.940	39	54	6
HOMO-4	-12.993	19	76	5
HOMO-5	-13.043	2	98	0

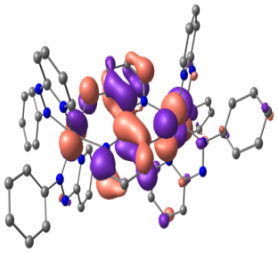
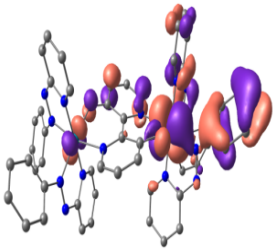
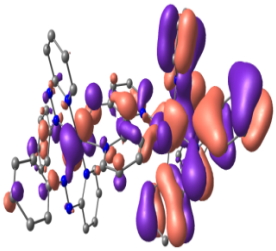
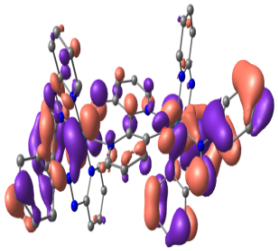
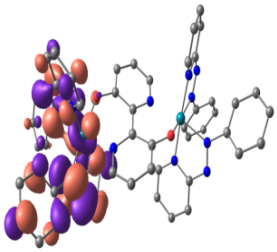
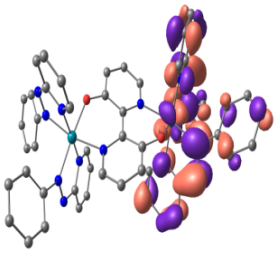
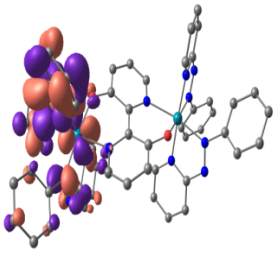
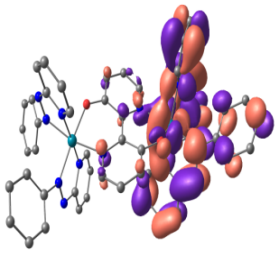
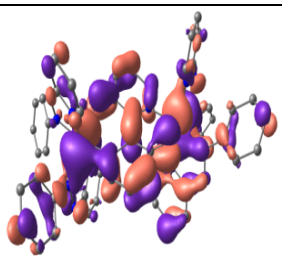
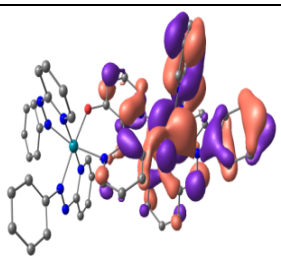
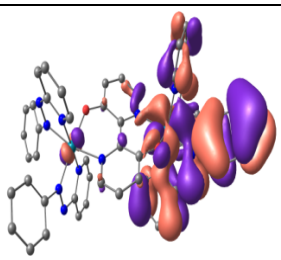
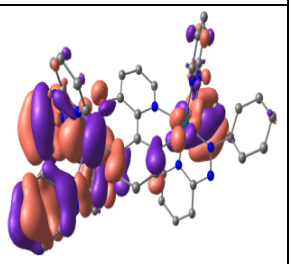
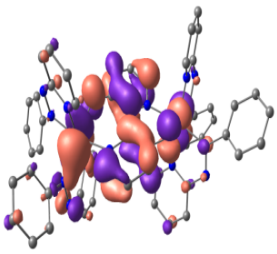
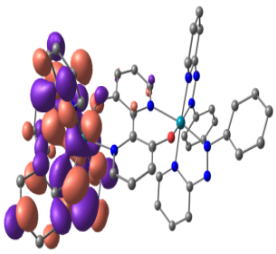
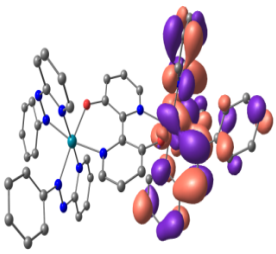
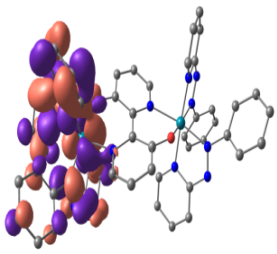
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **5a**$^{+}$ in *S* =1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-3.151	4	85	11
LUMO+4	-3.223	4	88	7
LUMO+3	-3.961	7	10	83
LUMO+2	-4.541	30	62	8
LUMO+1	-4.629	27	60	12
LUMO	-5.353	14	83	3
SOMO	-5.680	13	83	3
HOMO-1	-7.357	37	21	42
HOMO-2	-7.517	47	30	23
HOMO-3	-7.638	68	25	7
HOMO-4	-7.844	57	32	11
HOMO-5	-8.013	60	33	7
β-MO				
LUMO+5	-3.181	4	85	11
LUMO+4	-3.947	7	13	80
LUMO+3	-4.389	22	71	7
LUMO+2	-4.474	20	68	13
LUMO+1	-4.739	14	82	4
LUMO	-4.763	12	85	3
HOMO	-7.328	39	41	11
HOMO-1	-7.508	52	24	25
HOMO-2	-7.627	67	26	7
HOMO-3	-7.787	59	32	9
HOMO-4	-7.954	59	31	0
HOMO-5	-8.007	64	28	8

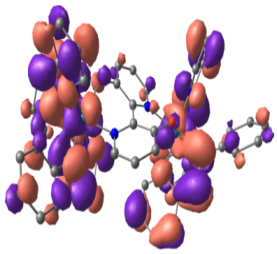
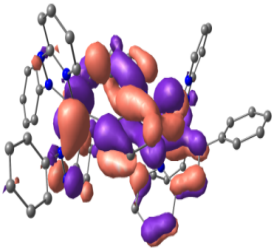
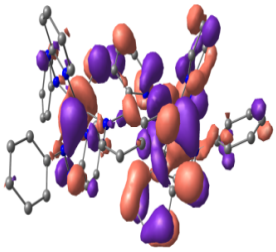
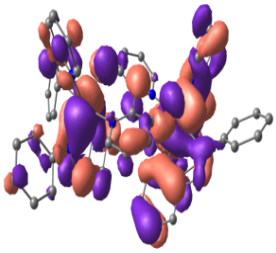
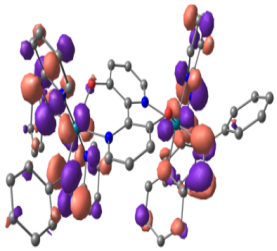
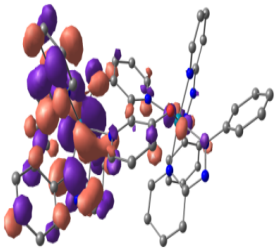
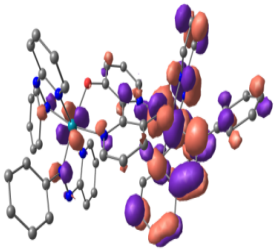
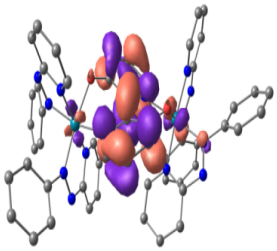
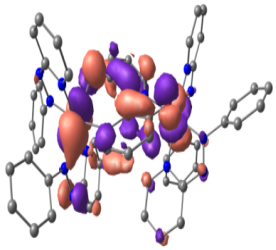
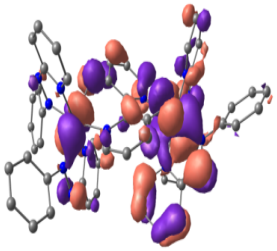
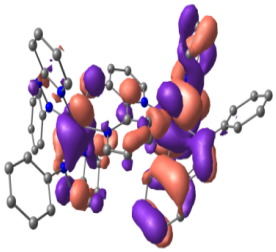
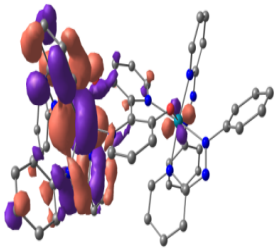
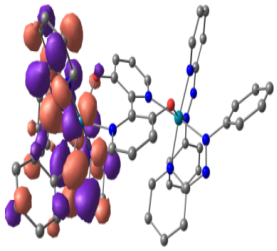
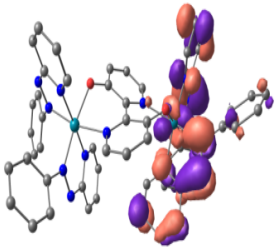
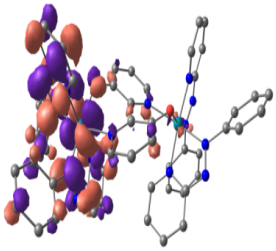
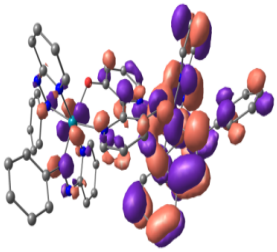
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **5a** in *S* =1 state, ($E_{\mathbf{BS(1,1)}\ S=0} - E_{S=1}$= 42.9503 cm^{-1})

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-0.686	4	87	9
LUMO+4	-0.737	6	74	20
LUMO+3	-0.837	4	88	8
LUMO+2	-1.556	11	14	75
LUMO+1	-2.016	34	52	14
LUMO	-2.185	32	52	16
SOMO1	-3.738	13	84	3
SOMO2	-3.743	13	84	3
HOMO-2	-4.970	44	23	33
HOMO-3	-5.038	48	36	16
HOMO-4	-5.125	63	27	10
HOMO-5	-5.439	55	30	15
β-MO				
LUMO+5	-0.764	4	79	17
LUMO+4	-1.523	11	28	61
LUMO+3	-1.774	18	62	19
LUMO+2	-1.949	17	67	17
LUMO+1	-2.196	10	86	4
LUMO	-2.236	13	80	6
HOMO	-4.918	44	21	35
HOMO-1	-5.018	54	26	20
HOMO-2	-5.070	67	25	8
HOMO-3	-5.286	59	32	8
HOMO-4	-5.435	63	28	9
HOMO-5	-5.530	65	25	9

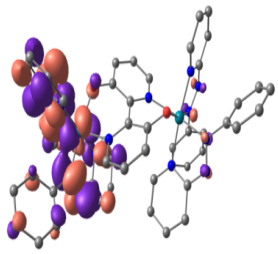
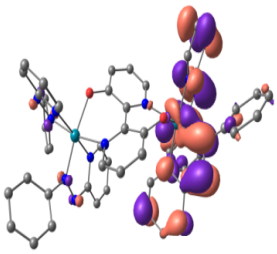
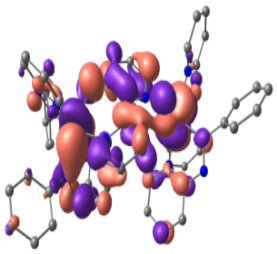
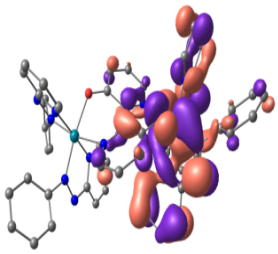
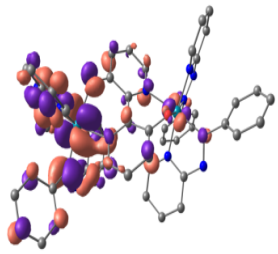
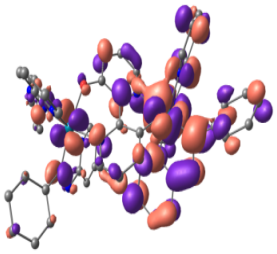
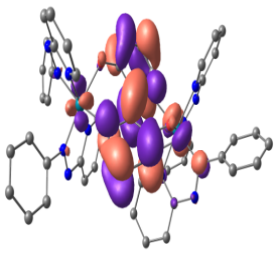
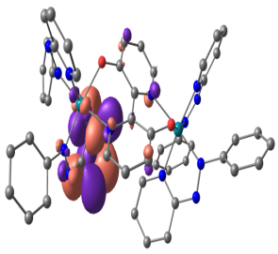
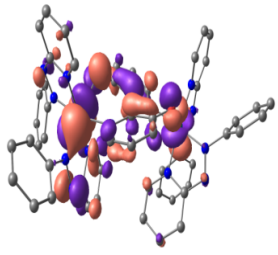
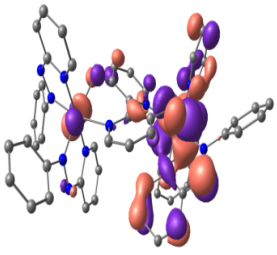
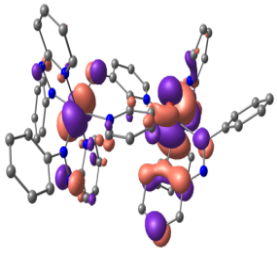
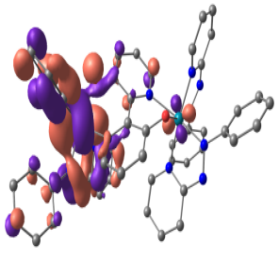
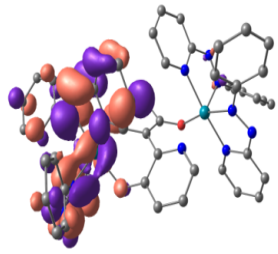
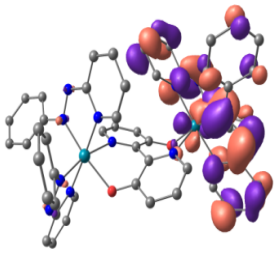
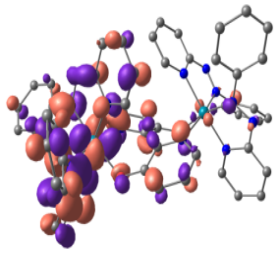
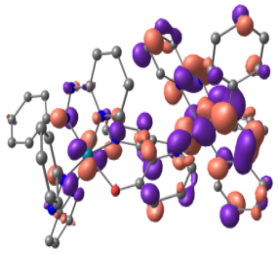
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for **5b**$^{2+}$ in *S* = 0 state

MO	Energy (eV)	% Composition		
		Os	pap	L
LUMO+5	-5.913	4	92	4
LUMO+4	-6.301	8	12	79
LUMO+3	-6.913	30	64	6
LUMO+2	-7.004	24	61	16
LUMO+1	-7.597	12	84	4
LUMO	-7.997	3	93	4
HOMO	-9.595	55	23	21
HOMO-1	-10.125	40	25	35
HOMO-2	-10.160	53	33	14
HOMO-3	-10.270	55	25	20
HOMO-4	-10.428	52	25	23
HOMO-5	-10.586	48	46	7

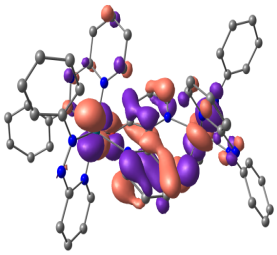
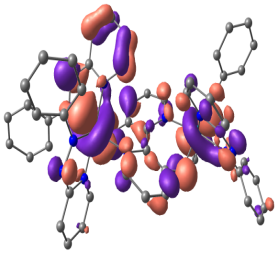
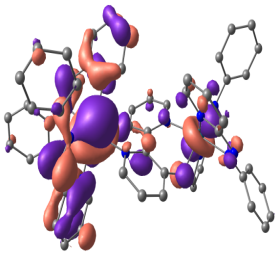
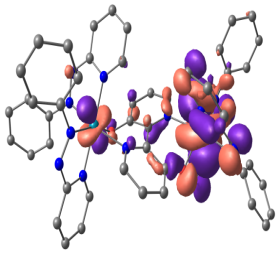
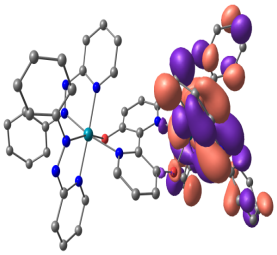
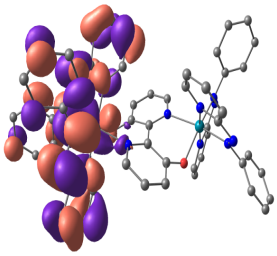
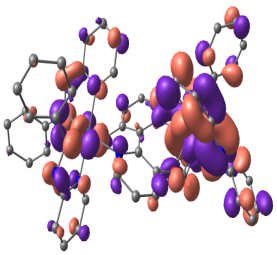
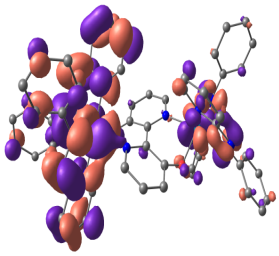
α-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **5b**$^{3+}$ in *S*=1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-8.197	4	52	44
LUMO+4	-9.049	5	8	86
LUMO+3	-9.578	20	75	5
LUMO+2	-9.621	19	72	9
LUMO+1	-9.890	10	87	3
LUMO	-9.943	9	88	3
SOMO1	-12.852	43	35	22
HOMO-1	-12.873	32	30	38
HOMO-2	-12.902	38	54	7
HOMO-3	-12.973	28	68	3
HOMO-4	-13.021	26	59	15
HOMO-5	-13.045	15	79	16
β-MO				
LUMO+5	-8.999	6	8	86
LUMO+4	-9.496	24	70	6
LUMO+3	-9.554	22	68	10
LUMO+2	-9.867	13	84	3
LUMO+1	-9.895	14	83	3
LUMO	-11.590	46	22	32
HOMO	-12.222	58	27	15
HOMO-1	-12.720	49	30	21
HOMO-2	-12.814	55	35	10
HOMO-3	-12.913	26	67	7
HOMO-4	-12.964	23	74	3
HOMO-5	-13.040	2	96	2

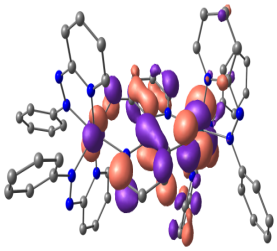
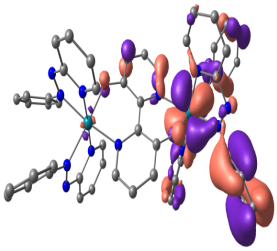
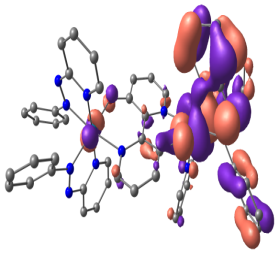
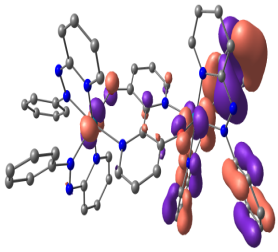
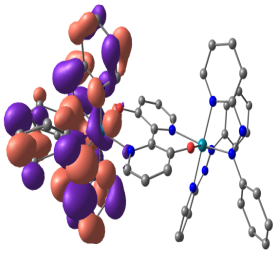
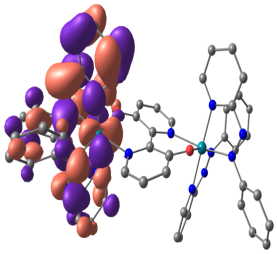
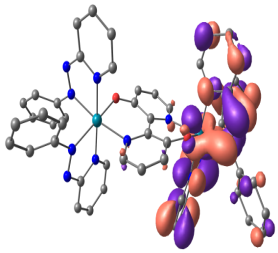
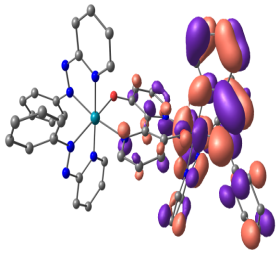
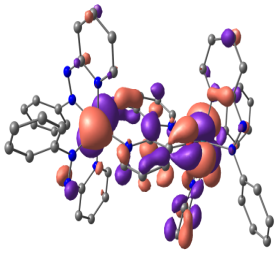
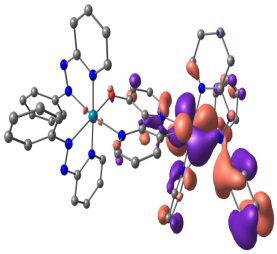
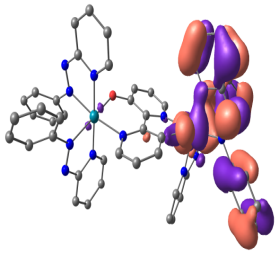
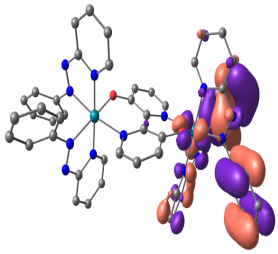
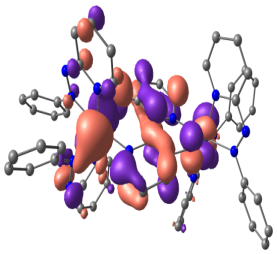
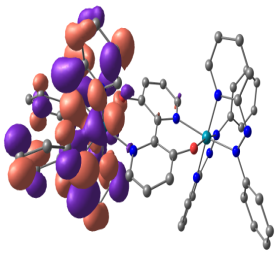
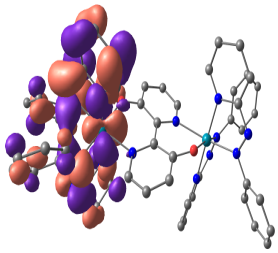
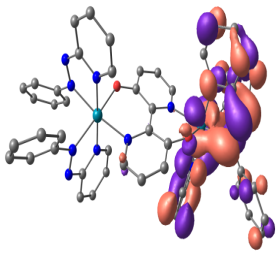
α-MO			
			
SOMO1	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **5b**$^{+}$ in *S*=1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-3.206	3	89	7
LUMO+4	-3.275	3	89	8
LUMO+3	-3.949	6	8	86
LUMO+2	-4.542	30	62	8
LUMO+1	-4.634	29	61	10
LUMO	-5.339	14	84	3
SOMO	-5.661	13	84	3
HOMO-1	-7.400	41	21	38
HOMO-2	-7.526	46	30	24
HOMO-3	-7.595	61	28	11
HOMO-4	-7.612	68	24	9
HOMO-5	-7.964	58	36	7
β-MO				
LUMO+5	-3.236	3	87	10
LUMO+4	-3.941	6	11	83
LUMO+3	-4.372	21	71	8
LUMO+2	-4.480	21	70	9
LUMO+1	-4.675	12	84	4
LUMO	-4.779	12	85	3
HOMO	-7.380	45	19	36
HOMO-1	-7.537	50	23	27
HOMO-2	-7.594	68	25	7
HOMO-3	-7.610	61	26	12
HOMO-4	-7.901	59	32	9
HOMO-5	-8.030	63	27	10

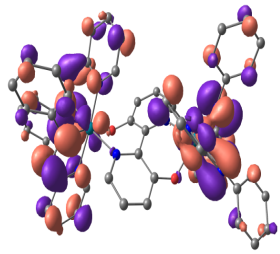
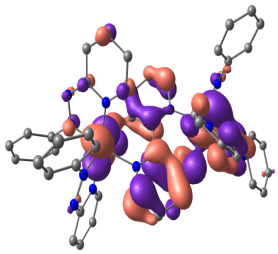
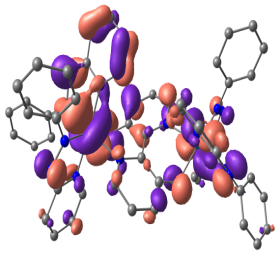
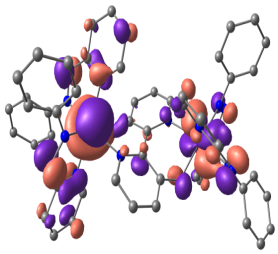
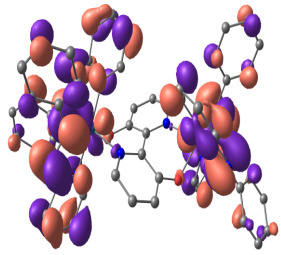
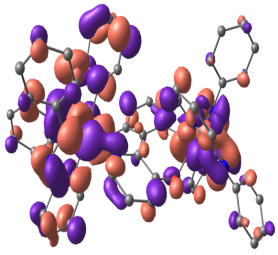
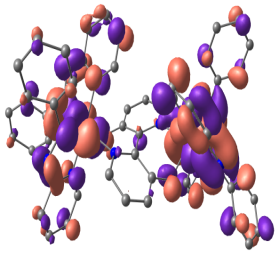
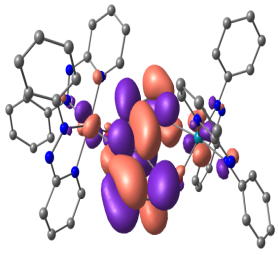
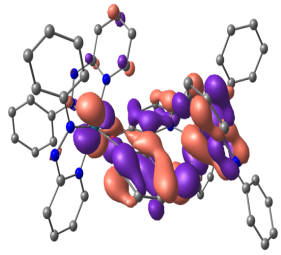
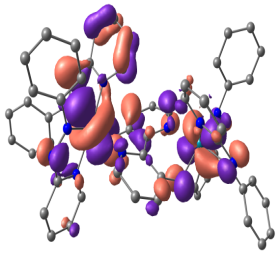
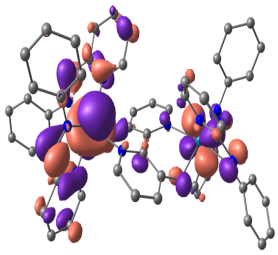
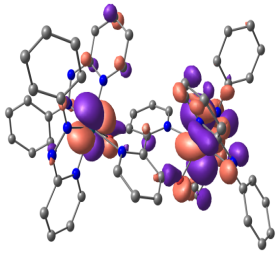
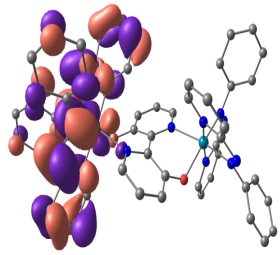
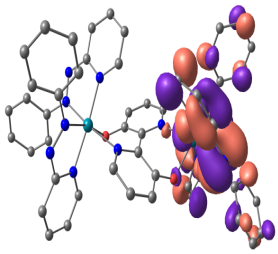
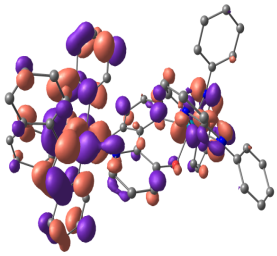
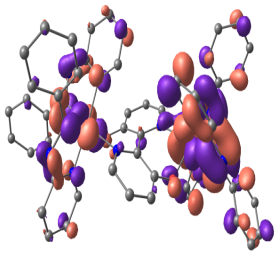
α-MO			
			
SOMO1	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S24 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for **5b** in *S*=1 state, ($E_{\mathbf{BS(1,1)}\ S=0} - E_{S=1}$= **24.5998** cm^{-1})

MO	Energy (eV)	% Composition		
		Os	pap	L
α-MO				
LUMO+5	-0.733	4	83	13
LUMO+4	-0.798	3	92	5
LUMO+3	-0.841	4	81	15
LUMO+2	-1.555	9	11	80
LUMO+1	-2.026	36	55	9
LUMO	-2.138	32	51	17
SOMO1	-3.744	12	85	2
SOMO2	-3.796	13	85	3
HOMO-2	-4.994	64	19	16
HOMO-3	-5.043	40	34	26
HOMO-4	-5.125	44	35	21
HOMO-5	-5.152	69	23	8
β-MO				
LUMO+5	-0.769	5	67	28
LUMO+4	-1.536	9	21	70
LUMO+3	-1.767	21	72	7
LUMO+2	-1.877	17	61	22
LUMO+1	-2.212	10	87	3
LUMO	-2.256	10	85	7
HOMO	-4.984	56	19	25
HOMO-1	-5.027	55	26	19
HOMO-2	-5.074	60	22	19
HOMO-3	-5.129	63	28	9
HOMO-4	-5.459	61	26	13
HOMO-5	-5.504	65	28	7

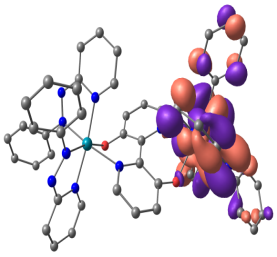
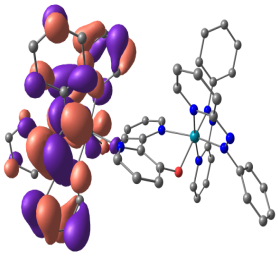
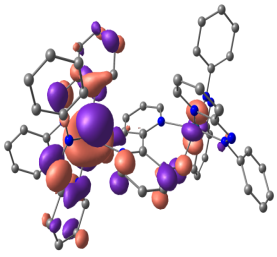
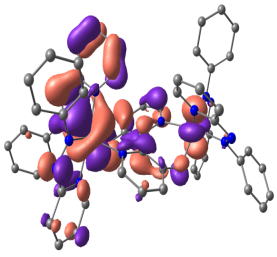
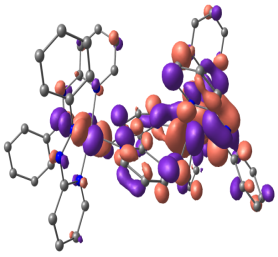
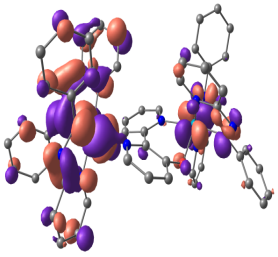
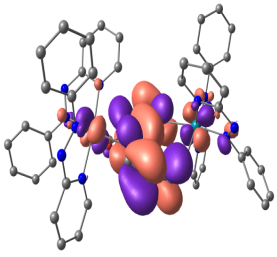
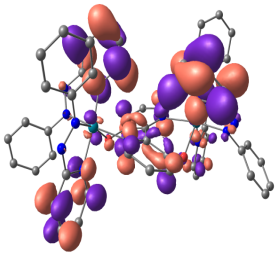
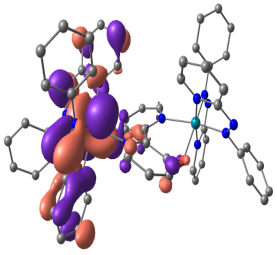
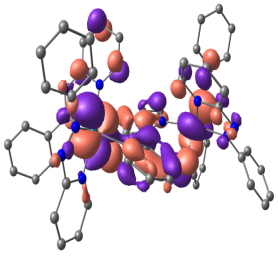
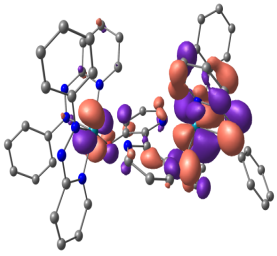
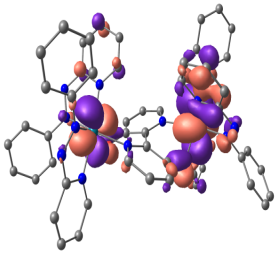
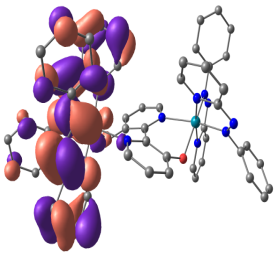
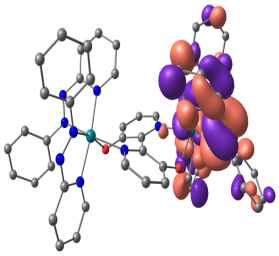
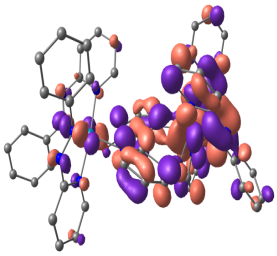
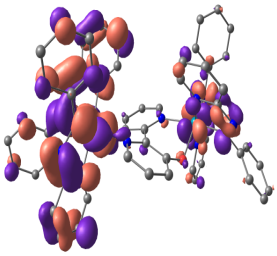
α-MO			
			
SOMO1	SOMO2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for **6** in *S* = 0 state

MO	Energy (eV)	% Composition		
		Os	pap	L/
LUMO+5	-0.128	4	95	2
LUMO+4	-0.194	2	96	1
LUMO+3	-0.879	5	93	2
LUMO+2	-0.995	4	94	2
LUMO+1	-2.250	32	59	9
LUMO	-2.891	18	76	6
HOMO	-4.683	8	9	83
HOMO-1	-5.157	15	14	71
HOMO-2	-5.260	26	42	32
HOMO-3	-5.388	34	25	41
HOMO-4	-5.507	43	12	46
HOMO-5	-5.764	39	12	48

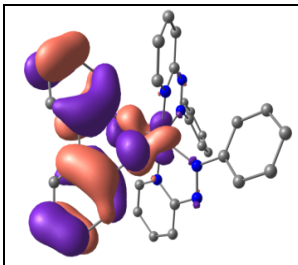
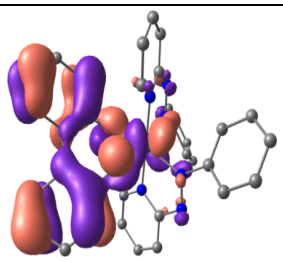
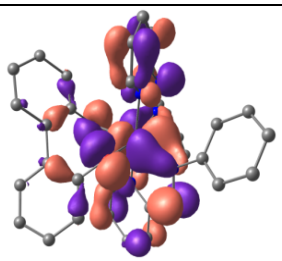
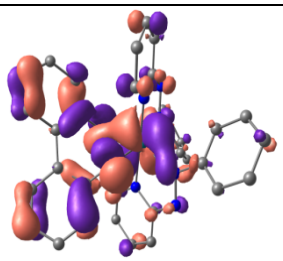
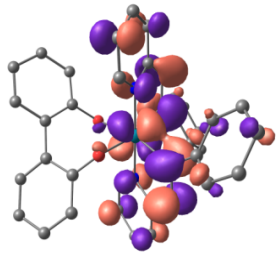
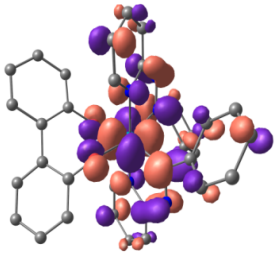
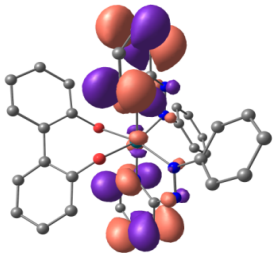
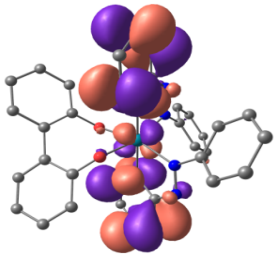
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{6}^{+}$ in *S*=1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L/
α-MO				
LUMO+5	-2.906	15	35	50
LUMO+4	-3.432	9	9	82
LUMO+3	-3.759	4	93	2
LUMO+2	-3.832	4	95	1
LUMO+1	-5.364	27	67	6
LUMO	-5.834	13	83	4
SOMO	-8.508	36	36	28
HOMO-1	-8.569	14	10	76
HOMO-2	-8.602	50	27	23
HOMO-3	-8.926	4	12	84
HOMO-4	-9.044	54	14	31
HOMO-5	-9.239	22	34	44
β-MO				
LUMO+5	-3.267	8	9	83
LUMO+4	-3.755	4	94	2
LUMO+3	-3.826	4	95	1
LUMO+2	-5.308	30	64	7
LUMO+1	-5.834	15	80	5
LUMO	-7.138	25	10	65
HOMO	-8.344	44	30	25
HOMO-1	-8.372	36	19	45
HOMO-2	-8.529	49	24	27
HOMO-3	-8.608	24	23	53
HOMO-4	-9.145	5	8	87
HOMO-5	-9.272	3	88	10

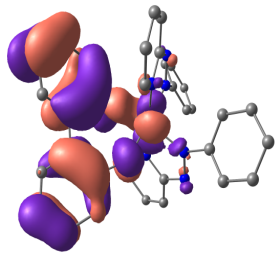
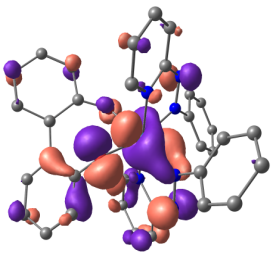
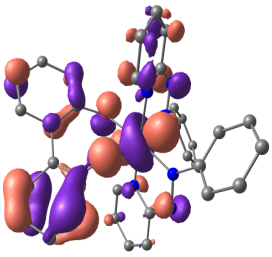
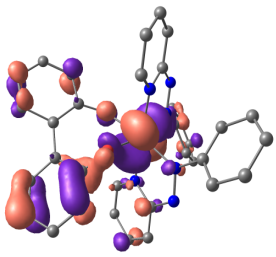
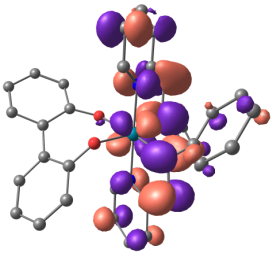
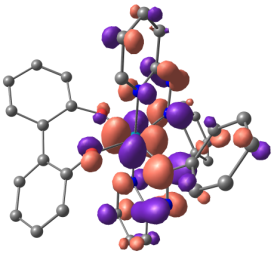
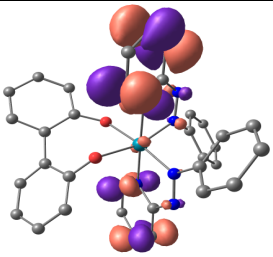
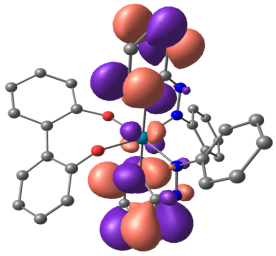
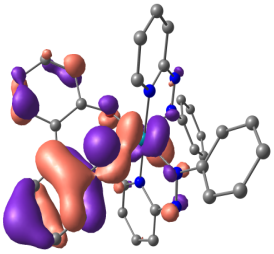
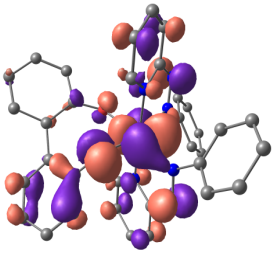
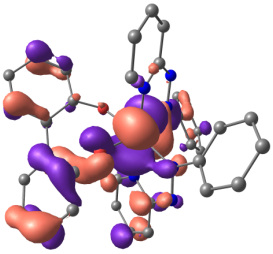
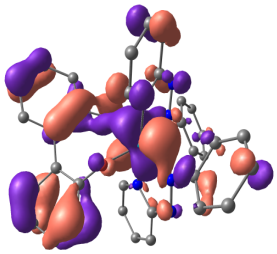
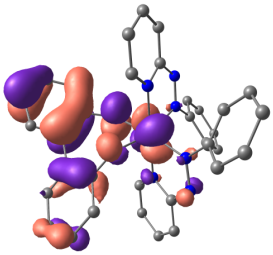
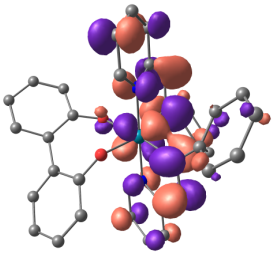
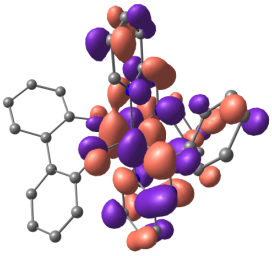
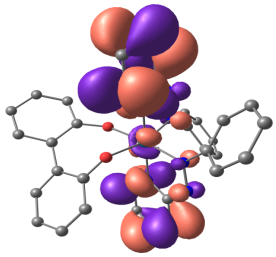
α-MO			
			
SOMO1	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S27 Calculated (uB3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{6}^{-}$ in S = 1/2 state

MO	Energy (eV)	% Composition		
		Os	pap	L/
α-MO				
LUMO+5	2.717	4	8	89
LUMO+4	2.658	3	96	1
LUMO+3	2.610	1	98	1
LUMO+2	2.254	5	94	2
LUMO+1	2.176	5	93	1
LUMO	1.032	40	49	11
SOMO	-0.674	18	77	5
HOMO-1	-1.868	49	20	31
HOMO-2	-2.024	21	48	31
HOMO-3	-2.151	44	25	31
HOMO-4	-2.348	36	14	50
HOMO-5	-2.591	5	15	80
β-MO				
LUMO+5	2.690	3	96	1
LUMO+4	2.641	2	98	1
LUMO+3	2.340	6	92	2
LUMO+2	2.241	5	93	1
LUMO+1	1.120	24	70	6
LUMO	0.884	17	78	6
HOMO	-1.821	48	28	24
HOMO-1	-1.828	47	28	25
HOMO-2	-1.931	39	22	39
HOMO-3	-2.336	36	13	51
HOMO-4	-2.585	4	15	81
HOMO-5	-3.186	2	3	95

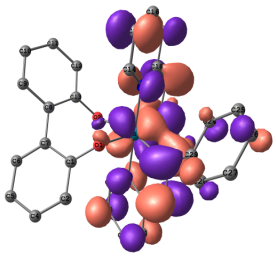
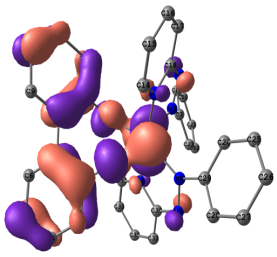
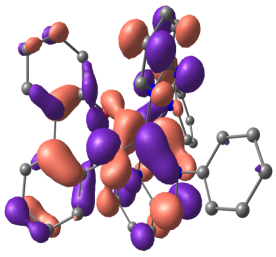
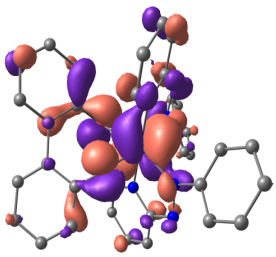
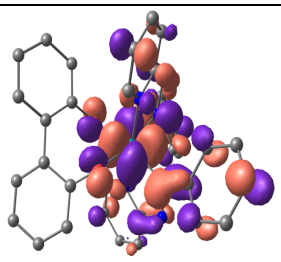
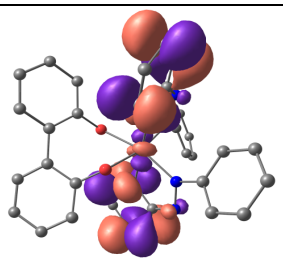
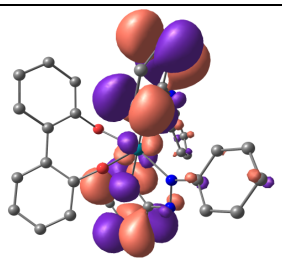
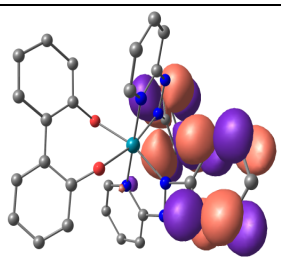
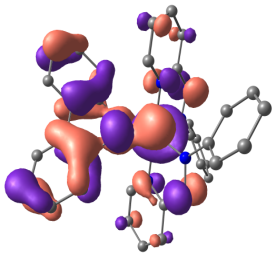
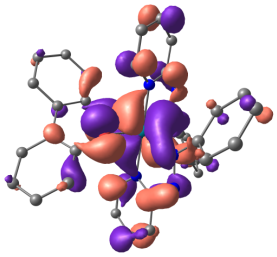
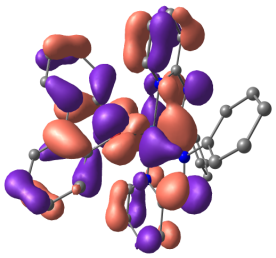
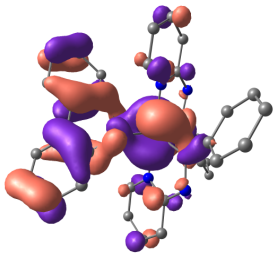
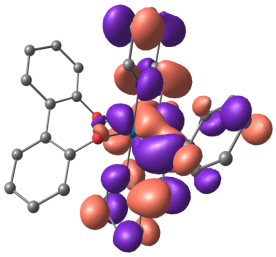
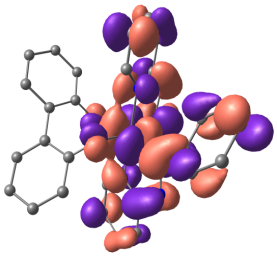
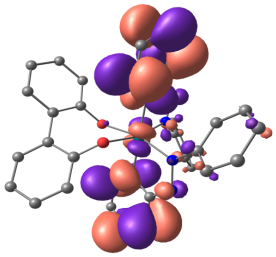
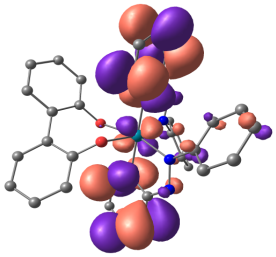
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S28 Calculated (B3LYP/6-31G*/LANL2DZ) MO compositions for $\mathbf{6}^{2-}$ in S = 0 state, ($E_{S=1}$-$E_{S=0}$=1505 cm^{-1})

MO	Energy (eV)	% Composition		
		Os	pap	L′
LUMO+5	5.545	3	96	1
LUMO+4	5.516	2	96	2
LUMO+3	5.424	6	92	2
LUMO+2	5.364	7	91	1
LUMO+1	5.263	2	4	94
LUMO	4.231	33	60	7
HOMO	2.708	15	80	5
HOMO-1	1.423	57	31	12
HOMO-2	1.221	54	26	20
HOMO-3	1.087	42	37	21
HOMO-4	0.495	10	10	79
HOMO-5	0.180	2	18	79

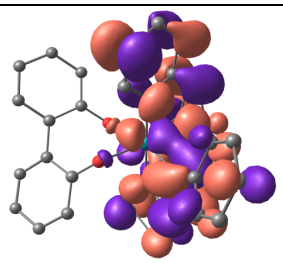
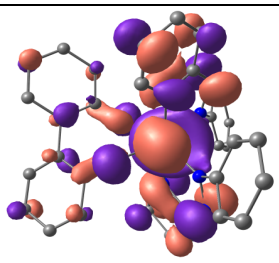
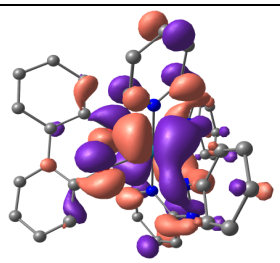
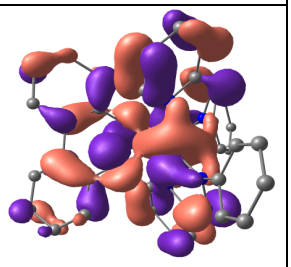
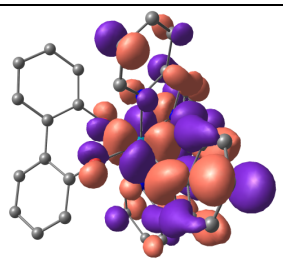
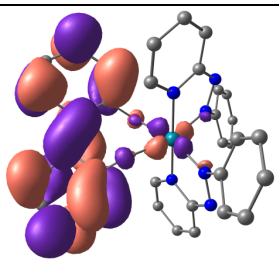
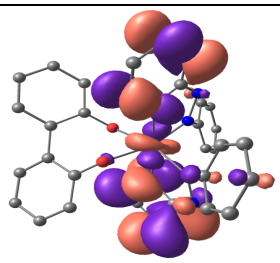
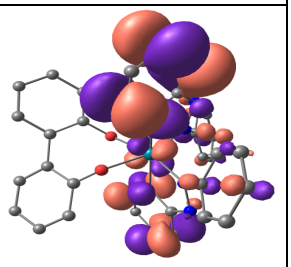
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S29 DFT calculated selected MO compositions for $\mathbf{2}^n$, $\mathbf{3}^n$, $\mathbf{4}^n$, $\mathbf{5a}^n$, $\mathbf{5b}^n$ and $\mathbf{6}^n$ by multiple methods and basis set

Complex	MO	Fragments	TZVP+LANL2DZ			6-31G* +LANL2DZ
			% Contribution			
			M06L	τ-HCTH	PBE	B3LYP
$\mathbf{2}^+$ (*S*=0)	HOMO LUMO	Os/pap/HL Os/pap/HL	0/19/81 7/89/4	0/22/77 8/89/3	0/23/76 8/89/3	1/4/96 12/84/4
$\mathbf{2}^{2+}$ (*S*=1/2)	β -LUMO	Os/pap/HL	16/15/69	9/11/79	11/13/76	1/2/97
2 (*S*=1/2)	SOMO β-LUMO	Os/pap/HL Os/pap/HL	7/89/4 5/89/5	7/89/4 6/89/5	7/89/4 6/89/5	12/84/4 28/67/4
$\mathbf{2}^-$ (*S*=0)	HOMO	Os/pap/HL	4/89/7	5/88/6	5/88/7	8/88/4
$\mathbf{3}^+$ (*S*=0)	HOMO LUMO	Os/pap/HL Os/pap/HL	29/31/40 11/81/8	27/34/39 12/78/11	29/32/38 12/78/10	22/21/58 14/82/3
$\mathbf{3}^{2+}$ (*S*=1/2)	β -LUMO	Os/pap/HL	30/29/41	31/29/40	33/30/37	32/22/46
3 (*S*=1/2)	SOMO β-LUMO	Os/pap/HL Os/pap/HL	8/83/9 5/86/8	8/81/11 5/83/11	11/77/12 10/75/15	14/83/3 12/78/10
$\mathbf{3}^-$ (*S*=0)	HOMO	Os/pap/HL	3/90/7	3/89/8	3/89/8	8/88/4
4 (*S*=0)	HOMO LUMO	Os/pap/L Os/pap/L	26/20/54 15/79/6	26/22/52 15/78/7	33/27/40 14/78/7	9/13/78 13/85/2
$\mathbf{4}^+$ (*S*=1/2)	SOMO β -LUMO	Os/pap/L Os/pap/L	14/23/63 33/23/44	14/25/61 29/26/46	17/22/62 24/35/41	14/14/72 33/18/49
$\mathbf{4}^-$ (*S*=1/2)	SOMO β -LUMO	Os/pap/L Os/pap/L	15/79/6 13/81/6	14/78/8 13/79/8	13/79/7 13/79/8	19/78/3 16/82/2
$\mathbf{4}^{2-}$ (*S*=0)	HOMO	Os/pap/L	23/70/7	25/66/9	24/68/8	10/88/2
$\mathbf{5a}^{2+}$ (*S*=0)	HOMO LUMO	Os/pap/L Os/pap/L	38/25/37 11/84/5	36/27/37 11/83/5	38/27/35 11/82/7	39/40/21 11/75/14
$\mathbf{5a}^{3+}$ (*S*=1/2)	β -HOMO β -LUMO	Os/pap/L Os/pap/L	55/26/18 37/26/38	52/30/18 35/27/38	52/30/18 35/26/38	54/28/11 40/23/37
$\mathbf{5a}^+$ (*S*=1/2)	SOMO α -LUMO	Os/pap/L Os/pap/L	8/83/9 11/79/11	11/80/8 12/80/8	10/82/8 10/82/8	13/83/3 14/83/3
5a (*S*=1)	SOMO1 β-LUMO	Os/pap/L Os/pap/L	12/82/6 7/83/10	10/85/4 7/79/13	10/85/5 8/79/13	13/84/3 13/80/6
$\mathbf{5b}^{2+}$ (*S*=0)	HOMO	Os/pap/L	31/30/39	31/30/39	32/31/37	55/23/21

	LUMO	Os/pap/L	13/81/6	11/84/4	12/83/5	3/93/4
5b^{3+} (*S*=1/2)	β–HOMO β -LUMO	Os/pap/L Os/pap/L	52/33/15 30/32/39	51/33/16 31/34/35	50/33/17 31/33/36	58/27/15 46/22/32
5b^{+} (*S*=1/2)	SOMO α -LUMO	Os/pap/L Os/pap/L	9/87/4 8/80/12	11/82/7 9/78/13	10/83/7 8/79/13	13/84/3 14/84/3
5b (*S*=1)	SOMO1 β -LUMO	Os/pap/L Os/pap/L	11/82/7 5/88/7	10/79/11 5/83/12	9/80/11 5/83/12	12/85/2 10/85/7
6 (*S*=0)	HOMO LUMO	Os/pap/ L$^{/}$ Os/pap/ L$^{/}$	24/21/55 15/72/12	19/21/60 13/75/12	23/22/55 13/74/13	8/9/83 18/76/6
6^{+} (*S*=1/2)	SOMO β -LUMO	Os/pap/ L$^{/}$ Os/pap/ L$^{/}$	21/17/61 20/21/59	17/18/65 16/20/64	18/19/63 18/21/61	36/36/28 25/10/65
6^{-} (*S*=1/2)	SOMO β -LUMO	Os/pap/ L$^{/}$ Os/pap/ L$^{/}$	15/73/11 14/72/13	14/73/13 13/73/14	13/74/13 14/72/14	18/77/5 17/78/6
6^{2-} (*S*=0)	HOMO	Os/pap/ L$^{/}$	17/71/12	17/67/15	17/68/15	15/80/5

Table S30 DFT Calculated energies (in kJ/Mole) of geometry optimized structures of $\mathbf{1}^n$, $\mathbf{2}^n$, $\mathbf{3}^n$, $\mathbf{4}^n$, $\mathbf{5a}^n$ and $\mathbf{5b}^n$ by multiple methods and basis set

Complex	TZVP+LANL2DZ			6-31G*+LANL2DZ
	M06L	τ-HCTH	PBE	B3LYP
$\mathbf{2}^{2+}$ (*S*=1/2)	–5024920.0783	–5024733.3411	–5019882.8715	-5023908.7813
$\mathbf{2}^{+}$ (*S*=0)	–5025790.4350	–5025621.2493	–5020763.4543	–5024761.8879
2 (*S*=1/2)	–5026304.1364	–5026148.4293	–5021281.2329	–5025256.2300
$\mathbf{2}^{-}$ (*S*=1)	–5026482.7563	–5026348.2109	–5021475.3931	–5025427.3574
$\mathbf{2}^{-}$ (*S*=0)	–5026515.3828	–5026376.8355	–5021506.4221	–5025435.2521
Δ*E*= 2^{-}(*S*=1)–2^{-} (*S*=0)	**33.0717 (2764.5776 cm^{-1})**	**28.6246 (2392.8292 cm^{-1})**	**31.0280 (2593.7377 cm^{-1})**	**7.8947 (659.9452 cm^{-1})**
$\mathbf{3}^{2+}$ (*S*=1/2)	–5024926.3760	–5024735.9160	–5019882.6006	–5023919.0451
$\mathbf{3}^{+}$ (*S*=0)	–5025790.2517	-5025609.9941	–5020748.9400	–5025375.1706
3 (*S*=1/2)	–5026275.4302	–5026108.6178	–5021238.1463	–5025237.6393
$\mathbf{3}^{-}$ (*S*=1)	–5026433.4993	–5026285.4841	–5021409.6214	–5025375.1706
$\mathbf{3}^{-}$ (*S*=0)	–5026460.9058	-5026310.1535	–5021436.2393	–5025388.8193
Δ*E*= 3^{-}(*S*=1)–3^{-} (*S*=0)	**27.4065 (2291.0040 cm^{-1})**	**24.6694 (2062.2004 cm^{-1})**	**26.6179 (2225.0822 cm^{-1})**	**13.6487 (1140.942 cm^{-1})**
$\mathbf{4}^{+}$ (*S*=1/2)	–5024027.1913	–5023833.0805	–5018970.0214	–5023011.3714
4 (*S*=0)	–5024617.9987	–5024422.4307	–5019571.9362	–5023581.5751
$\mathbf{4}^{-}$ (*S*=1/2)	–5024832.8074	–5024653.8780	–5019792.8930	–5023785.6739
$\mathbf{4}^{2-}$ (*S*=1)	–5024727.8452	–5024562.1716	–5019695.3699	–5023652.4474
$\mathbf{4}^{2-}$ (*S*=0)	–5024746.2772	–5024585.1807	–5019718.8376	–5023681.1121
Δ*E*= 4^{2-}(*S*=1)–4^{2-}(*S*=0)	**18.4320 (1540.7945 cm^{-1})**	**23.0091 (1923.4101 cm^{-1})**	**23.4677 (1961.7461 cm^{-1})**	**28.6647 (2396.1813cm^{-1})**
$\mathbf{5a}^{3+}$ (*S*=1/2)	–8354396.4251	–8354325.0619	–8346032.8826	–8352723.9688

5a^{2+} (*S*=0)	–8355424.1514	–8355341.8220	–8347045.7450	–8353733.2392
5a^{+} (*S*=1/2)	–8356105.9210	–8356029.3253	–8347725.6647	–8354375.8217
5a (*S*=1)	–8356563.8067	–8356496.0074	–8348183.1922	–8354831.9948
5a (*S*=0)	–8356467.6554	–8356478.9847	–8348169.9148	–8354773.8680
5a (BS(1,1) *S*=0)	—	—	—	–8354831.4810
Δ*E*= 5a BS(1,1) – 5a(*S*=1)	—	—	—	**0.5138 (42.9503 cm^{-1})**
5b^{3+} (*S*=1/2)	–8354392.9802	–8354324.9926	–8346031.9782	–8352724.8993
5b^{2+} (*S*=0)	–8355417.9725	–8355350.2982	–8347054.4191	–8353722.9793
5b^{+} (*S*=1/2)	–8356082.6305	–8356019.2617	– 8347710.7083	–8354364.6626
5b (*S*=1)	–8356550.6472	–8356489.8375	–8348172.2662	–8354824.2955
5b (*S*=0)	–8356526.7651	–8356472.7525	–8348158.0796	–8354764.3417
5b (BS(1,1) *S*=0)	—	–8356489.8443	–8348172.2757	–8354824.0017
Δ*E*= 5b BS(1,1) – 5b(*S*=1)	—	**–0.0098 (–0.8192 cm^{-1})**	**–0.0095 (–0.7941 cm^{-1})**	**0.2938 (24.5998 cm^{-1})**
6^{+} (*S*=1/2)	–4939826.3513	–4939672.3200	–4934800.0286	–4938832.3965
6 (*S*=0)	–4940389.8052	–4940240.0177	–4935365.1321	–4939378.2207
6^{-} (*S*=1/2)	–4940595.4039	–4940442.0061	–4935575.0676	–4939569.3224
6^{2-} (*S*=1)	–4940475.2505	–4940353.5136	–4935459.9974	–4939420.3287
6^{2-} (*S*=0)	–4940493.2677	–4940375.6130	–4935482.6930	–4939438.3336
Δ*E*= 6^{2-}(*S*=1)–6^{2-}(*S*=0)	**18.0171 (1506.1116 cm^{-1})**	**22.0994 (1839.8418 cm^{-1})**	**22.6956 (1897.2036 cm^{-1})**	**18.0049 (1505.0918 cm^{-1})**

Table S31 DFT calculated Mulliken spin distributions for **2**^{n}, **3**^{n}, **4**^{n}, **5a**^{n}**, 5b**^{n} and **6**^{n} by multiple methods and basis set

Complex	TZVP+LANL2DZ									6-31G*+LANL2DZ		
	M06L			τ-HCTH			PBE			B3LYP		
	Os	HL/L/ L$^{/}$	pap	Os	HL/L/ L$^{/}$	pap	Os	HL/L/ L$^{/}$	pap	Os	HL/L/L$^{/}$	pap
2^{2+} (*S*=1/2)	0.104	0.901	-0.004	0.116	0.885	-0.009	0.156	0.844	-0.001	-0.014	1.018	-0.001
2 (*S*=1/2)	-0.064	-0.019	1.045	-0.016	0.018	0.997	-0.001	0.020	0.980	-0.174	0.014	1.163
3^{2+} (*S*=1/2)	0.546	0.467	-0.014	0.503	0.524	-0.029	0.485	0.505	0.013	0.566	0.462	-0.024
3 (*S*=1/2)	-0.040	-0.003	1.086	0.020	-0.003	0.984	0.033	-0.002	0.970	-0.194	-0.008	1.183
4^{+} (*S*=1/2)	0.322	0.736	-0.062	0.320	0.750	-0.068	0.408	0.450	0.196	0.251	0.841	-0.064
4^{-} (*S*=1/2)	0.075	-0.014	0.940	0.101	-0.014	0.914	0.131	-0.006	0.874	-0.173	-0.036	1.206
5a^{3+} (*S*=1/2)	0.668	0.371	-0.047	0.624	0.423	-0.048	0.596	0.409	-0.006	0.587	0.467	-0.063
5a^{+} (*S*=1/2)	0.037	0.009	0.955	0.059	0.007	0.902	0.097	0.015	0.882	-0.139	-0.001	1.179
5a (*S*=1)	0.096	0.004	1.877	0.147	0.004	1.839	0.199	-0.004	1.792	-0.281	-0.021	2.365
5b^{3+} (*S*=1/2)	0.667	0.359	-0.019	0.634	0.394	-0.033	0.615	0.373	0.014	0.618	0.421	-0.040
5b^{+} (*S*=1/2)	-0.006	-0.004	1.002	0.046	0.001	0.955	0.068	0.006	0.928	-0.180	-0.014	1.203
5b (*S*=1)	-0.036	-0.003	2.005	0.062	-0.010	1.965	0.114	0.001	1.88	-0.352	0.030	2.378
6^{+} (*S*=1/2)	0.299	0.769	-0.069	0.313	0.785	-0.099	0.316	0.715	-0.068	0.218	0.822	-0.036
6^{-} (*S*=1/2)	0.182	-0.016	0.834	0.193	-0.014	0.824	0.222	-0.007	0.782	-0.059	-0.031	1.088

Table S32 DFT Calculated single point energies (in kJ/Mole) of $\mathbf{2}^n$, $\mathbf{3}^n$, $\mathbf{4}^n$, $\mathbf{6}^n$ by multiple methods and basis set (ground sate are highlighted in bold)

Complex	TZVP+LANL2DZ			6-31G*+LANL2DZ
	M06L	τ-HCTH	PBE	B3LYP
$\mathbf{2}^-$ (BS(1,1), *S*=0)	–5026479.9994	–5026353.6491	–5021478.6637	–5025426.9353
$\mathbf{2}^-$ (*S*=1)	–5026480.0867	–5026348.3136	–5021475.1999	–5025427.0881
2^- (*S*=0)	–**5026513.0814**	–**5026376.4682**	–**5021505.8830**	–**5025434.8858**
$\mathbf{3}^-$ (BS(1,1), *S*=0)	–5026434.7952	–5026284.8621	–5021409.8869	–5025359.2835
$\mathbf{3}^-$ (*S*=1)	–5026432.9676	–5026285.3565	–5021409.1796	–5025374.7676
$\mathbf{3}^-$ (*S*=0)	–**5026459.0509**	–**5026311.4269**	–**5021436.1382**	–**5025388.8705**
$\mathbf{4}^{2-}$ (BS(1,1), *S*=0)	—	—	—	–5023651.2732
$\mathbf{4}^{2-}$ (*S*=1)	—	—	—	–5023652.2531
$\mathbf{4}^{2-}$ (*S*=0)	—	—	—	–**5023681.6505**
$\mathbf{6}^{2-}$ (BS(1,1), *S*=0)	—	—	—	–4939418.7085
$\mathbf{6}^{2-}$ (*S*=1)	—	—	—	–4939420.3783
$\mathbf{6}^{2-}$ (*S*=0)	—	—	—	–**4939437.9022**

Table S33 Selected DFT calculated ((u)B3LYP/6-31G*/LANL2DZ) bond lengths for $\mathbf{2}^n$

Bond length (Å)	DFT			
	$\mathbf{2}^{2+}$ S=1/2	$\mathbf{2}^{+}$ S=0	**2** S=1/2	$\mathbf{2}^{-}$ S=0
Os1-N1	2.106	2.105	2.118	2.136
Os1- N2	2.105	2.101	2.118	2.133
Os1-N3	2.095	2.081	2.083	2.073
Os1-N5	2.074	2.053	2.042	2.022
Os1-N6	2.080	2.059	2.038	2.020
Os1-N8	2.096	2.082	2.082	2.073
C4-O1	1.260	1.306	1.286	1.294
C7-O2	1.304	1.278	1.309	1.315
C5-C6	1.453	1.475	1.477	1.478
N4-N5	1.287	1.293	1.328	1.365
N6-N7	1.287	1.293	1.327	1.364
O1-H1	1.030	1.090	1.105	1.114
O2⋯H1	1.433	1.319	1.293	1.280
O1⋯ O2	2.449	2.403	2.393	2.390

Table S34 Selected DFT calculated ((u)B3LYP/6-31G*/LANL2DZ) bond lengths for $\mathbf{3}^{n}$

Bond length (Å)	DFT			
	$\mathbf{3}^{2+}$ S=1/2	$\mathbf{3}^{+}$ S=0	**3** S=1/2	$\mathbf{3}^{-}$ S=0
Os1-N1	2.162	2.173	2.192	2.213
Os1-O2	1.972	2.041	2.081	2.124
Os1-N3	2.089	2.080	2.092	2.091
Os1-N5	2.088	2.025	1.998	1.979
Os1-N6	2.086	2.035	2.021	1.992
Os1-N8	2.099	2.071	2.075	2.070
C4-O1	1.317	1.329	1.336	1.343
C10-O2	1.320	1.319	1.308	1.295
C5-C6	1.477	1.482	1.482	1.482
N4-N5	1.280	1.295	1.327	1.364
N6-N7	1.286	1.301	1.341	1.381
O1-H1	1.017	1.015	1.014	1.016
N2⋯H1	1.581	1.594	1.598	1.588
O1⋯N2	2.499	2.517	2.524	2.521

Table S35 Selected DFT calculated ((u)B3LYP/6-31G*/LANL2DZ) bond lengths for $\mathbf{4}^{n}$

Bond length (Å)	DFT			
	$\mathbf{4}^{+}$ S=1/2	**4** S=0	$\mathbf{4}^{-}$ S=1/2	$\mathbf{4}^{2-}$ S=0
Os1-N1	2.071	2.059	2.071	2.076
Os1-N3	2.020	2.011	2.000	1.976
Os1-N6	2.071	2.059	2.071	2.076
Os1-N8	2.020	2.011	2.000	1.976
Os1-O1	2.044	2.048	2.092	2.142
Os1-O2	2.044	2.048	2.092	2.142
C15-O1	1.312	1.346	1.331	1.316
C20-O2	1.312	1.346	1.331	1.316
C21-C16	1.478	1.496	1.495	1.494
N2-N3	1.298	1.312	1.347	1.389
N7-N8	1.298	1.312	1.347	1.389

Table S36 Selected DFT calculated ((u)B3LYP/6-31G*/LANL2DZ) bond Lengths for $\mathbf{6}^{n}$

Bond length (Å)	DFT			
	$\mathbf{6}^{+}$ S=1/2	**6** S=0	$\mathbf{6}^{-}$ S=1/2	$\mathbf{6}^{2-}$ S=0
Os1-N1	2.064	2.045	2.063	2.079
Os1-N3	2.025	2.007	1.993	1.976
Os1-N4	1.999	2.009	1.997	1.978
Os1-N6	2.060	2.044	2.063	2.081
Os1-O1	2.040	2.043	2.082	2.128
Os1-O2	2.051	2.040	2.077	2.123
C1-O1	1.332	1.349	1.334	1.319
C12-O2	1.301	1.349	1.335	1.319
C6-C7	1.470	1.486	1.486	1.485
N2-N3	1.299	1.316	1.355	1.400
N4-N5	1.304	1.315	1.355	1.400

Table S37 Selected DFT calculated ((u)B3LYP/6-31G*/LANL2DZ) bond lengths for **5a**^{n}

Bond length (Å)	DFT			
	5a^{3+} *S*=1/2	**5a**$^{2+}$ *S*=0	**5a**$^{+}$ *S*=1/2	**5a** *S*=1
Os1-N1	2.081	2.076	2.066	2.071
Os1-N3	2.050	2.025	2.016	2.011
Os1-N4	2.057	2.034	2.009	1.988
Os1-N6	2.088	2.067	2.092	2.098
Os1-N7	2.193	2.195	2.193	2.205
Os1-O2	2.021	2.058	2.076	2.086
Os2-N8	2.085	2.092	2.082	2.094
Os2-N10	2.049	2.024	1.998	1.987
Os2-N11	2.054	2.004	2.003	1.992
Os2-N13	2.096	2.070	2.095	2.099
Os2-N14	2.188	2.185	2.193	2.209
Os2-O1	1.999	2.054	2.067	2.079
C26-O1	1.304	1.310	1.309	1.307
C53-O2	1.297	1.315	1.313	1.312
C27-C54	1.478	1.487	1.485	1.484
N2-N3	1.298	1.294	1.324	1.349
N4-N5	1.286	1.304	1.311	1.329
N9-N10	1.296	1.291	1.311	1.347
N11-N12	1.285	1.311	1.329	1.337
Os1…Os2	6.601	6.422	6.358	6.362

Table S38 Selected DFT calculated ((u)B3LYP/6-31G*/LANL2DZ) bond lengths for **5b**^{n}

Bond length (Å)	DFT			
	5b^{3+} *S*=1/2	**5b**$^{2+}$ *S*=0	**5b**$^{+}$ *S*=1/2	**5b** *S*=1
Os1-N1	2.099	2.069	2.081	2.088
Os1-N3	2.046	2.015	2.008	1.990
Os1-N4	2.037	2.026	2.0191	2.011
Os1-N6	2.083	2.099	2.069	2.073
Os1-N7	2.190	2.180	2.205	2.217
Os1-O2	2.032	2.051	2.071	2.080
Os2-N8	2.099	2.093	2.075	2.076
Os2-N10	2.079	2.021	2.031	2.017
Os2-N11	2.078	2.004	2.010	1.996
Os2-N13	2.094	2.071	2.078	2.084
Os2-N14	2.169	2.188	2.203	2.213
Os2-O1	1.983	2.054	2.061	2.078
C26-O1	1.310	1.309	1.317	1.315
C53-O2	1.295	1.308	1.314	1.314
C27-C54	1.482	1.488	1.487	1.486
N2-N3	1.285	1.313	1.314	1.331
N4-N5	1.303	1.290	1.325	1.348
N9-N10	1.288	1.291	1.317	1.341
N11-N12	1.280	1.309	1.310	1.329
Os1…Os2	6.616	6.433	6.448	6.445