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Supporting Information

Diosmium compounds bridged by bis(imidazole)-*p*-quinone ligands

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Table S1 Selected crystallographic parameters

	[**1**]$(ClO_4)_2$•CH_2Cl_2	[**2**]$(ClO_4)_2$•CH_2Cl_2	[**3**]$(ClO_4)_2$
empirical formula	$C_{59}H_{42}Cl_4N_{14}O_{10}Os_2$	$C_{59}H_{42}Cl_4N_{14}O_{10}Os_2$	$C_{31}H_{23}ClN_6O_5Os$
formula weight	1629.26	1629.26	785.20
crystal system	triclinic	monoclinic	triclinic
space group	$P\,\bar{1}$	$P2_1/c$	$P\,\bar{1}$
a (Å)	12.1356(2)	10.48690(10)	9.43780(10)
b (Å)	14.8336(4)	18.5944(2)	12.8016(2)
c (Å)	17.2502(4)	33.9047(4)	13.6171(3)
α (deg)	75.546(2)	90	101.594(2
β (deg)	89.585(2)	93.9530(10)	106.424(2)
γ (deg)	88.763(2)	90	94.7480(10)
V (Å^3)	3006.30(12)	6595.61(12)	1528.72(5)
Z	2	4	2
μ (mm^{-1})	4.472	4.076	4.308
ρ_{calcd} (g cm^{-3})	1.800	1.641	1.706
Temperature (K)	150(2)	150(2)	150(2)
F (000)	1588.0	3176.0	768.0
θ range (deg)	1.687 to 25	1.628 to 24.999	1.604 to 25
data/restraints/parameters	10553/54/802	11607/0/802	5381/0/39
$R1$, wR_2 [$I > 2\sigma(I)$]	0.0414, 0.0983	0.0378, 0.0949	0.0218, 0.0531
$R1$, wR_2(all data)	0.0529, 0.1047	0.0430, 0.0976	0.0241, 0.0541
GOF on F^2	1.028	1.071	1.044
largest difference in peak and hole (e Å^{-3})	1.6, -1.95	1.39, -1.21	0.92, -0.71

Table S2 Selected experimental and calculated bond lengths (Å)

	[**1**$^{2+}$]		[**2**$^{2+}$]	
bond	X-ray	DFT (*S*=0)	X-ray	DFT (*S*=0)
Os1-N1	2.095(5)	2.124	2.078(4)	2.130
Os1-N2	2.090(5)	2.134	2.087(4)	2.130
Os1-N7	2.049(5)	2.085	2.045(5)	2.075
Os1-N8	2.041(5)	2.083	2.032(5)	2.068
Os1-N9	2.043(5)	2.084	2.043(5)	2.088
Os1-N10	2.052(6)	2.083	2.064(5)	2.099
Os2-N4	2.072(5)	2.124	2.085(4)	2.135
Os2-N5	2.083(5)	2.134	2.073(5)	2.126
Os2-N11	2.043(6)	2.082	2.035(5)	2.074
Os2-N12	2.054(5)	2.084	2.049(5)	2.083
Os2-N13	2.046(5)	2.085	2.051(5)	2.079
Os2-N14	2.059(6)	2.084	2.055(5)	2.095
C1-O1	1.223(7)	1.228	1.220(6)	1.237
C1-C2	1.464(9)	1.474	1.483(7)	1.483
C2-N1	1.375(8)	1.370	1.370(7)	1.379
C2-C3	1.406(9)	1.414	1.398(7)	1.416
C3-N3	1.356(8)	1.352	1.370(7)	1.346
C3-C4	1.465(9)	1.483	1.458(8)	1.481
C4-O2	1.233(7)	1.228	1.234(7)	1.219
C4-C5	1.460(9)	1.475	1.462(8)	1.479
C5-N4	1.369(8)	1.370		
C5-N6			1.363(7)	1.346
C5-C6	1.399(9)	1.414	1.409(8)	1.416
C6-C1	1.464(9)	1.482	1.462(8)	1.482
C6-N6	1.366(8)	1.351		
C6-N4			1.374(7)	1.378
C7-N1	1.372(8)	1.373	1.379(7)	1.374
C7-N3	1.339(8)	1.337	1.331(7)	1.335
Os1---Os2	9.347	9.457	7.586	7.811

Table S3 Selected experimental and calculated bond angles (deg)

	[**1**$^{2+}$]		[**2**$^{2+}$]	
bond (deg)	X-ray	DFT (*S*=0)	X-ray	DFT (*S*=0)
N1-Os1-N2	78.4(2)	76.971	78.34(17)	77.393
N1-Os1-N7	94.1(2)	88.582	99.15(17)	101.668
N1-Os1-N8	99.04(19)	101.495	93.64(17)	93.461
N1-Os1-N9	169.1(2)	169.306	168.67(18)	166.223
N1-Os1-N10	93.8(2)	95.352	92.88(18)	91.710
N2-Os1-N7	97.5(2)	98.232	175.70(18)	176.076
N2-Os1-N8	175.4(2)	175.372	97.93(18)	98.583
N2-Os1-N9	93.3(2)	94.522	93.79(18)	93.220
N2-Os1-N10	86.8(2)	85.222	86.64(18)	84.865
N7-Os1-N8	78.8(2)	77.310	78.67(19)	77.630
N7-Os1-N9	94.1(2)	99.164	89.17(18)	88.357
N7-Os1-N10	171.6(2)	175.280	97.01(19)	98.992
N8-Os1-N9	89.7(2)	87.476	95.5(2)	97.948
N8-Os1-N10	97.2(2)	99.299	172.68(19	174.308
N9-Os1-N10	78.5(2)	77.283	78.4(2)	77.264
N4-Os2-N5	78.0(2)	77.097	78.00(18)	77.109
N4-Os2-N11	88.5(2)	89.931	97.44(18)	97.461
N4-Os2-N12	102.6(2)	101.193	172.52(18)	170.327
N4-Os2-N13	171.9(2)	168.623	103.48(17)	96.948
N4-Os2-N14	96.3(2)	94.436	85.49(19)	84.680
N5-Os2-N11	97.9(2	97.786	91.62(19)	92.123
N5-Os2-N12	175.7(2)	174.960	95.51(19)	94.629
N5-Os2-N13	96.1(2)	94.311	172.6(2)	167.976
N5-Os2-N14	85.1(2)	86.326	94.8(2)	91.417
N11-Os2-N12	77.9(2)	77.409	78.86(18)	77.609
N11-Os2-N13	98.0(2)	98.711	95.37(19)	99.064
N11-Os2-N14	174.9(2)	174.586	173.4(2)	176.199
N12-Os2-N13	83.7(2)	87.977	83.43(18)	92.080
N12-Os2-N14	99.0(2)	98.565	98.88(19)	100.724
N13-Os2-N14	77.5(2)	77.392	78.2(2)	77.518

Table S4 Selected experimental and calculated bond lengths (Å)

	[**3**$^{2+}$]	
bond	X-ray	DFT (*S*=0)
Os1-O1	2.093(2)	2.149
Os1-N1	2.150(3)	2.167
Os1-N3	2.057(3)	2.078
Os1-N4	2.031(3)	2.058
Os1-N5	2.059(3)	2.084
Os1-N6	2.032(3)	2.069
C1-O1	1.274(4)	1.273
C1-C2	1.431(5)	1.433
C2-N1	1.363(4)	1.364
C2-C3	1.379(5)	1.399
C3-N2	1.363(4)	1.353
C4-N2	1.351(5)	1.352
C4-N1	1.382(4)	1.382
C4-C5	1.469(5)	1.470
C5-C6	1.389(5)	1.400
C6-C7	1.390(6)	1.395
C7-C8	1.380(7)	1.400
C8-C11	1.524(6)	1.509
C8-C9	1.391(7)	1.405
C9-C10	1.376(7)	1.390
C10-C5	1.394(6)	1.407
Os1---Os1′	7.938	8.042

Table S5 Selected experimental and calculated bond angles (deg)

[**3**$^{2+}$]		
bond (deg)	X-ray	DFT (*S*=0)
N1-Os1-O1	79.64(10)	78.554
N1-Os1-N3	84.98(11)	85.368
N1-Os1-N4	104.45(11)	100.899
N1-Os1-N5	164.42(11)	167.335
N1-Os1-N6	96.57(11)	97.047
O1-Os1-N3	95.36(11)	96.137
O1-Os1-N4	172.17(10)	173.692
O1-Os1-N5	85.36(10)	87.344
O1-Os1-N6	88.33(11)	89.655
N3-Os1-N4	78.53(12)	77.558
N3-Os1-N5	100.71(12)	100.638
N3-Os1-N6	176.21(11)	176.113
N4-Os1-N5	90.94(11)	91.328
N4-Os1-N6	97.72(12)	98.953
N5-Os1-N6	78.68(12)	77.601

Table S6 Intermolecular interactions (Å)

	CH---π		π---π	
[**1**]$(ClO_4)_2$	C47---H10	2.863	C9---C45	3.516
	C45---H9	2.752	C4---C10	3.445
	C31---H45	2.758	C3---C4	3.447
	C30---H42	2.797	C2---C12	3.591
[**2**]$(ClO_4)_2$	C54---H11	2.896	C11---C2	3.495
	C55---H11	2.885	C11---C3	3.565
			C11---C1	3.458
			C11---C6	3.590
			C11---C55	3.502
			C12---C4	3.598
			C12---C2	3.564
[**3**]$(ClO_4)_2$	C15---H9	2.875	C8---C10	3.461
			C9---C9	3.377
			C17---C19	3.542
			C18---C20	3.478

Table S7 Energies of DFT (M06L/lanL2DZ/6-31G**) optimized structures

Complex	*E* (Hartrees)					$E_{(HE-LE)}$[a]
	S = 0	*S* = 1/2	*S* = 1	*S* = 3/2	*S* = 2	
[**1**$^{3+}$]		-3332.6959				
[**1**$^{2+}$]	-3333.0397					
[**1**$^{+}$]		-333.2450				
[**1**]	-333.3662		-3333.3719			0.0057 Hartrees 14.97 KJ mol^{-1} 1258 cm^{-1}
[**1**$^{-}$]		-3333.4117		-3330.4101		0.0016 Hartrees 4.20 KJ mol^{-1} 351 cm^{-1}
[**1**$^{2-}$]	-3333.3722		-3333.3654		-3333.3693	0.0068 Hartrees 17.85 KJ mol^{-1} 1492 cm^{-1}
[**2**$^{3+}$]		-333.6617				
[**2**$^{2+}$]	-3333.0175					
[**2**$^{+}$]		-3333.2363				
[**2**]	-3333.3710		-3333.3688			0.0023 Hartrees 6.039 KJ mol^{-1} 505 cm^{-1}
[**2**$^{-}$]	-3333.4162			-3333.3629		0.0533 Hartrees 139 KJ mol^{-1} 11698 cm^{-1}
[**2**$^{2-}$]	-333.3745		-3333.3726		-3333.3706	0.0039 Hartrees 10.24 KJ mol^{-1} 856 cm^{-1}
[**3**$^{4+}$]	-3378.7383		-3378.7590			0.0206 Hartrees 54.08 KJ mol^{-1} 4521 cm^{-1}
[**3**$^{3+}$]		-3379.1962				
[**3**$^{2+}$]	-3379.5543					
[**3**$^{+}$]		-3379.7677				
[**3**]	-3379.8970		-3379.8946			0.0024 Hartrees 6.30 KJ mol^{-1} 527 cm^{-1}
[**3**$^{-}$]		-3379.9440		-3379.9401		0.039 Hartrees 10.24 KJ mol^{-1} 855 cm^{-1}
[**3**$^{2-}$]	-3379.9064		-3379.9059		-3379.9025	0.0039 Hartrees 10.24 KJ mol^{-1} 856 cm^{-1}

Table S8 Selected DFT calculated bond lengths (Å) for [**1**^{n}]

bond	DFT					
	[**1**$^{3+}$] (*S*=1/2)	[**1**$^{2+}$] (*S*=0)	[**1**$^{+}$] (*S*=1/2)	[**1**] (*S*=1)	[**1**$^{-}$] (*S*=1/2)	[**1**$^{2-}$] (*S*=0)
Os1-N1	2.100	2.124	2.109	2.110	2.109	2.125
Os1-N2	2.126	2.134	2.127	2.120	2.113	2.107
Os1-N7	2.082	2.085	2.064	2.058	2.057	2.049
Os1-N8	2.084	2.083	2.065	2.059	2.063	2.060
Os1-N9	2.092	2.084	2.076	2.076	2.078	2.064
Os1-N10	2.095	2.083	2.086	2.086	2.089	2.072
Os2-N4	2.099	2.124	2.107	2.109	2.108	2.126
Os2-N5	2.124	2.134	2.125	2.117	2.111	2.107
Os2-N11	2.082	2.082	2.065	2.060	2.058	2.051
Os2-N12	2.083	2.084	2.064	2.057	2.060	2.055
Os2-N13	2.095	2.085	2.077	2.075	2.077	2.064
Os2-N14	2.095	2.084	2.086	2.085	2.087	2.073
C1-O1	1.227	1.228	1.230	1.230	1.233	1.232
C1-C2	1.464	1.474	1.463	1.463	1.461	1.462
C2-N1	1.361	1.370	1.362	1.361	1.362	1.363
C2-C3	1.413	1.414	1.413	1.414	1.418	1.418
C3-N3	1.350	1.352	1.350	1.349	1.350	1.349
C3-C4	1.476	1.483	1.472	1.472	1.472	1.476
C4-O2	1.227	1.228	1.231	1.231	1.233	1.232
C4-C5	1.465	1.475	1.464	1.464	1.462	1.464
C5-N4	1.361	1.370	1.363	1.362	1.363	1.363
C5-C6	1.413	1.414	1.413	1.415	1.418	1.418
C6-C1	1.476	1.482	1.349	1.349	1.471	1.475
C6-N6	1.350	1.351	1.471	1.472	1.350	1.349
C7-N1	1.383	1.373	1.373	1.374	1.374	1.374
C7-N3	1.332	1.337	1.337	1.338	1.339	1.342

Table S9 Selected DFT calculated bond lengths (Å) for [**2**^{n}]

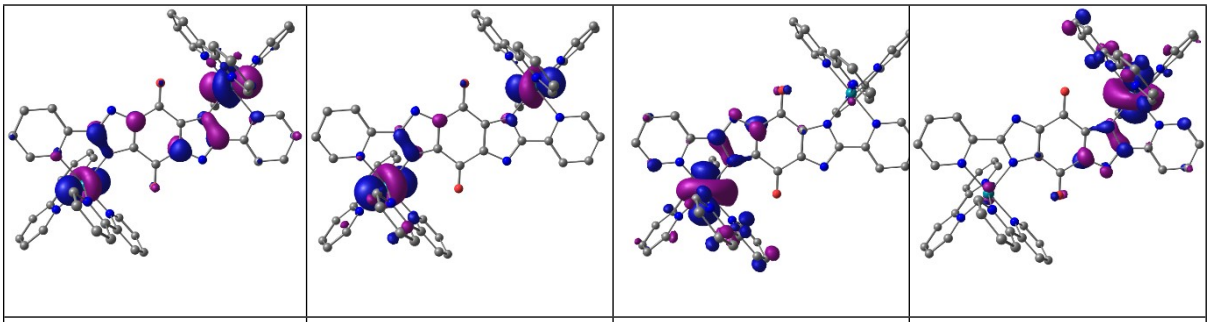
bond	DFT					
	[**2**$^{3+}$] (S=1/2)	[**2**$^{2+}$] (S=0)	[**2**$^{+}$] (*S*=1/2)	[**2**] (*S*=1)	[**2**$^{-}$] (*S*=1/2)	[**2**$^{2-}$] (*S*=0)
Os1-N1	2.086	2.103	2.101	2.105	2.106	2.120
Os1-N2	2.1237	2.131	2.128	2.122	2.115	2.113
Os1-N7	2.073	2.064	2.064	2.056	2.059	2.051
Os1-N8	2.069	2.053	2.054	2.048	2.049	2.046
Os1-N9	2.101	2.083	2.077	2.076	2.076	2.066
Os1-N10	2.106	2.097	2.091	2.085	2.085	2.078
Os2-N4	2.104	2.110	2.095	2.107	2.108	2.128
Os2-N5	2.114	2.126	2.120	2.108	2.101	2.091
Os2-N11	2.077	2.061	2.062	2.063	2.062	2.050
Os2-N12	2.090	2.072	2.075	2.071	2.070	2.064
Os2-N13	2.079	2.067	2.075	2.077	2.071	2.070
Os2-N14	2.101	2.092	2.087	2.076	2.073	2.072
C1-O1	1.236	1.240	1.239	1.236	1.237	1.236
C1-C2	1.471	1.465	1.459	1.463	1.461	1.465
C2-N1	1.367	1.368	1.363	1.361	1.361	1.363
C2-C3	1.420	1.414	1.416	1.416	1.418	1.420
C3-N3	1.346	1.346	1.347	1.348	1.349	1.349
C3-C4	1.475	1.478	1.479	1.476	1.474	1.472
C4-O2	1.216	1.219	1.222	1.224	1.228	1.231
C4-C5	1.472	1.475	1.476	1.474	1.474	1.471
C5-N6	1.343	1.347	1.349	1.348	1.350	1.351
C5-C6	1.420	1.413	1.414	1.415	1.417	1.418
C6-C1	1.469	1.464	1.461	1.462	1.462	1.466
C6-N4	1.363	1.365	1.360	1.360	1.360	1.362
C7-N1	1.389	1.373	1.373	1.373	1.376	1.377
C7-N3	1.326	1.335	1.338	1.339	1.340	1.341

Table S10 Selected DFT calculated bond lengths (Å) for [$\mathbf{3}^{n}$]

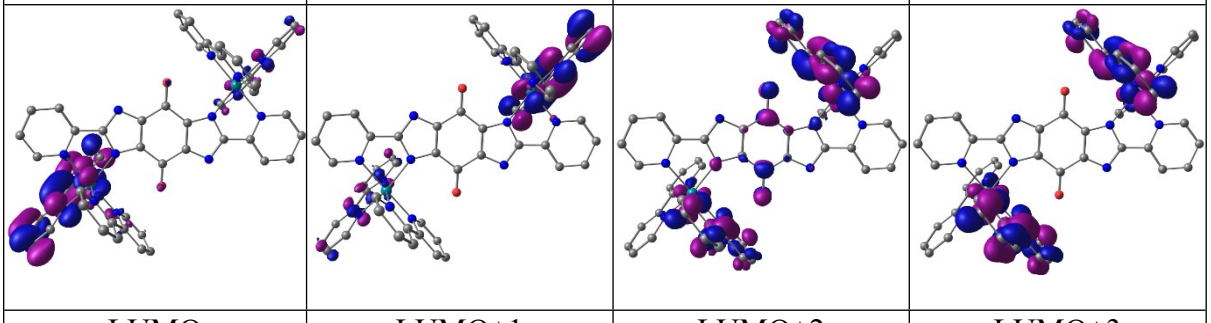
bond	DFT						
	[$\mathbf{3}^{4+}$] (*S*=1)	[$\mathbf{3}^{3+}$] (*S*=1/2)	[$\mathbf{3}^{2+}$] (*S*=0)	[$\mathbf{3}^{+}$] (*S*=1/2)	[**3**] (*S*=0)	[$\mathbf{3}^{-}$] (*S*=1/2)	[$\mathbf{3}^{2-}$] (*S*=0)
Os1-O1	2.095	2.145	2.153	2.133	2.114	2.127	2.127
Os1-N1	2.194	2.155	2.144	2.137	2.137	2.160	2.182
Os1-N3	2.101	2.083	2.075	2.065	2.066	2.062	2.061
Os1-N4	2.079	2.058	2.045	2.039	2.034	2.036	2.043
Os1-N5	2.069	2.069	2.062	2.053	2.050	2.047	2.036
Os1-N6	2.087	2.086	2.074	2.059	2.058	2.063	2.056
C1-O1	1.283	1.275	1.277	1.302	1.308	1.305	1.302
C1-C2	1.421	1.427	1.428	1.417	1.412	1.415	1.414
C2-N1	1.350	1.352	1.360	1.366	1.369	1.366	1.368
C2-C3	1.421	1.412	1.398	1.406	1.409	1.410	1.411
C3-N2	1.335	1.343	1.354	1.363	1.365	1.366	1.362
C4-N2	1.361	1.352	1.347	1.342	1.342	1.345	1.347
C4-N1	1.395	1.395	1.376	1.376	1.377	1.376	1.376
C4-C5	1.434	1.442	1.457	1.458	1.458	1.456	1.455
C5-C6	1.410	1.404	1.399	1.400	1.401	1.401	1.402
C6-C7	1.380	1.384	1.387	1.387	1.388	1.387	1.387
C7-C8	1.410	1.404	1.400	1.399	1.399	1.397	1.399
C8-C11	1.485	1.490	1.496	1.497	1.498	1.498	1.499
C8-C9	1.411	1.406	1.399	1.398	1.398	1.399	1.399
C9-C10	1.377	1.380	1.387	1.388	1.388	1.388	1.387
C10-C5	1.416	1.410	1.400	1.400	1.401	1.403	1.404
Os1---Os1′	8.031	8.036	8.014	7.967	7.960	8.001	8.047

Table S11 Composition and energies of selected molecular orbitals of [$\mathbf{1}^{2+}$] (S=0)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
HOMO–5	-8.718	29	34	13	23
HOMO–4	-8.615	29	19	35	17
HOMO–3	-8.522	57	05	17	21
HOMO–2	-8.508	6	62	13	19
HOMO–1	-8.221	59	7	16	17
HOMO	-8.155	4	6	18	19
LUMO	-6.673	8	2	6	85
LUMO+1	-6.603	1	7	3	90
LUMO+2	-6.359	9	1	9	81
LUMO+3	-6.280	2	9	7	82
LUMO+4	-6.088	3	5	64	28
LUMO+5	-5.914	0	4	13	83



HOMO	HOMO–1	HOMO–2	HOMO–3



LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Composition and energies of selected molecular orbitals of [$\mathbf{1}^{3+}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-11.322	40	30	12	18
HOMO–4	-11.257	30	36	18	16
HOMO–3	-11.212	67	5	10	17
HOMO–2	-11.190	8	64	10	18
HOMO–1	-11.148	27	40	15	17
SOMO	-11.005	13	17	56	15
LUMO	-8.930	3	2	15	81
LUMO+1	-8.906	3	4	3	90
LUMO+2	-8.770	3	3	49	44
LUMO+3	-8.639	5	4	2	89
LUMO+4	-8.582	4	6	24	67
LUMO+5	-8.257	3	3	89	5
β-spin					
HOMO–5	-11.272	28	19	35	18
HOMO–4	-11.193	38	32	11	20
HOMO–3	-11.132	29	34	23	15
HOMO–2	-11.047	42	27	14	18
HOMO–1	-10.995	13	39	28	19
HOMO	-10.630	37	38	9	16
LUMO	-10.597	33	32	20	15
LUMO+1	-8.921	3	2	14	81
LUMO+2	-8.896	3	4	4	90
LUMO+3	-8.748	4	3	46	47
LUMO+4	-8.621	5	4	2	88
LUMO+5	-8.555	4	6	27	63

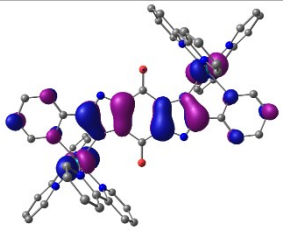
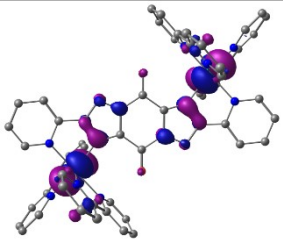
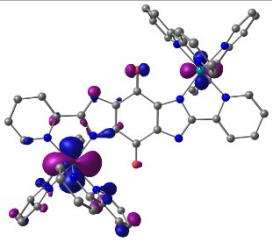
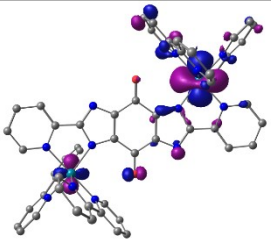
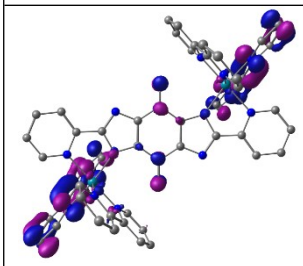
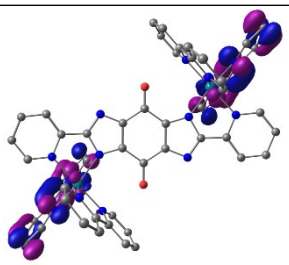
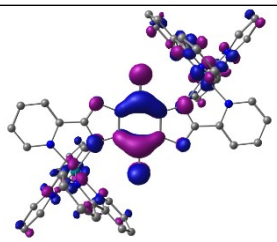
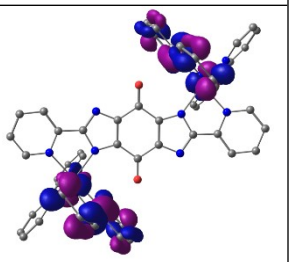
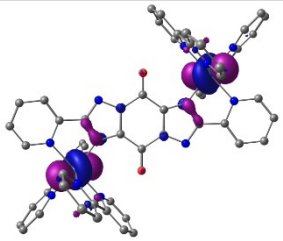
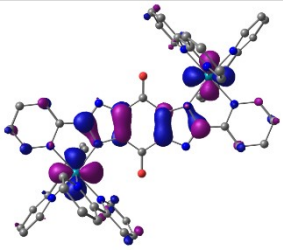
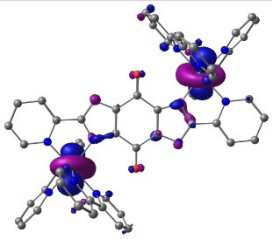
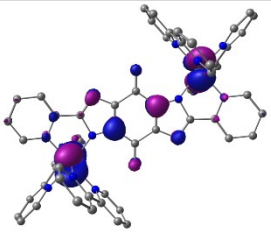
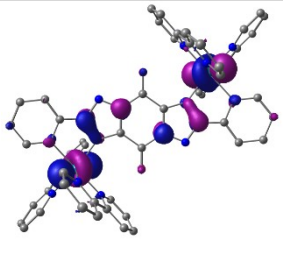
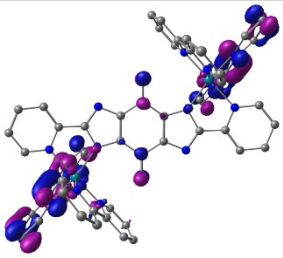
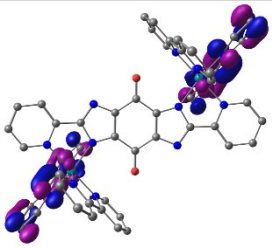
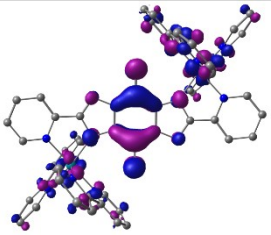
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Composition and energies of selected molecular orbitals of [**1**$^{+}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-6.373	22	36	24	18
HOMO–4	-6.285	61	4	15	20
HOMO–3	-6.261	5	63	12	21
HOMO–2	-5.945	40	35	9	16
HOMO–1	-5.930	31	37	16	16
SOMO 1	-4.418	2	2	9	87
LUMO	-4.400	3	3	5	89
LUMO+1	-4.233	9	2	8	81
LUMO+2	-4.193	3	9	2	86
LUMO+3	-3.954	4	4	70	22
LUMO+4	-3.756	4	4	85	7
LUMO+5	-3.582	3	1	26	71
β-spin					
HOMO–5	-6.417	41	27	10	22
HOMO–4	-6.348	23	36	24	17
HOMO–3	-6.278	60	5	15	20
HOMO–2	-6.253	6	62	12	21
HOMO–1	-5.938	38	37	9	16
HOMO	-5.924	33	35	16	16
LUMO	-4.272	2	1	15	82
LUMO+1	-4.231	2	3	6	89
LUMO+2	-4.115	11	0	3	86
LUMO+3	-4.090	0	11	3	85
LUMO+4	-3.905	4	4	69	24
LUMO+5	-3.736	4	4	93	9

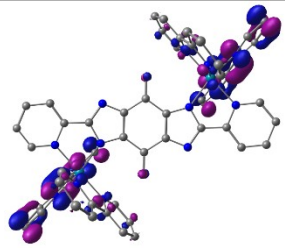
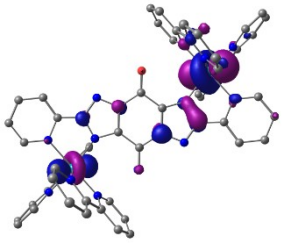
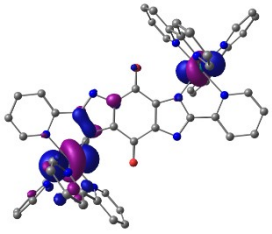
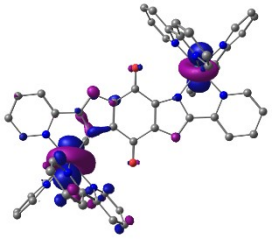
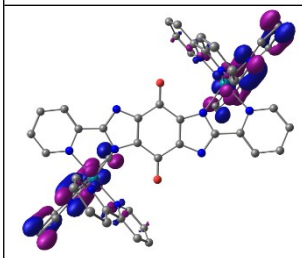
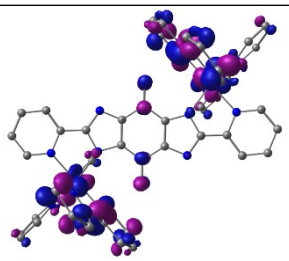
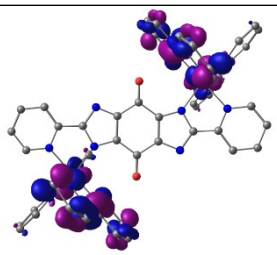
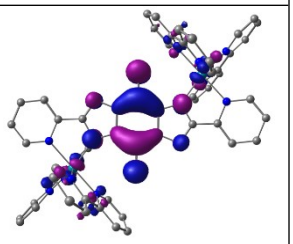
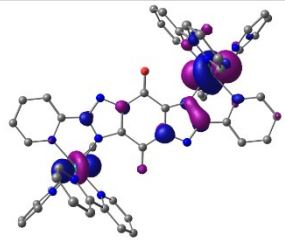
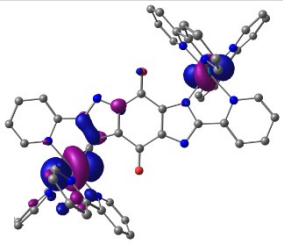
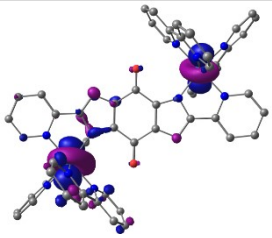
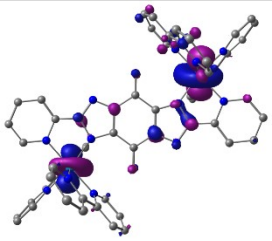
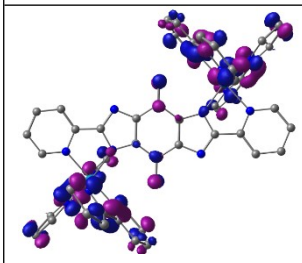
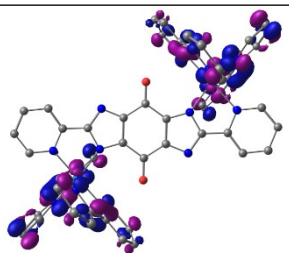
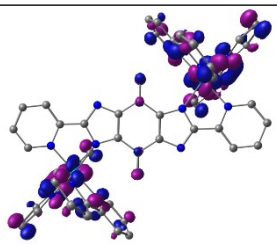
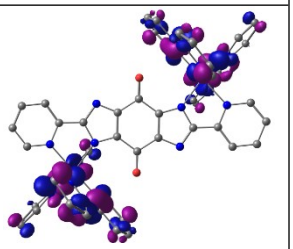
α-spin			
			
SOMO1	HOMO-1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Composition and energies of selected molecular orbitals of [**1**] (*S*=1)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-4.048	57	8	14	21
HOMO–4	-4.022	9	58	11	22
HOMO–3	-3.694	22	52	8	17
HOMO–2	-3.690	50	20	14	16
SOMO 2	-2.220	2	2	11	85
SOMO 1	-2.196	3	2	7	88
LUMO	-2.044	10	2	6	82
LUMO+1	-2.012	2	11	2	85
LUMO+2	-1.775	4	2	70	22
LUMO+3	-1.652	4	4	84	8
LUMO+4	-1.427	1	2	65	3
LUMO+5	-1.370	3	2	16	79
β-spin					
HOMO–5	-4.158	42	26	10	22
HOMO–4	-4.101	23	38	20	19
HOMO–3	-4.029	55	11	13	20
HOMO–2	-4.003	12	56	11	21
HOMO–1	-3.677	4	69	9	17
HOMO	-3.674	68	3	13	15
LUMO	-1.990	2	1	24	73
LUMO+1	-1.928	3	3	10	85
LUMO+2	-1.773	7	2	15	76
LUMO+3	-1.747	2	8	8	83
LUMO+4	-1.685	4	4	59	33
LUMO+5	-1.577	5	5	67	23

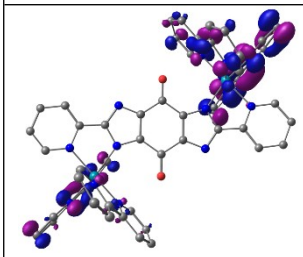
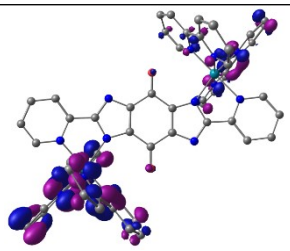
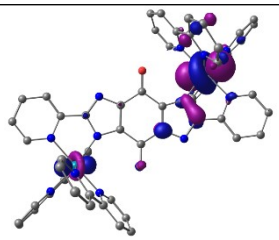
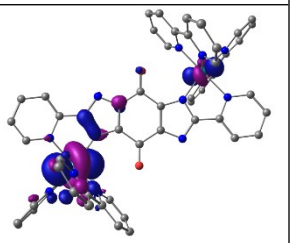
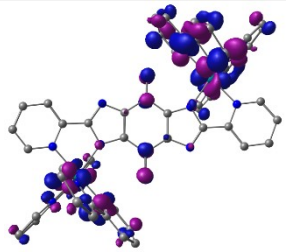
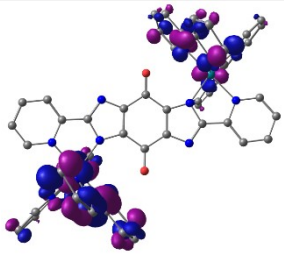
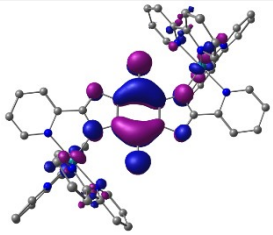
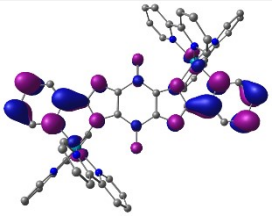
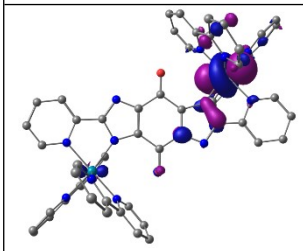
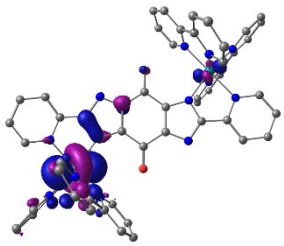
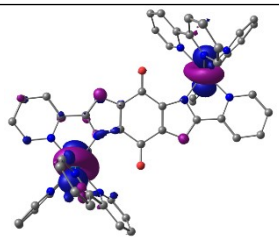
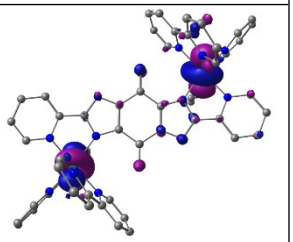
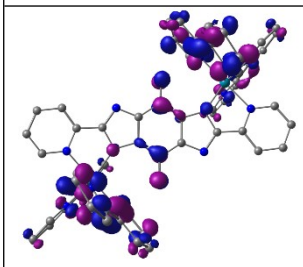
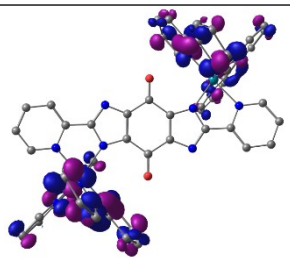
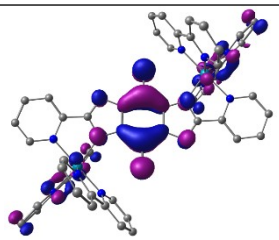
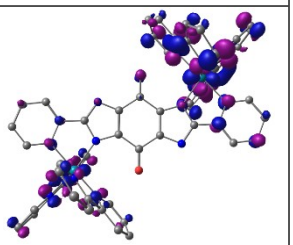
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 Composition and energies of selected molecular orbitals of [**1**$^{-}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-1.814	32	35	13	20
HOMO–4	-1.784	36	32	13	19
HOMO–3	-1.473	1	72	10	18
HOMO–2	-1.462	72	1	11	16
HOMO–1	-0.146	0	5	5	95
HOMO	-0.143	5	0	5	95
LUMO	0.272	5	4	23	68
LUMO+1	0.326	6	7	3	84
LUMO+2	0.420	5	5	83	7
LUMO+3	0.454	5	5	61	30
LUMO+4	0.673	3	3	81	12
LUMO+5	0.822	2	2	54	42
β-spin					
HOMO–5	-1.892	28	32	18	23
HOMO–4	-1.812	35	31	14	20
HOMO–3	-1.779	32	35	13	20
HOMO–2	-1.465	1	71	9	18
HOMO–1	-1.453	72	2	10	16
HOMO	0.023	2	2	12	84
LUMO	0.059	3	3	5	89
LUMO+1	0.358	5	3	49	43
LUMO+2	0.380	3	4	72	21
LUMO+3	0.417	4	6	12	78
LUMO+4	0.508	7	6	40	47
LUMO+5	0.700	4	4	16	77

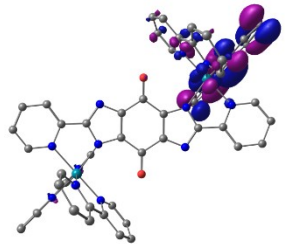
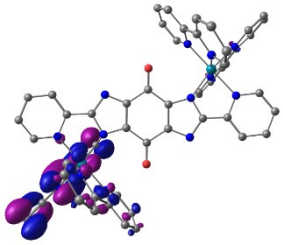
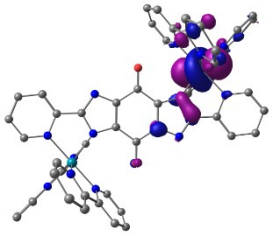
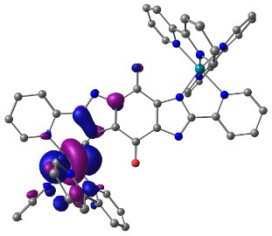
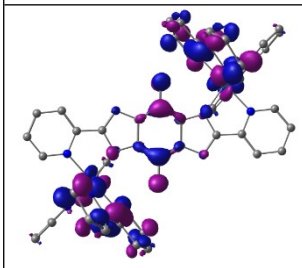
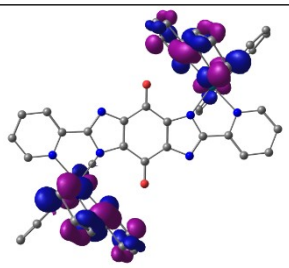
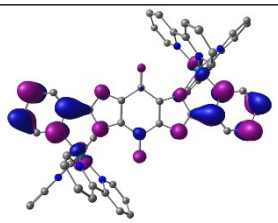
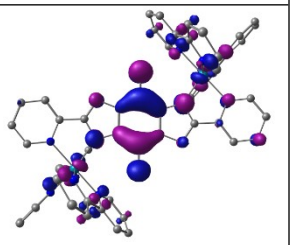
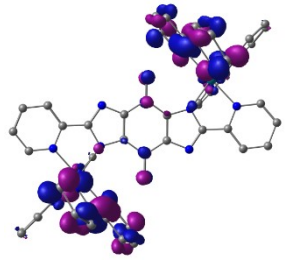
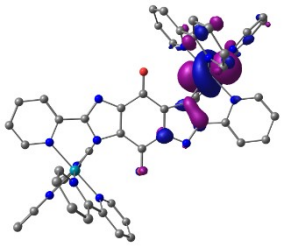
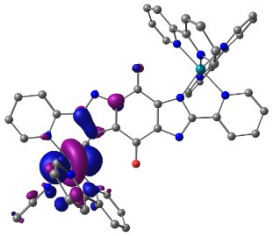
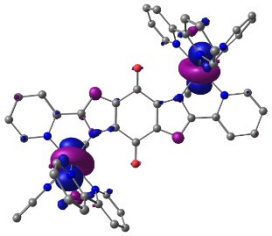
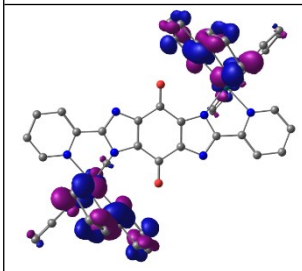
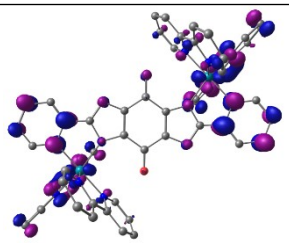
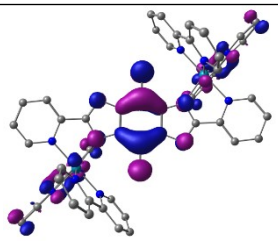
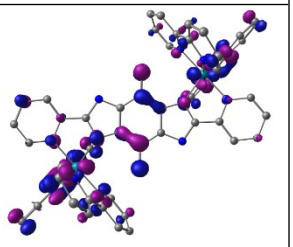
α-spin			
			
SOMO1	SOMO2	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 Composition and energies of selected molecular orbitals of [$\mathbf{1}^{2-}$] (S=0)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
HOMO–5	0.392	46	19	14	21
HOMO–4	0.423	20	46	12	21
HOMO–3	0.748	4	67	11	18
HOMO–2	0.753	68	6	10	16
HOMO–1	2.194	2	1	11	86
HOMO	2.207	1	2	11	86
LUMO	2.409	8	3	9	80
LUMO+1	2.435	4	4	4	83
LUMO+2	2.619	5	6	77	12
LUMO+3	2.628	5	4	69	23
LUMO+4	2.847	3	4	82	11
LUMO+5	3.001	2	2	64	32

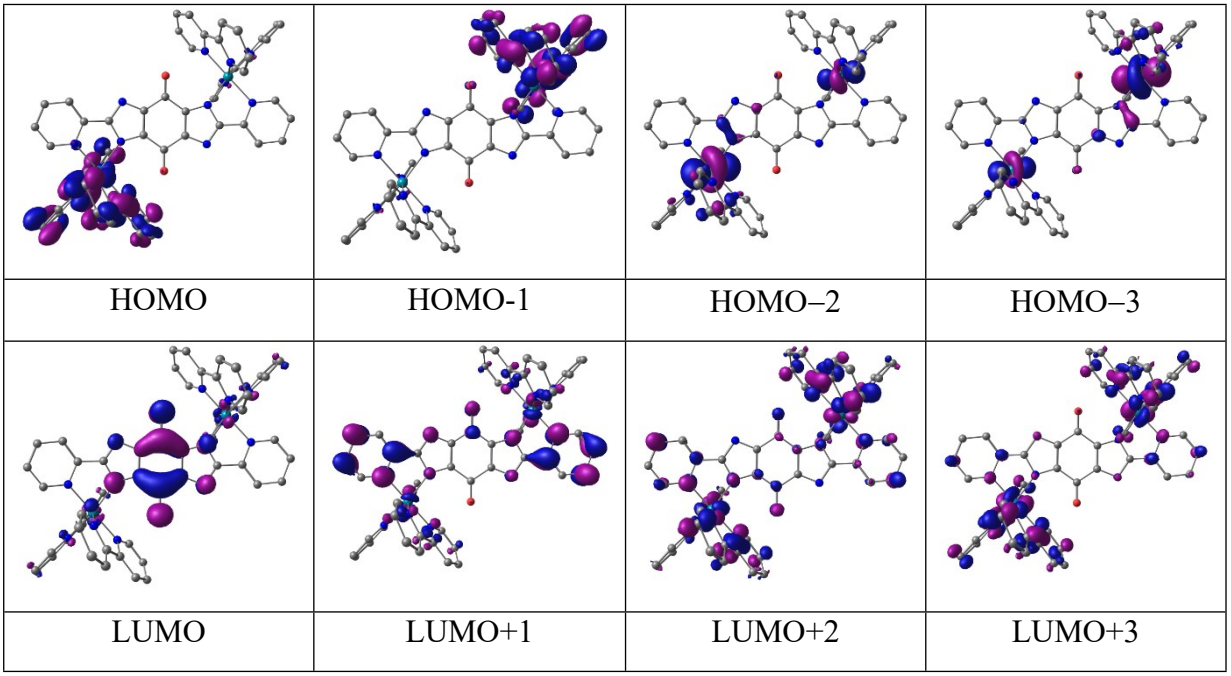


Table S17. Composition and Energies of Selected Molecular Orbitals of [$\mathbf{2}^{2+}$] (S=0)

MO	Energy(ev)				
		Os1	Os2	L1	bpy
HOMO–5	-8.880	5	56	22	17
HOMO–4	-8.826	70	1	12	17
HOMO–3	-8.812	25	24	36	15
HOMO–2	-8.555	20	29	39	12
HOMO–1	-8.543	3	16	76	5
HOMO	-8.416	35	11	41	12
LUMO	-7.062	1	4	3	93
LUMO+1	-7.054	6	1	3	91
LUMO+2	-6.941	0	10	1	88
LUMO+3	-6.795	13	0	3	84
LUMO+4	-6.402	1	2	32	65
LUMO+5	-6.270	2	5	54	39

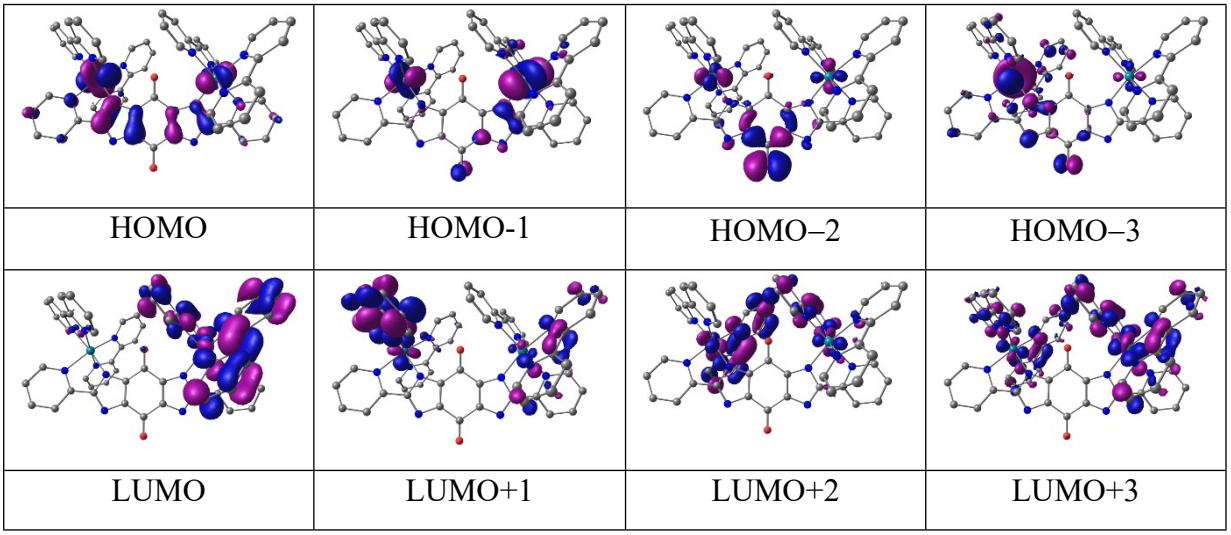


Table S18 Composition and energies of selected molecular orbitals of [$\mathbf{2}^{3+}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-11.651	37	30	16	16
HOMO–4	-11.611	72	1	12	16
HOMO–3	-11.569	1	65	15	18
HOMO–2	-11.538	49	15	23	13
HOMO–1	-11.375	17	13	63	7
SOMO1	-11.345	3	2	93	2
LUMO	-9.421	4	1	11	84
LUMO+1	-9.291	1	7	2	90
LUMO+2	-9.268	1	7	8	85
LUMO+3	-9.206	10	1	3	87
LUMO+4	-9.102	4	4	74	18
LUMO+5	-8.558	1	2	11	86
β-spin					
HOMO–5	-11.616	15	55	8	22
HOMO–4	-11.506	64	5	16	15
HOMO–3	-11.457	7	58	17	19
HOMO–2	-11.426	22	12	58	9
HOMO–1	-11.312	7	7	80	5
HOMO	-11.104	38	33	15	14
LUMO	-11.008	26	30	33	12
LUMO+1	-9.404	5	1	10	85
LUMO+2	-9.282	1	7	2	90
LUMO+3	-9.255	1	8	6	85
LUMO+4	-9.193	11	1	3	86
LUMO+5	-9.051	4	4	76	16

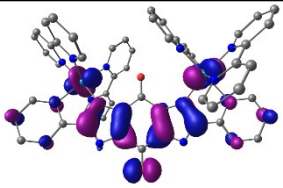
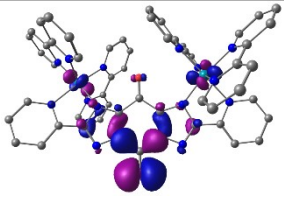
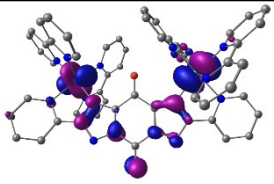
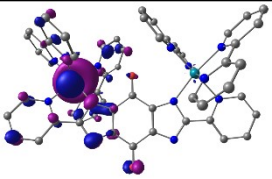
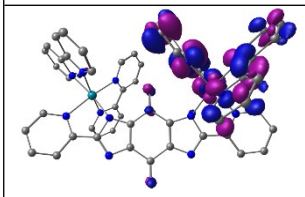
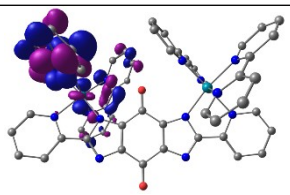
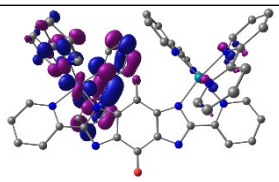
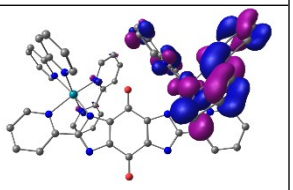
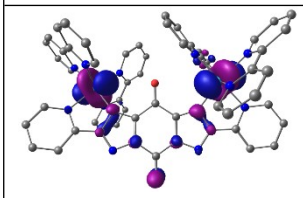
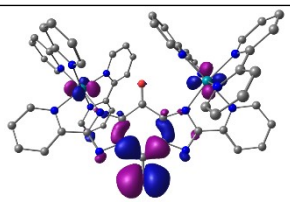
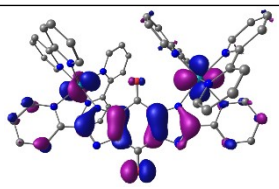
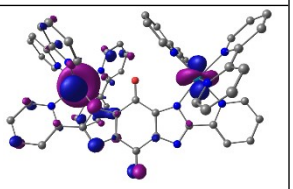
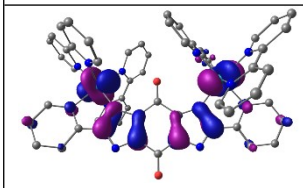
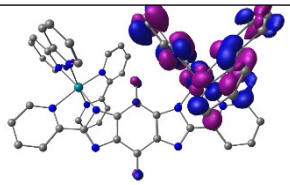
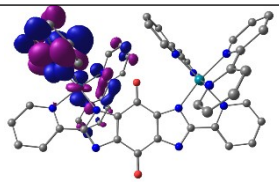
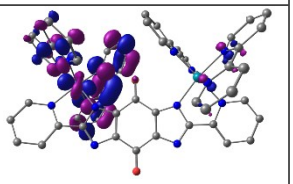
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S19 Composition and energies of selected molecular orbitals of [$\mathbf{2}^{+}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-6.568	45	11	28	16
HOMO–4	-6.538	10	51	19	20
HOMO–3	-6.465	53	6	23	18
HOMO–2	-6.238	17	53	16	14
HOMO–1	-6.155	53	12	21	15
SOMO 1	-4.702	3	3	9	86
LUMO	-4.635	3	5	3	89
LUMO+1	-4.595	0	10	4	85
LUMO+2	-4.457	13	0	4	83
LUMO+3	-4.218	4	4	78	13
LUMO+4	-3.886	1	2	16	81
LUMO+5	-3.848	1	3	57	39
β-spin					
HOMO–5	-6.637	6	10	80	5
HOMO–4	-6.556	44	12	29	15
HOMO–3	-6.526	8	53	19	20
HOMO–2	-6.453	54	5	22	18
HOMO–1	-6.231	16	54	17	14
HOMO	-6.145	53	11	21	15
LUMO	-4.569	1	3	13	83
LUMO+1	-4.499	2	5	3	89
LUMO+2	-4.465	1	8	3	88
LUMO+3	-4.323	11	1	4	84
LUMO+4	-4.176	5	4	74	17
LUMO+5	-3.860	1	2	17	80

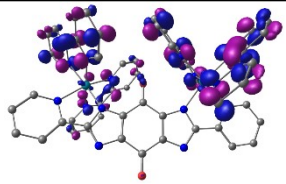
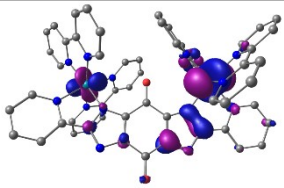
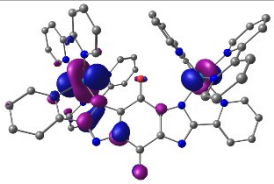
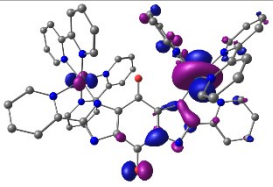
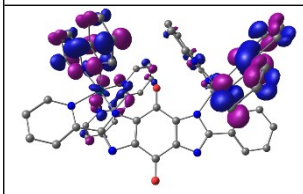
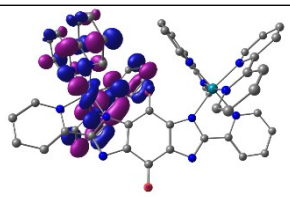
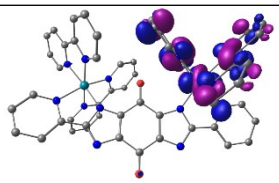
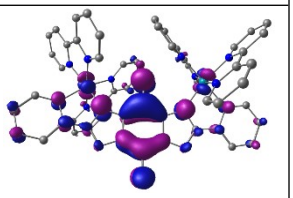
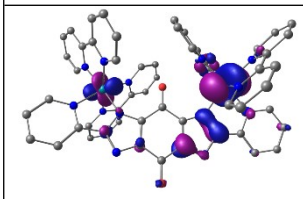
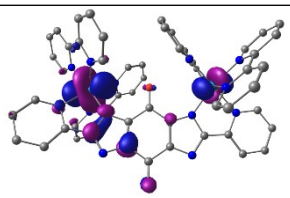
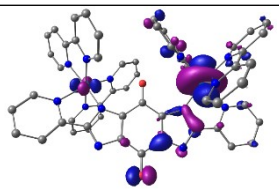
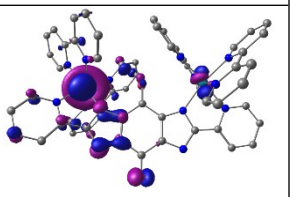
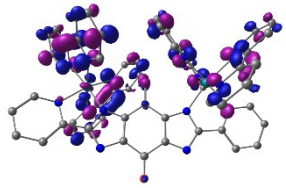
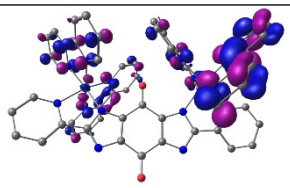
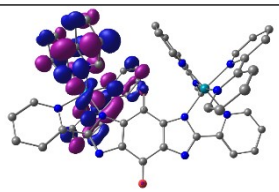
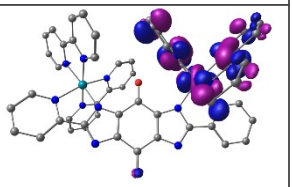
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 Composition and energies of selected molecular orbitals of [**2**] (*S*=1)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-4.175	22	42	14	22
HOMO–4	-4.140	43	21	15	21
HOMO–3	-3.873	35	38	12	15
HOMO–2	-3.821	36	32	17	15
SOMO 2	-2.394	3	1	13	83
SOMO 1	-2.302	2	5	4	89
LUMO	-2.251	0	11	5	84
LUMO+1	-2.157	12	1	5	82
LUMO+2	-1.970	5	5	73	17
LUMO+3	-1.666	2	2	84	12
LUMO+4	-1.584	4	2	51	44
LUMO+5	-1.491	1	4	22	73
β-spin					
HOMO–5	-4.278	22	47	9	23
HOMO–4	-4.219	39	22	21	18
HOMO–3	-4.142	29	36	15	20
HOMO–2	-4.115	36	29	15	20
HOMO–1	-3.853	33	39	12	15
HOMO	-3.801	37	31	17	15
LUMO	-2.159	1	2	31	66
LUMO+1	-2.058	2	5	5	88
LUMO+2	-1.961	1	8	5	86
LUMO+3	-1.906	8	3	26	63
LUMO+4	-1.861	6	3	42	49
LUMO+5	-1.614	3	3	73	16

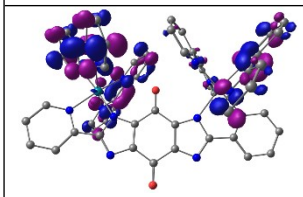
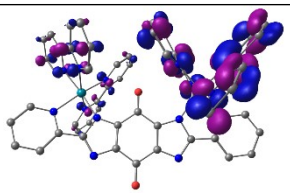
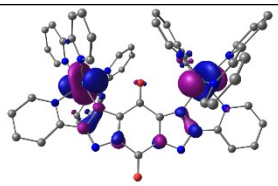
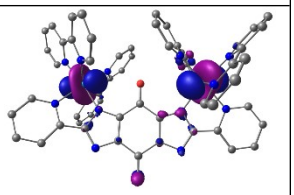
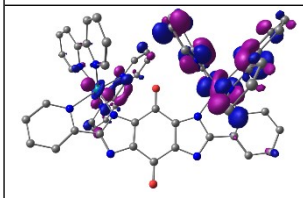
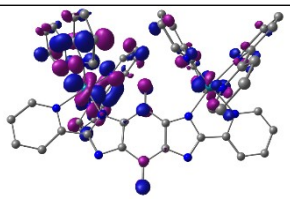
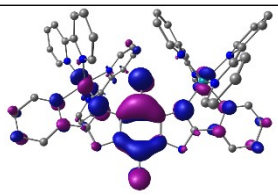
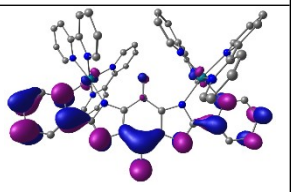
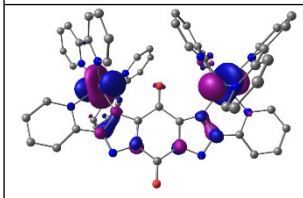
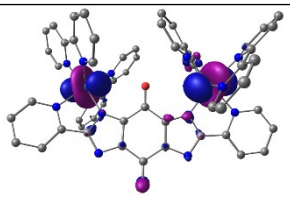
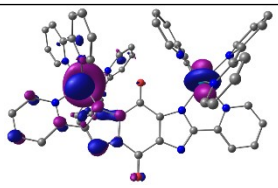
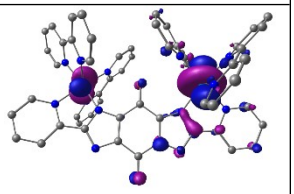
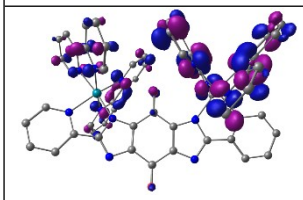
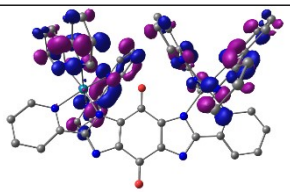
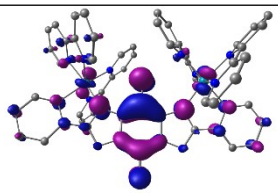
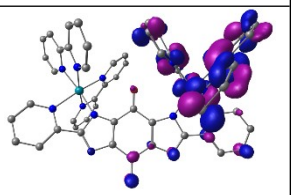
α-spin			
			
SOMO1	SOMO2	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 Composition and energies of selected molecular orbitals of [**2**$^{-}$] (*S*=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
α-spin					
HOMO–5	-1.788	1	66	10	23
HOMO–4	-1.702	1	61	14	24
HOMO–3	-1.543	70	2	12	17
HOMO–2	-1.380	1	70	14	15
HOMO–1	-0.104	4	0	11	85
HOMO	0.106	4	3	16	77
LUMO	0.147	9	2	7	82
LUMO+1	0.356	6	6	65	23
LUMO+2	0.494	0	8	15	77
LUMO+3	0.567	5	1	83	12
LUMO+4	0.671	2	5	55	37
LUMO+5	0.808	4	2	34	59
β-spin					
HOMO–5	-1.872	20	46	12	22
HOMO–4	-1.819	59	4	15	22
HOMO–3	-1.696	1	64	14	21
HOMO–2	-1.516	69	3	11	17
HOMO–1	-1.393	2	69	14	14
HOMO	0.046	1	8	7	84
LUMO	0.163	5	3	12	81
LUMO+1	0.327	6	1	52	41
LUMO+2	0.458	4	2	20	74
LUMO+3	0.523	3	5	42	49
LUMO+4	0.639	6	1	65	28
LUMO+5	0.704	4	4	54	38

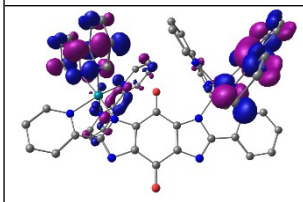
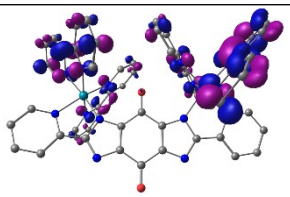
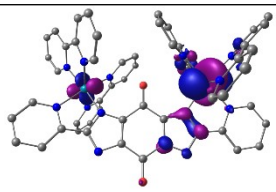
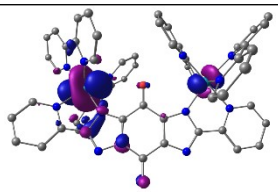
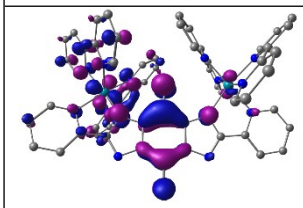
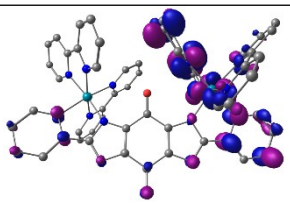
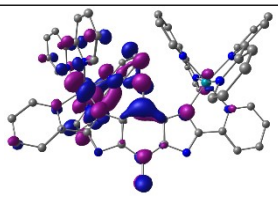
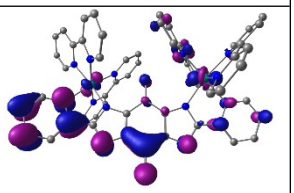
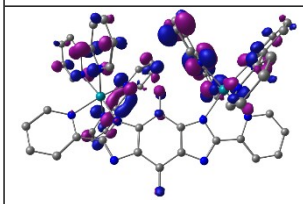
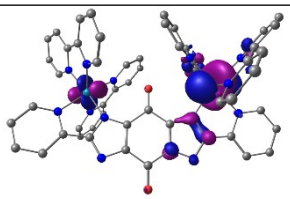
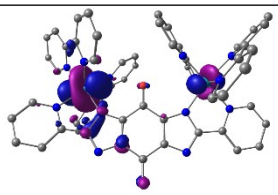
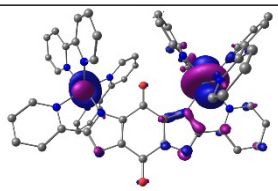
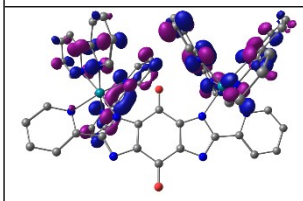
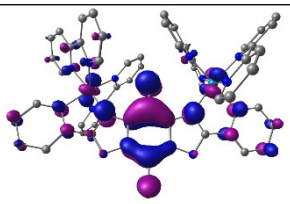
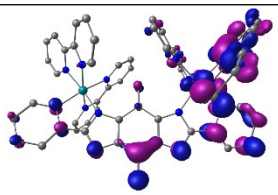
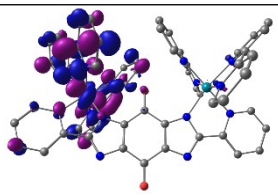
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22 Composition and energies of selected molecular orbitals of [$\mathbf{2}^{2-}$] (S=0)

MO	Energy(ev)	Composition			
		Os1	Os2	L1	bpy
HOMO–5	0.485	46	19	16	18
HOMO–4	0.534	23	44	15	18
HOMO–3	0.754	34	39	10	17
HOMO–2	0.799	38	34	11	17
HOMO–1	2.202	1	1	11	87
HOMO	2.321	1	2	5	92
LUMO	2.448	1	4	71	18
LUMO+1	2.497	3	1	69	28
LUMO+2	2.686	3	9	28	60
LUMO+3	2.701	3	9	34	54
LUMO+4	2.805	10	3	59	29
LUMO+5	2.983	2	2	82	14

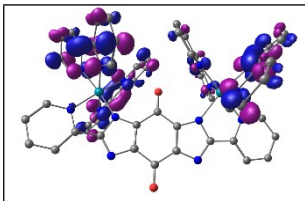
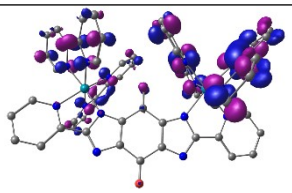
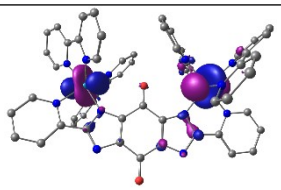
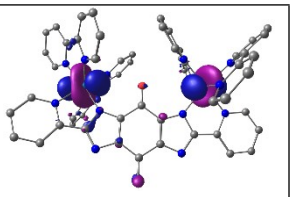
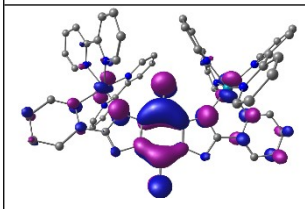
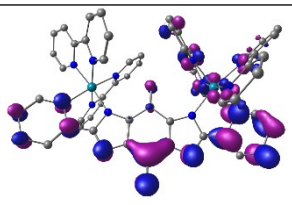
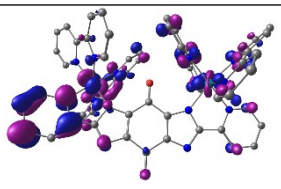
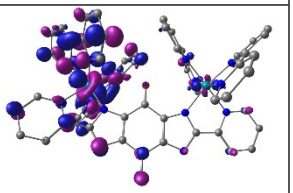
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 Composition and energies of selected molecular orbitals of [$\mathbf{3}^{2+}$] (S=0)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
HOMO–5	-8.845	32	32	11	24
HOMO–4	-8.840	33	33	9	24
HOMO–3	-8.607	31	31	20	18
HOMO–2	-8.502	33	33	19	16
HOMO–1	-8.437	34	34	12	19
HOMO	-8.292	9	9	79	4
LUMO	-8.279	4	4	74	17
LUMO+1	-6.698	5	5	2	89
LUMO+2	-6.660	6	6	5	83
LUMO+3	-6.606	6	6	2	87
LUMO+4	-6.596	6	6	4	84
LUMO+5	-5.953	1	1	3	94

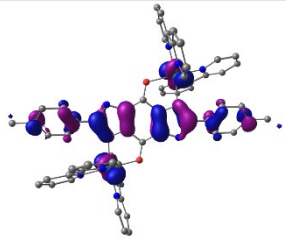
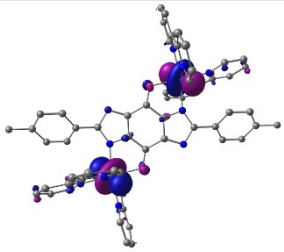
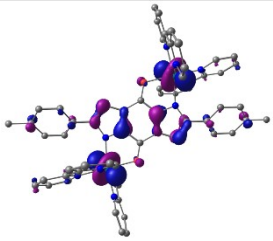
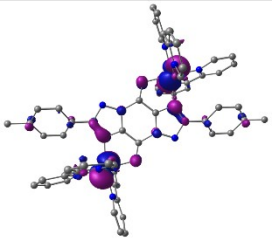
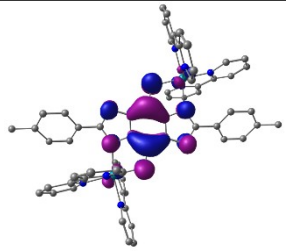
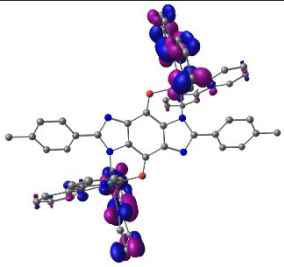
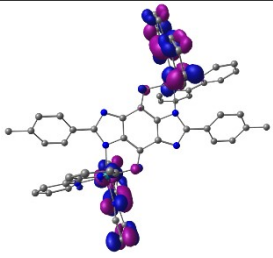
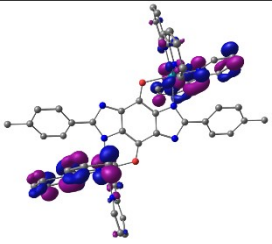
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S24 Composition and energies of selected molecular orbitals of [$\mathbf{3}^{3+}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
α-spin					
HOMO–5	-11.417	35	39	7	19
HOMO–4	-11.415	36	32	14	18
HOMO–3	-11.221	36	36	12	17
HOMO–2	-11.195	37	37	8	18
HOMO–1	-11.119	32	32	18	18
SOMO	-11.014	5	5	87	3
LUMO	-9.872	6	6	80	8
LUMO+1	-8.944	4	4	2	91
LUMO+2	-8.924	4	4	3	88
LUMO+3	-8.883	5	5	2	88
LUMO+4	-8.882	5	5	2	88
LUMO+5	-8.102	1	1	5	93
β-spin					
HOMO–5	-11.521	33	33	16	18
HOMO–4	-11.294	33	33	13	21
HOMO–3	-11.278	36	35	7	22
HOMO–2	-11.032	30	30	24	16
HOMO–1	-10.928	23	23	43	12
HOMO	-10.873	39	39	6	16
LUMO	-10.781	23	23	45	8
LUMO+1	-9.848	6	6	79	9
LUMO+2	-8.935	4	4	2	90
LUMO+3	-8.914	5	5	3	88
LUMO+4	-8.873	5	6	2	87
LUMO+5	-8.873	5	6	2	88

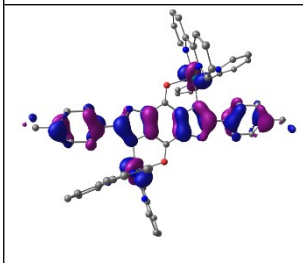
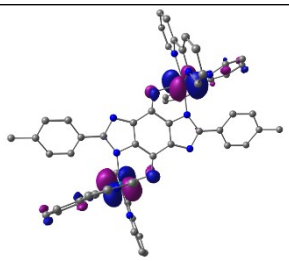
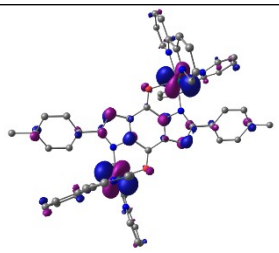
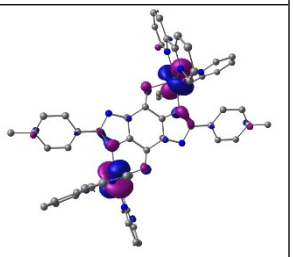
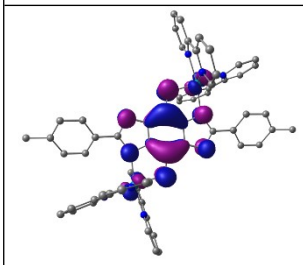
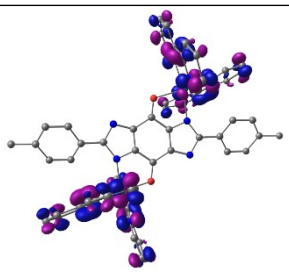
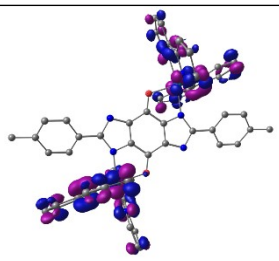
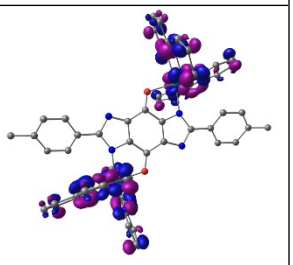
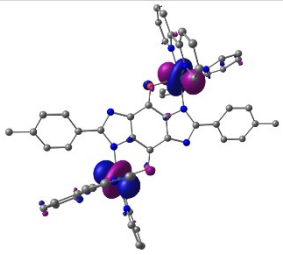
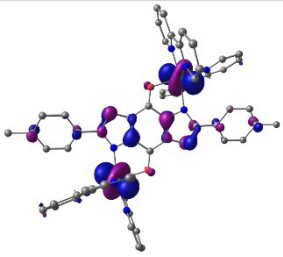
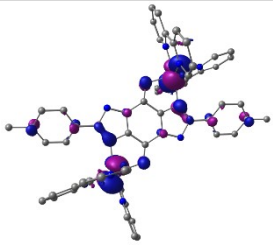
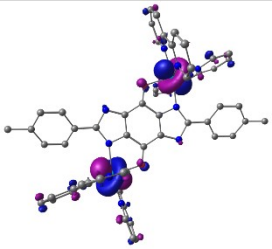
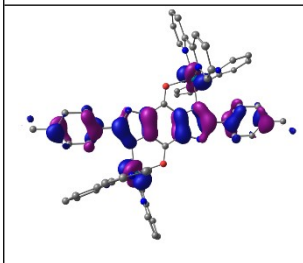
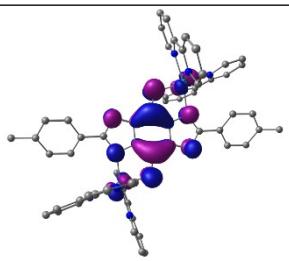
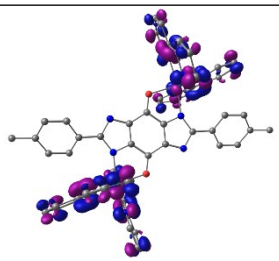
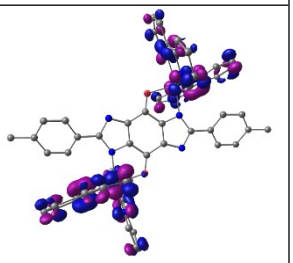
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25 Composition and energies of selected molecular orbitals of [$\mathbf{3}^{4+}$] (S=1)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
α-spin					
HOMO–5	-14.174	2	1	94	3
HOMO–4	-14.088	23	23	43	12
HOMO–3	-14.035	34	34	9	22
HOMO–2	-14.017	35	35	8	22
SOMO 2	-13.713	18	18	54	10
SOMO 1	-13.404	20	20	94	20
LUMO	-12.414	5	5	83	6
LUMO+1	-11.237	3	4	2	91
LUMO+2	-11.230	4	4	2	90
LUMO+3	-11.155	4	4	2	90
LUMO+4	-11.147	4	4	1	91
LUMO+5	-10.325	1	1	5	93
β-spin					
HOMO–5	-14.087	33	33	16	18
HOMO–4	-13.901	21	21	48	10
HOMO–3	-13.846	1	69	9	21
HOMO–2	-13.845	69	1	9	21
HOMO–1	-13.510	21	21	49	10
HOMO	-13.270	29	29	29	14
LUMO	-13.237	38	38	7	17
LUMO+1	-13.145	15	15	64	5
LUMO+2	-12.368	6	6	81	7
LUMO+3	-11.209	4	4	2	91
LUMO+4	-11.201	4	4	2	89
LUMO+5	-11.129	4	4	2	90

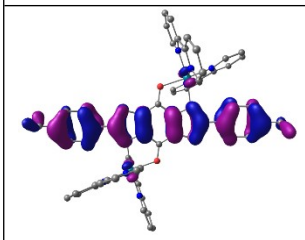
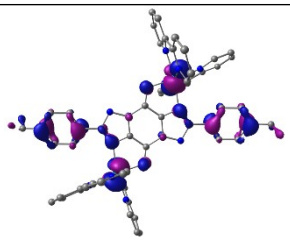
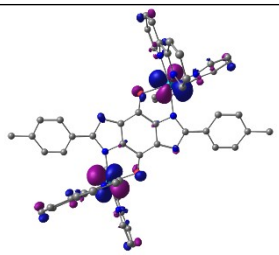
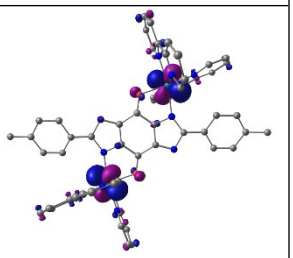
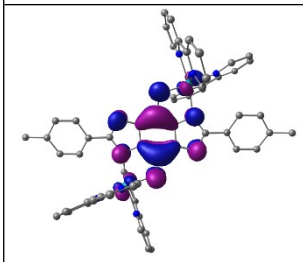
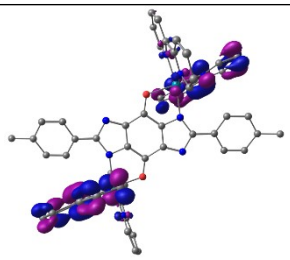
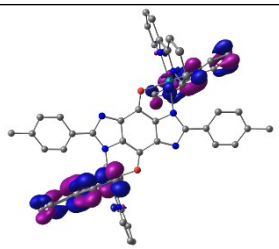
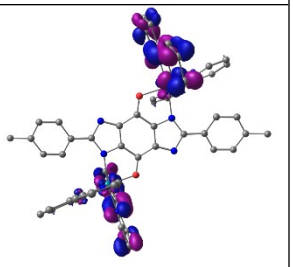
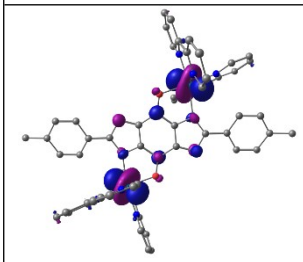
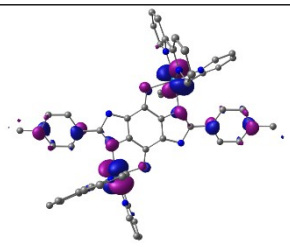
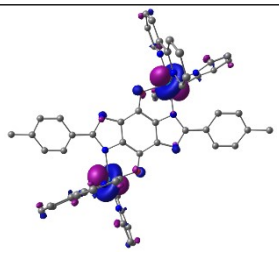
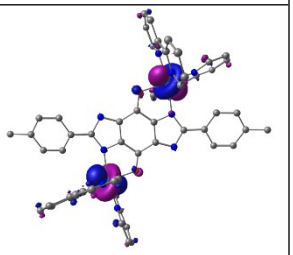
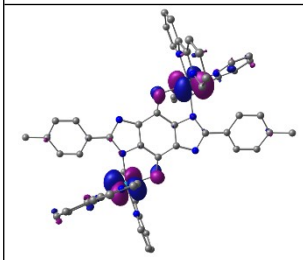
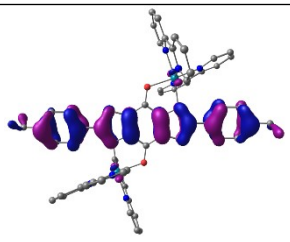
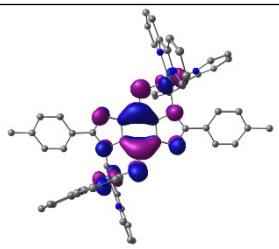
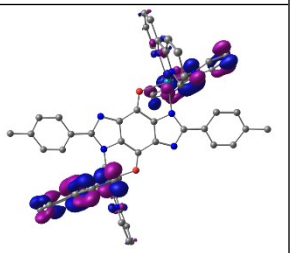
α-spin			
			
SOMO1	SOMO2	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26 Composition and energies of selected molecular orbitals of [$\mathbf{3}^{+}$] (S=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
α-spin					
HOMO–5	-6.498	33	32	9	26
HOMO–4	-6.190	30	30	21	20
HOMO–3	-6.093	34	33	18	15
HOMO–2	-6.087	37	37	8	17
HOMO–1	-5.878	7	7	82	4
HOMO	-4.751	1	1	56	42
LUMO	-4.521	5	5	2	88
LUMO+1	-4.432	7	7	8	79
LUMO+2	-4.419	6	6	2	85
LUMO+3	-4.394	7	7	23	63
LUMO+4	-3.759	1	1	3	95
LUMO+5	-3.756	1	1	3	95
β-spin					
HOMO–5	-6.495	27	38	10	25
HOMO–4	-6.495	37	26	12	25
HOMO–3	-6.175	29	29	23	19
HOMO–2	-6.076	37	36	10	17
HOMO–1	-6.074	34	34	17	15
HOMO	-5.856	6	6	85	3
LUMO	-4.536	2	2	17	79
LUMO+1	-4.456	5	5	2	89
LUMO+2	-4.372	6	6	2	86
LUMO+3	-4.370	6	6	2	86
LUMO+4	-4.153	6	6	67	20
LUMO+5	-3.743	1	1	3	95

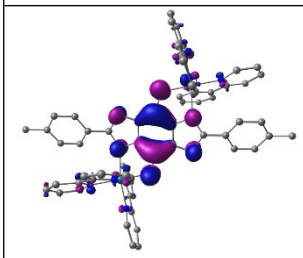
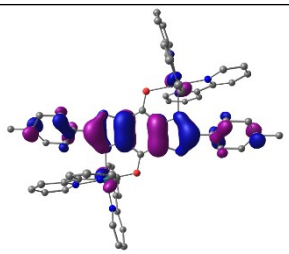
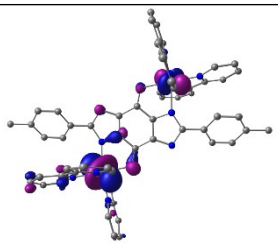
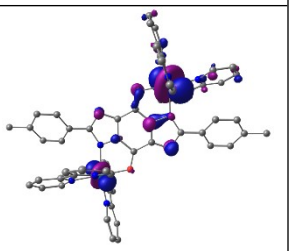
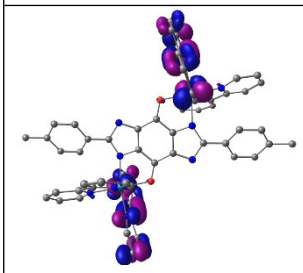
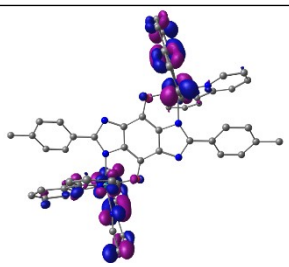
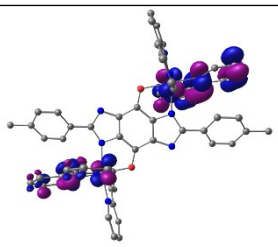
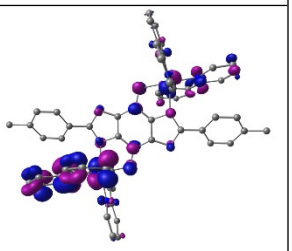
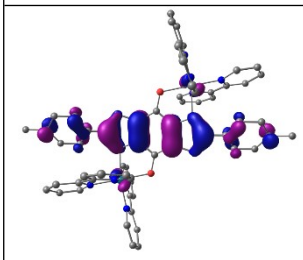
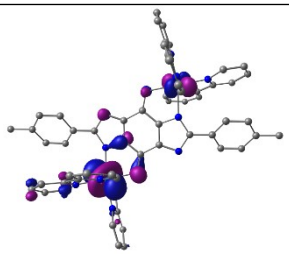
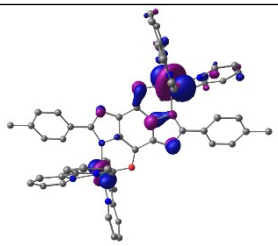
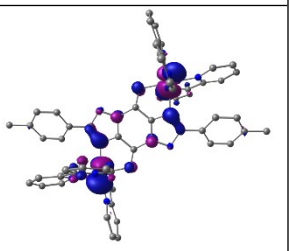
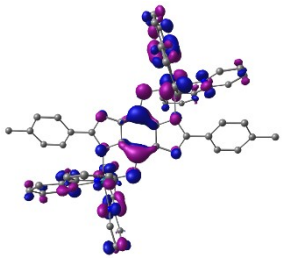
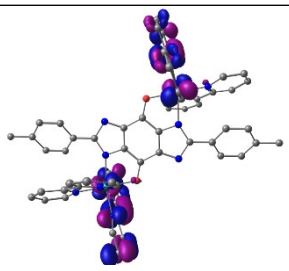
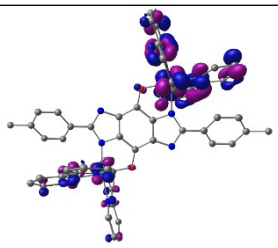
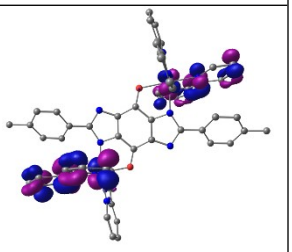
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S27 Composition and energies of selected molecular orbitals of [**3**] (*S*=0)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
HOMO–5	-4.172	14	49	10	26
HOMO–4	-3.909	28	31	20	21
HOMO–3	-3.766	49	14	22	15
HOMO–2	-3.740	18	52	11	18
HOMO–1	-3.607	10	8	77	5
HOMO	-2.367	1	1	41	57
LUMO	-2.189	4	8	2	86
LUMO+1	-2.148	1	12	2	85
LUMO+2	-2.135	4	8	4	84
LUMO+3	-1.976	7	9	41	44
LUMO+4	-1.482	2	0	4	94
LUMO+5	-1.473	0	2	3	95

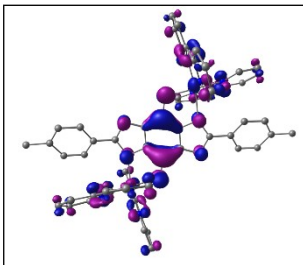
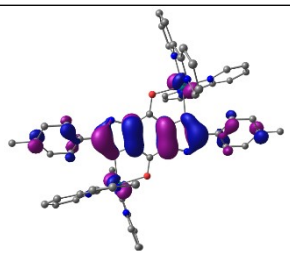
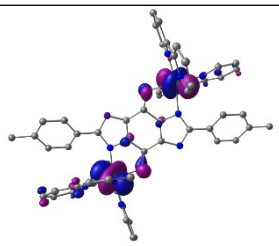
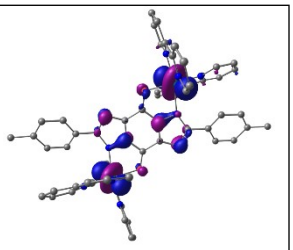
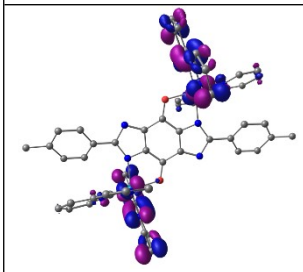
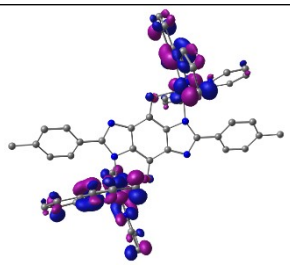
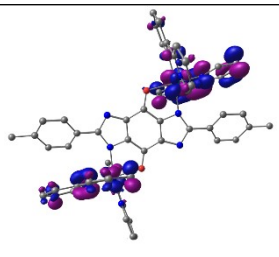
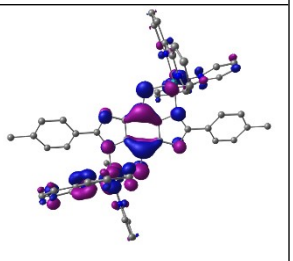
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S28 Composition and energies of selected molecular orbitals of [**3**$^{-}$] (*S*=1/2)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
α-spin					
HOMO–5	-1.623	28	30	19	23
HOMO–4	-1.531	11	7	75	7
HOMO–3	-1.414	41	28	12	19
HOMO–2	-1.390	23	39	24	14
HOMO–1	-0.192	2	1	22	74
HOMO	-0.052	6	6	3	85
LUMO	0.024	14	1	2	83
LUMO+1	0.041	1	13	3	83
LUMO+2	0.287	7	8	58	27
LUMO+3	0.768	2	0	4	94
LUMO+4	0.795	0	2	4	94
LUMO+5	0.986	5	0	2	93
β-spin					
HOMO–5	-1.847	7	56	10	27
HOMO–4	-1.568	30	31	16	22
HOMO–3	-1.539	9	8	75	7
HOMO–2	-1.402	48	21	11	20
HOMO–1	-1.368	18	46	21	15
HOMO	-0.223	2	2	61	35
LUMO	0.128	7	5	3	85
LUMO+1	0.192	7	8	11	75
LUMO+2	0.264	9	3	3	85
LUMO+3	0.319	4	10	11	75
LUMO+4	0.815	3	0	4	93
LUMO+5	0.838	0	3	4	93

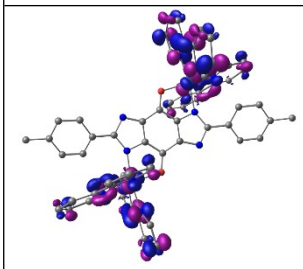
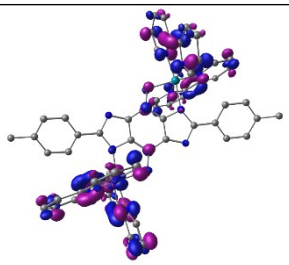
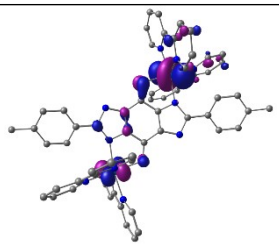
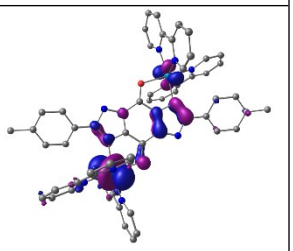
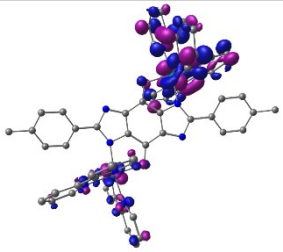
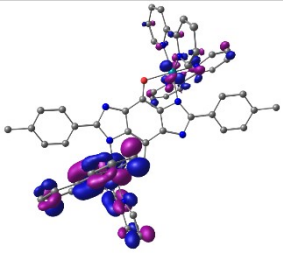
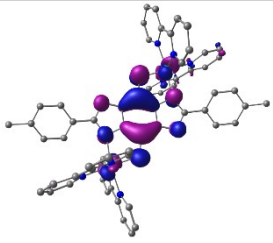
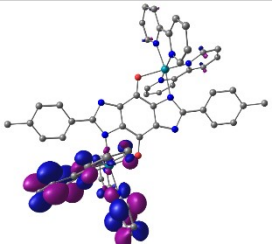
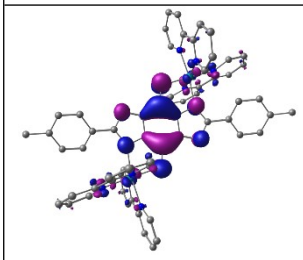
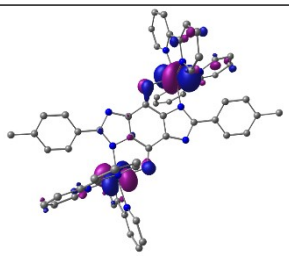
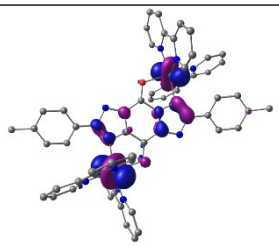
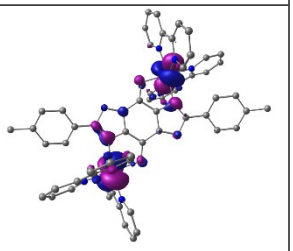
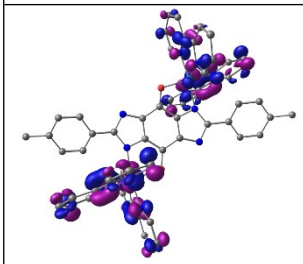
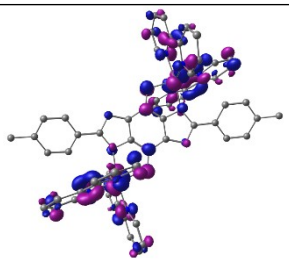
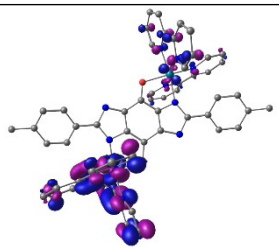
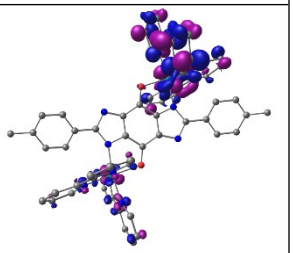
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S29 Composition and energies of selected molecular orbitals of [$\mathbf{3}^{2-}$] (S=0)

MO	Energy(ev)	Composition			
		Os1	Os2	L2	bpy
HOMO–5	0.667	6	6	80	7
HOMO–4	0.725	30	30	16	23
HOMO–3	0.922	3	67	11	19
HOMO–2	0.937	68	2	12	18
HOMO–1	2.120	1	1	45	53
HOMO	2.368	6	6	3	85
LUMO	2.420	0	13	2	85
LUMO+1	2.438	13	0	2	85
LUMO+2	2.554	8	9	36	47
LUMO+3	3.065	0	2	5	93
LUMO+4	3.073	2	0	4	93
LUMO+5	3.269	0	6	4	90

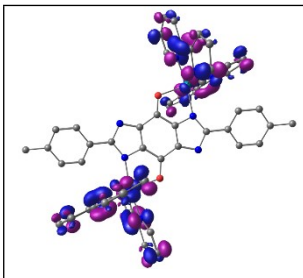
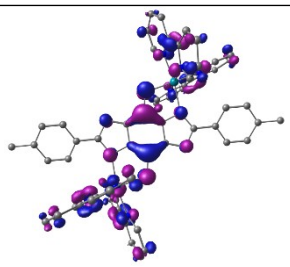
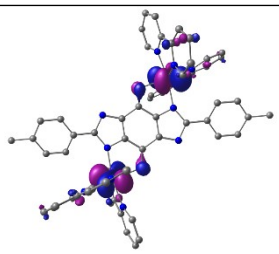
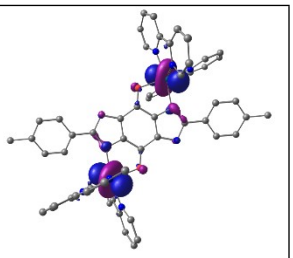
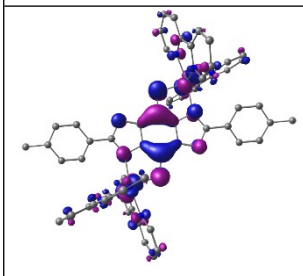
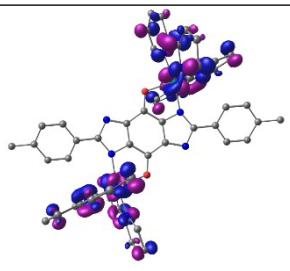
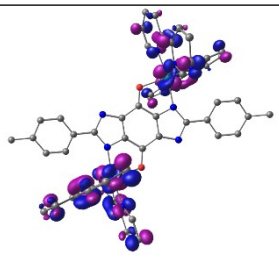
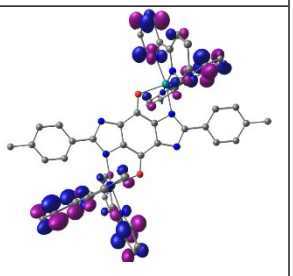
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S30 TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions for [$\mathbf{1}^n$]

λ/nm (DFT) (f)	Transitions	Character
	[$\mathbf{1}^{3+}$] (S=1/2)	
1637(0.008)	HOMO−2(β)→LUMO(β)(0.97)	Os(dπ)→Os(dπ)/L_1(π*)
1308(0.02)	HOMO−3(β)→LUMO(β)(0.91)	Os(dπ)/L_1(π)→Os(dπ)/L_1(π*)
767(0.006)	HOMO−4(β)→LUMO(β)(0.74)	Os(dπ)/bpy(π)→Os(dπ)/L_1(π*)
	HOMO−5(β)→LUMO(β)(0.43)	Os(dπ)/L_1(π)→Os(dπ)/L_1(π*)
	HOMO−5(β)→LUMO(β)(0.42)	L_1(π)→Os(dπ)/L_1(π*)
653(0.07)	HOMO(β)→LUMO+2(β)(0.44)	Os(dπ)→bpy(π*)
	HOMO(α)→LUMO+1(α)(0.41)	L_1(π)/Os(dπ)→bpy(π*)
	HOMO(β)→LUMO+1(β)(0.37)	Os(dπ)→ bpy(π*)
543(0.03)	HOMO−2(α)→LUMO+1(α)(0.42)	Os(dπ)→bpy(π*)
	HOMO−2(β)→LUMO+2(β)(0.39)	Os(dπ)→bpy(π*)
	HOMO−2(β)→LUMO+1(β)(0.33)	Os(dπ)→bpy(π*)
497(0.04)	HOMO(β)→LUMO+5(β)(0.47)	Os(dπ)→bpy(π*)
	HOMO(α)→LUMO+4(α)(0.46)	L_1(π)/Os(dπ)→bpy(π*)/L_1(π*)
473(0.11)	HOMO−2(α)→LUMO+3(α)(0.43)	Os(dπ)→bpy(π*)
	HOMO−2(β)→LUMO+4(β)(0.35)	Os(dπ)→bpy(π*)
	HOMO−1(α)→LUMO+5(α)(0.33)	Os(dπ)→L_1(π*)
444(0.05)	HOMO−2(β)→LUMO+6(β)(0.41)	Os(dπ)→L_1(π*)
	HOMO−2(α)→LUMO+5(α)(0.40)	Os(dπ)→L_1(π*)
	HOMO−1(α)→LUMO+3(α)(0.33)	Os(dπ)→L_1(π*)
416(0.04)	HOMO−13(β)→LUMO(β)(0.41)	bpy(π)→Os(dπ)/L_1(π*)
	HOMO−16(β)→LUMO(β)(0.41)	L_1(π)→Os(dπ)/L_1(π*)
392(0.05)	HOMO−3(β)→LUMO+4(β)(0.65)	Os(dπ)/L_1(π)→bpy(π*)
	HOMO−3(α)→LUMO+3(α)(0.63)	Os(dπ)→L_1(π*)
372(0.15)	HOMO−3(β)→LUMO+5(β)(0.45)	Os(dπ)/L_1(π)→bpy(π*)/L_1(π*)
	HOMO−3(α)→LUMO+4(α)(0.39)	Os(dπ)→bpy(π*)/L_1(π*)
	HOMO−1(β)→LUMO+12(β)(0.36)	Os(dπ)/L_1(π)→bpy(π*)
	HOMO−1(α)→LUMO+11(α)(0.35)	Os(dπ)→bpy(π*)

369(0.28)	HOMO−3(α)→LUMO+5(α)(0.45)	Os(dπ)→L_1(π*)
	HOMO−3(β)→LUMO+6(β)(0.44)	Os(dπ)/L_1(π)→L_1(π*)
	[$\mathbf{1}^{2+}$] (S=0)	
699(0.03)	HOMO−1→LUMO+2(0.68)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
636(0.10)	HOMO−2→LUMO(0.63)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
513(0.05)	HOMO−6→LUMO(0.58)	L_1(π)/bpy(π)/Os(dπ)→bpy(π*)
508(0.01)	HOMO−6→LUMO+1(0.59)	L_1(π)/bpy(π)/Os(dπ)→bpy(π*)
470(0.02)	HOMO−6→LUMO+3(0.62)	L_1(π)/bpy(π)/Os(dπ)→bpy(π*)
461(0.06)	HOMO−4→LUMO+5(0.52)	Os(dπ)/L_1(π)/bpy(π)→bpy(π*)/ L_1(π*)
	HOMO→LUMO+9(0.41)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)/L-$_1$(π*)
408(0.13)	HOMO−5→LUMO+8(0.42)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
	HOMO−3→LUMO+9(0.39)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)/L-$_1$(π*)
391(0.04)	HOMO−5→LUMO+12(0.40)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)/L-$_1$(π*)
	HOMO−3→LUMO+11(0.24)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
348(0.09)	HOMO−11→LUMO(0.60)	L_1(π)→bpy(π*)
332(0.15)	HOMO−6→LUMO+15(0.61)	L_1(π)/Os(dπ)/bpy(π)→L_1(π*)
	[$\mathbf{1}^{+}$] (S=1/2)	
1856(0.006)	HOMO(α)→LUMO+4(α)(0.99)	bpy(π)→L_1(π*)
1333(0.0006)	HOMO(α)→LUMO+5(α)(0.99)	bpy(π)→bpy(π*)/L_1(π*)
1266(0.001)	HOMO(α)→LUMO+6(α)(0.99)	bpy(π)→bpy(π*)
1026(0.003)	HOMO(α)→LUMO+8(α)(0.99)	bpy(π)→bpy(π*)
936(0.004)	HOMO(α)→LUMO+12(α)(0.99)	bpy(π)→bpy(π*)/L_1(π*)
780(0.011)	HOMO−1(β)→LUMO(β)(0.90)	Os(dπ)→bpy(π*)
689(0.009)	HOMO−1(β)→LUMO+2(β)(0.85)	Os(dπ)→bpy(π*)
634(0.05)	HOMO−1(β)→LUMO+4(β)(0.49)	Os(dπ)→L_1(π*)/bpy(π*)
585(0.04)	HOMO−2(β)→LUMO+2(β)(0.87)	Os(dπ)/bpy(π)→bpy(π*)
531(0.08)	HOMO−2(β)→LUMO+4(β)(0.45)	Os(dπ)/bpy(π)→L_1(π*)/bpy(π*)

	HOMO−6(β)→LUMO+1(β)(0.39)	L_1(π)/Os(dπ) →bpy(π*)
472(0.04)	HOMO−6(β)→LUMO+3(β)(0.62)	L_1(π)/Os(dπ) →bpy(π*)
	HOMO−7(β)→LUMO+1(β)(0.41)	L_1(π)→bpy(π*)
	[**1**] (S=1)	
1979(0.004)	HOMO(α)→LUMO+3(α)(0.98)	bpy(π)→L_1(π*)
1889(0.004)	HOMO−1(α)→LUMO+3(α)(0.99)	bpy(π)→L_1(π*)
1353(0.004)	HOMO(α)→LUMO+4(α)(0.99)	bpy(π)→L_1(π*)/bpy(π*)
1110(0.001)	HOMO(α)→LUMO+6(α)(0.80)	bpy(π)→bpy(π*)/L_1(π*)
	HOMO−1(α)→LUMO+5(α)(0.57)	bpy(π)→bpy(π*)
891(0.007)	HOMO(α)→LUMO+12(α)(0.97)	bpy(π)→bpy(π*)/L_1(π*)
781(0.04)	HOMO(β)→LUMO(β)(0.80)	Os(dπ)→bpy(π*)/L_1(π*)
654(0.03)	HOMO−2(β)→LUMO(β)(0.65)	Os(dπ)/bpy(π)→bpy(π*)/L_1(π*)
530(0.04)	HOMO−3(β)→LUMO+3(β)(0.46)	Os(dπ)/bpy(π)→bpy(π*)
500(0.09)	HOMO−5(β)→LUMO+4(β)(0.54)	Os(dπ)/bpy(π)→L_1(π*)/bpy(π*)
421(0.06)	HOMO−1(β)→LUMO+16(β)(0.65)	Os(dπ)→bpy(π*)
	1$^-$ (S=1/2)	
1864(0.02)	HOMO(β)→LUMO+4(β)(0.74)	bpy(π)→bpy(π*)/L_1(π*)
1841(0.02)	HOMO(β)→LUMO+4(β)(0.54)	bpy(π)→bpy(π*)/L_1(π*)
1625(0.003)	HOMO−1(α)→LUMO+3(α)(0.95)	bpy(π)→L_1(π*)/bpy(π*)
1344(0.006)	HOMO(α)→LUMO+5(α)(0.92)	bpy(π)→L_1(π*)/bpy(π*)
1226(0.003)	HOMO−1(α)→LUMO+4(α)(0.99)	bpy(π)→L_1(π*)/bpy(π*)
840(0.007)	HOMO−1(α)→LUMO+11(α)(0.98)	bpy(π)→bpy(π*)
771(0.01)	HOMO−2(α)→LUMO+1(α)(0.73)	Os(dπ)→bpy(π*)
643(0.03)	HOMO−1(β)→LUMO+3(β)(0.61)	Os(dπ)→bpy(π*)
535(0.05)	HOMO−4(β)→LUMO+3(β)(0.52)	Os(dπ)/bpy(π)→bpy(π*)
465(0.06)	HOMO(β)→LUMO+4(β)(0.54)	bpy(π)→bpy(π*)/L_1(π*)
425(0.04)	HOMO−4(α)→LUMO+16(α)(0.48)	Os(dπ)→bpy(π*)
	[**1**$^{2-}$] (S=0)	
1720(0.02)	HOMO→LUMO+3(0.64)	bpy(π)→L_1(π*)/bpy(π*)
1324(0.04)	HOMO−1→LUMO+5(0.53)	bpy(π)→L_1(π*)/bpy(π*)
	HOMO−1→LUMO+3(0.30)	bpy(π)→L_1(π*)/bpy(π*)

1247(0.07)	HOMO−1→LUMO+5(0.33)	bpy(π)→L_1(π*)/bpy(π*)
	HOMO−1→LUMO+2(0.31)	bpy(π)→L_1(π*)
785(0.04)	HOMO−2→LUMO(0.66)	Os(dπ)→bpy(π*)
654(0.05)	HOMO−4→LUMO(0.46)	Os(dπ)/bpy(π)→bpy(π*)
546(0.08)	HOMO−5→LUMO+1(0.44)	Os(dπ)/bpy(π)→bpy(π*)
486(0.10)	HOMO−7→LUMO+2(0.40)	Os(dπ)/bpy(π)→L_1(π*)
363(0.22)	HOMO−8→LUMO+5(0.60)	L_1(π)→L_1(π*)/bpy(π*)

Table S31 TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions for [$\mathbf{2}^n$]

λ/nm (DFT) (f)	Transitions	Character
	[$\mathbf{2}^{3+}$] (S=1/2)	
1593(0.01)	HOMO−5(β)→LUMO(β)(0.97)	Os(dπ)/bpy(π)→Os(dπ)/L_1(π*)
906(0.006)	HOMO−7(β)→LUMO(β)(0.98)	L_1(π)→Os(dπ)/L_1(π*)
881(0.004)	HOMO−8(β)→LUMO(β)(0.98)	L_1(π)→Os(dπ)/L_1(π*)
753(0.008)	HOMO(β)→LUMO+1(β)(0.98)	Os(dπ)→bpy(π*)
538(0.02)	HOMO−5(β)→LUMO+1(β)(0.72)	Os(dπ)/bpy(π)→bpy(π*)
472(0.04)	HOMO(α)→LUMO+5(α)(0.42)	L_1(π)→bpy(π*)
412(0.06)	HOMO−5(β)→LUMO+6(β)(0.54)	Os(dπ)/bpy(π)→bpy(π*)
	[$\mathbf{2}^{2+}$] (S=0)	
636(0.04)	HOMO−3→LUMO(0.58)	Os(dπ)/L_1(π)→bpy(π*)
500(0.02)	HOMO−6→LUMO+1(0.32)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
	HOMO−5→LUMO+2(0.21)	Os(dπ)/L_1(π)→bpy(π*)
	HOMO→LUMO+6(0.21)	Os(dπ)/L_1(π)→bpy(π*)
497(0.04)	HOMO−6→LUMO+1(0.49)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
	HOMO−6→LUMO+2(0.21)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
	HOMO−6→LUMO+3(0.22)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)
459(0.02)	HOMO−6→LUMO+4(0.20)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)/L_1(π*)
	HOMO−4→LUMO+5(0.50)	Os(dπ)→L_1(π*)/bpy(π*)
401(0.07)	HOMO−3→LUMO+10(0.31)	Os(dπ)/L_1(π)→bpy(π*)
400(0.05)	HOMO−6→LUMO+5(0.26)	Os(dπ)/bpy(π)/L_1(π)→L_1(π*)/bpy(π*)
	HOMO−1→LUMO+16(0.63)	L_1(π)→L_1(π*)
353(0.10)	HOMO−11→LUMO(0.55)	L_1(π)→bpy(π*)
346(0.06)	HOMO−3→LUMO+13(0.48)	Os(dπ)/bpy(π)/L_1(π)→bpy(π*)/L_1(π*)
330(0.08)	HOMO−3→LUMO+15(0.55)	Os(dπ)/bpy(π)/L_1(π)→L_1(π*)

	[**2**$^{+}$] (S=1/2)	
1276(0.009)	HOMO(α)→LUMO+5(α)(0.99)	bpy(π)→L_1(π*)/bpy(π*)
959(0.003)	HOMO(α)→LUMO+10(α)(0.97)	bpy(π)→bpy(π*)
770(0.004)	HOMO−1(β)→LUMO(β)(0.55)	Os(dπ)→bpy(π*)
	HOMO−1(α)→LUMO+1(α)(0.54)	Os(dπ)/L_1(π)→bpy(π*)
	HOMO−2(α)→LUMO(α)(0.52)	Os(dπ)→bpy(π*)
570(0.02)	HOMO(β)→LUMO+5(β)(0.65)	Os(dπ)/L_1(π)→bpy(π*)
	HOMO−1(α)→LUMO+4(α)(0.38)	Os(dπ)/L_1(π)→bpy(π*)
493(0.04)	HOMO−6(β)→LUMO+2(β)(0.32)	Os(dπ)/bpy(π)→bpy(π*)
407(0.05)	HOMO−6(α)→LUMO+6(α)(0.34)	L_1(π)→bpy(π*)
	HOMO−5(β)→LUMO+7(β)(0.31)	L_1(π)→bpy(π*)
	[**2**] (S=1)	
1977(0.03)	HOMO(α)→LUMO+3(α)(0.62)	bpy(π)→L_1(π*)
	HOMO(α)→LUMO+2(α)(0.36)	bpy(π)→L_1(π*)
1713(0.01)	HOMO−1(α)→LUMO+3(α)(0.94)	bpy(π)→L_1(π*)
1418(0.004)	HOMO(α)→LUMO+4(α)(0.99)	bpy(π)→L_1(π*)/bpy(π*)
1268(0.004)	HOMO−1(α)→LUMO+4(α)(0.99)	bpy(π)→L_1(π*)/bpy(π*)
1142(0.004)	HOMO(α)→LUMO+6(α)(0.92)	bpy(π)→bpy(π*)/L_1(π*)
812(0.01)	HOMO(β)→LUMO(β)(0.83)	Os(dπ)→bpy(π*)/L_1(π*)
683(0.05)	HOMO−2(β)→LUMO(β)(0.80)	Os(dπ)/bpy(π)→bpy(π*)
	HOMO−6(α)→LUMO+6(α)(0.44)	L_1(π)→bpy(π*)
566(0.04)	HOMO−4(β)→LUMO+2(β)(0.62)	Os(dπ)/L_1(π)→bpy(π*)
	HOMO−5(β)→LUMO+1(β)(0.49)	Os(dπ)/bpy(π)→bpy(π*)
468(0.04)	HOMO(α)→LUMO+16(α)(0.76)	bpy(π)→bpy(π*)
	[**2**$^{-}$] (S=1/2)	
1970(0.01)	HOMO(α)→LUMO+3(α)(0.82)	bpy(π)→L_1(π*)
1813(0.02)	HOMO−1(α)→LUMO+3(α)(0.69)	bpy(π)→L_1(π*)
1557(0.04)	HOMO(β)→LUMO+3(β)(0.63)	bpy(π)→bpy(π*)/L_1(π*)
	HOMO−1(α)→LUMO(α)(0.38)	bpy(π)→bpy(π*)
1282(0.009)	HOMO−1(α)→LUMO+4(α)(0.94)	bpy(π)→L_1(π*)/bpy(π*)
1105(0.005)	HOMO(α)→LUMO+5(α)(0.81)	bpy(π)→bpy(π*)/L_1(π*)

806(0.006)	HOMO−1(β)→LUMO(β)(0.87)	Os(dπ)→bpy(π*)
680(0.02)	HOMO−1(β)→LUMO+2(β)(0.55)	Os(dπ)→bpy(π*)/L_1(π*)
	HOMO−2(α)→LUMO+2(α)(0.51)	Os(dπ)→bpy(π*)
579(0.04)	HOMO−3(β)→LUMO+2(β)(0.46)	Os(dπ)/bpy(π)→bpy(π*)/L_1(π*)
	HOMO−5(α)→LUMO+2(α)(0.40)	Os(dπ)/bpy(π)→bpy(π*)
421(0.03)	HOMO−3(β)→LUMO+9(β)(0.36)	Os(dπ)/bpy(π)→bpy(π*)/L_1(π*)
	[$\mathbf{2}^{2-}$] (S=0)	
1850(0.03)	HOMO→LUMO+2(0.60)	bpy(π)→bpy(π*)/L_1(π*)
1534(0.01)	HOMO→LUMO+3(0.51)	bpy(π)→bpy(π*)/L_1(π*)
	HOMO−1→LUMO+3(0.42)	bpy(π)→bpy(π*)/L_1(π*)
1329(0.06)	HOMO−1→LUMO+2(0.57)	bpy(π)→bpy(π*)/L_1(π*)
1241(0.10)	HOMO−1→LUMO+3(0.52)	bpy(π)→bpy(π*)/L_1(π*)
1012(0.01)	HOMO−1→LUMO+4(0.46)	bpy(π)→L_1(π*)/bpy(π*)
	HOMO→LUMO+6(0.45)	bpy(π)→L_1(π*)/bpy(π*)
725(0.03)	HOMO→LUMO+14(0.35)	bpy(π)→bpy(π*)
599(0.07)	HOMO−4→LUMO(0.57)	Os(dπ)→L_1(π*)
464(0.16)	HOMO−5→LUMO+2(0.38)	Os(dπ)→bpy(π*)/L_1(π*)
376(0.26)	HOMO−5→LUMO+1(0.39)	L_1(π)→L_1(π*)/bpy(π*)

Table S32 TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions for [$\mathbf{3}^n$]

λ/nm (DFT) (f) [c]	Transitions	Character
	[$\mathbf{3}^{4+}$] (S=1)	
1568(0.06)	HOMO−4(β)→LUMO+1(β)(0.91)	L(π)/Os(dπ)→L_2(π*)/Os(dπ)
1017(0.41)	HOMO−5(β)→LUMO(β)(0.97)	Os(dπ)→Os(dπ)
912(0.01)	HOMO−2(β)→LUMO+2(β)(0.93)	Os(dπ)/bpy(π)→L_2(π*)
818(0.13)	HOMO−5(α)→LUMO(α)(0.53)	L_2(π)→L_2(π*)
767(0.28)	HOMO−5(α)→LUMO(α)(0.68)	L_2(π)→L_2(π*)
	SOMO2(α)→LUMO(α)(0.47)	L_2(π)/Os(dπ)→L_2(π*)
668(0.02)	HOMO−12(β)→LUMO+1(β)(0.99)	bpy(π)→L_2(π*)/Os(dπ)
619(0.23)	HOMO−7(α)→LUMO(α)(0.83)	Os(dπ)→L_2(π*)
	HOMO−5(β)→LUMO+2(β)(0.52)	Os(dπ)→L_2(π*)
491(0.04)	HOMO−14(β)→LUMO(β)(0.99)	L_2(π)→Os(dπ)
434(0.15)	HOMO(β)→ LUMO+7(β)(0.67)	Os(dπ)/L_2(π)→bpy(π*)
	SOMO1(α)→LUMO+5(α)(0.59)	L_2(π)→bpy(π*)
423(0.10)	HOMO−4(β)→LUMO+7(β)(0.55)	L_2(π)/Os(dπ)→bpy(π*)
409(0.36)	HOMO−22(β)→LUMO(β)(0.63)	L_2(π)/bpy(π)→Os(dπ)
	SOMO1(α)→LUMO+5(α)(0.50)	L_2(π)→bpy(π*)
	[$\mathbf{3}^{3+}$] (S=1/2)	
1300(0.004)	HOMO(β)→LUMO+2(β)(0.98)	Os(dπ)→L_2(π*)
1091(0.16)	HOMO−6(β)→LUMO(β)(0.98)	L_2(π)→Os(dπ)/L_2(π*)
893(0.02)	HOMO−3(β)→LUMO+1(β)(0.90)	Os(dπ)/bpy(π)→L_2(π*)
810(0.14)	HOMO−5(α)→LUMO(α)(0.84)	Os(dπ)/bpy(π)→L_2(π*)
771(0.50)	HOMO−1(α)→LUMO(α)(0.56)	Os(dπ)→L_2(π*)
	HOMO−5(α)→LUMO(α)(0.48)	Os(dπ)/bpy(π)→L_2(π*)
595(0.05)	HOMO−7(α)→LUMO(α)(0.66)	L_2(π)→L_2(π*)
	HOMO−6(β)→LUMO+1(β)(0.59)	L_2(π)→L_2(π*)
476(0.06)	HOMO−5(β)→LUMO+2(β)(0.57)	Os(dπ)→bpy(π*)
	HOMO−5(α)→LUMO+2(α)(0.41)	Os(dπ)/bpy(π)→bpy(π*)
381(0.05)	SOMO1(α)→LUMO+13(α)(0.91)	L_2(π)→L_2(π*)

375(0.40)	SOMO1(α)→LUMO+7(α)(0.42)	L_2(π)→bpy(π*)
	HOMO−1(β)→LUMO+10(β)(0.37)	Os(dπ)/L_2(π)→bpy(π*)
	HOMO−1(α)→LUMO+11(α)(0.31)	Os(dπ)→bpy(π*)
	[**3**$^{2+}$] (S=0)	
1165(0.003)	HOMO−1→LUMO(0.69)	Os(dπ)→L_2(π*)
891(0.10)	HOMO−4→LUMO(0.58)	Os(dπ)/bpy(π)→L_2(π*)
816(0.51)	HOMO−4→LUMO(0.40)	Os(dπ)/bpy(π)→L_2(π*)
	HOMO−2→LUMO(0.55)	Os(dπ)→L_2(π*)
665(0.01)	HOMO−1→LUMO+2(0.69)	Os(dπ)/bpy(π)→bpy(π*)
488(0.10)	HOMO−6→LUMO+4(0.62)	Os(dπ)→bpy(π*)
470(0.03)	HOMO−1→LUMO+6(0.65)	Os(dπ)→bpy(π*)
	HOMO→LUMO+5(0.22)	L_2(π)→bpy(π*)
441(0.02)	HOMO−1→LUMO+7(0.47)	Os(dπ)→bpy(π*)
	HOMO→LUMO+9(0.35)	L_2(π)→bpy(π*)
367(0.09)	HOMO−5→LUMO+13(0.31)	Os(dπ)/bpy(π)→L_2(π*)
	HOMO−3→LUMO+13(0.47)	Os(dπ)/L_2(π)→L_2(π*)
	[**3**$^{+}$] (S=1/2)	
1687(0.005)	HOMO(α)→LUMO(α)(0.99)	L_2(π)/bpy(π)→bpy(π*)
1572(0.01)	HOMO(α)→LUMO+2(α)(0.99)	L_2(π)/bpy(π)→bpy(π*)
910(0.03)	HOMO−1(β)→LUMO(β)(0.99)	Os(dπ)→bpy(π*)
792(0.15)	HOMO−2(β)→LUMO(β)(0.93)	Os(dπ)→bpy(π*)
699(0.02)	HOMO−4(β)→LUMO(β)(0.61)	Os(dπ)/bpy(π)→bpy(π*)
	HOMO−1(β)→LUMO+4(β)(0.47)	Os(dπ)→L_2(π*)/bpy(π*)
	HOMO−2(α)→LUMO+3(α)(0.35)	Os(dπ)→bpy(π*)/L_2(π*)
645(0.02)	HOMO−3(α)→LUMO+3(α)(0.58)	Os(dπ)→bpy(π*)/L_2(π*)
	HOMO−2(β)→LUMO+2(β)(0.55)	Os(dπ)→bpy(π*)
608(0.11)	HOMO(α)→LUMO+12(α)(0.76)	L_2(π)/bpy(π)→L_2(π*)
	HOMO−2(β)→LUMO+4(β)(0.41)	Os(dπ)→L_2(π*)
548(0.03)	HOMO−7(α)→LUMO+2(α)(0.66)	Os(dπ)/bpy(π)→bpy(π*)
	HOMO−7(α)→LUMO(α)(0.32)	Os(dπ)/bpy(π)→bpy(π*)
	HOMO−5(α)→LUMO+3(α)(0.31)	Os(dπ)/bpy(π)→bpy(π*)/L_2(π*)

522(0.09)	HOMO−7(α)→ LUMO+2(α)(0.59)	Os(dπ)/bpy(π)→bpy(π*)
508(0.05)	HOMO−2(α)→ LUMO+5(α)(0.72)	Os(dπ)→bpy(π*)
	HOMO−1(β)→LUMO+6(β)(0.46)	Os(dπ)→bpy(π*)
462(0.05)	HOMO−2(β)→LUMO+7(β)(0.53)	Os(dπ)→bpy(π*)
	HOMO−1(β)→LUMO+10(β)(0.42)	Os(dπ)→bpy(π*)
	HOMO−2(α)→LUMO+9(α)(0.39)	Os(dπ)→bpy(π*)
443(0.03)	HOMO−3(α)→LUMO+6(α)(0.59)	Os(dπ)→bpy(π*)
	HOMO−2(β)→LUMO+7(β)(0.53)	Os(dπ)→bpy(π*)
	[**3**] (S=0)	
2145(0.26)	HOMO→LUMO(0.52)	bpy(π)/L_2(π)→bpy(π*)
	HOMO→LUMO+2(0.46)	bpy(π)/L_2(π)→bpy(π*)
1641(0.003)	HOMO→LUMO+3(0.69)	bpy(π)/L_2(π)→bpy(π*)/L_2(π*)
893(0.01)	HOMO→LUMO+8(0.70)	bpy(π)/L_2(π)→bpy(π*)
826(0.02)	HOMO→LUMO+10(0.70)	bpy(π)/L_2(π)→bpy(π*)
673(0.02)	HOMO−4→LUMO+1(0.61)	Os(dπ)/bpy(π)→bpy(π*)
624(0.07)	HOMO−4→LUMO+3(0.60)	Os(dπ)/bpy(π)→bpy(π*)/L_2(π*)
534(0.09)	HOMO−7→LUMO+2(0.38)	Os(dπ)/bpy(π)→bpy(π*)
413(0.15)	HOMO−5→LUMO+5(0.30)	Os(dπ)/bpy(π)→bpy(π*)
380(0.38)	HOMO−3→LUMO+12(0.34)	Os(dπ)/L_2(π)→L_2(π*)
361(0.21)	HOMO−6→LUMO+12(0.51)	Os(dπ)/bpy(π)→L_2(π*)
	[$\mathbf{3}^-$] (S=1/2)	
1653(0.02)	HOMO(β)→LUMO+2(β)(0.86)	L_2(π)/bpy(π)→bpy(π*)
977(0.009)	HOMO(α)→LUMO+7(α)(0.62)	bpy(π)→bpy(π*)
	HOMO(α)→LUMO+8(α)(0.61)	bpy(π)→bpy(π*)
	HOMO(α)→LUMO+6(α)(0.44)	bpy(π)→bpy(π*)
876(0.02)	HOMO−2(α)→LUMO(α)(0.74)	Os(dπ)/L_2(π)→bpy(π*)
754(0.05)	HOMO−3(β)→LUMO+1(β)(0.48)	L_2(π)→bpy(π*)
	HOMO−1(β)→LUMO+1(β)(0.39)	Os(dπ)/L_2(π)→bpy(π*)
692(0.05)	HOMO−5(α)→LUMO+2(α)(0.47)	Os(dπ)/bpy(π)/L_2(π)→bpy(π*)
570(0.09)	HOMO−5(β)→LUMO+1(β)(0.49)	Os(dπ)/bpy(π)→bpy(π*)
437(0.04)	HOMO−2(β)→LUMO+12(β)(0.40)	Os(dπ)/bpy(π)→L_2(π*)

	[$\mathbf{3}^{2-}$] (S=0)	
1515(0.14)	HOMO−1→LUMO+1(0.53)	bpy(π)/L_2(π)→bpy(π*)
	HOMO→LUMO+2(0.50)	bpy(π)→bpy(π*)/L_2(π*)
840(0.03)	HOMO−2→LUMO(0.47)	Os(dπ)→bpy(π*)
730(0.14)	HOMO−4→LUMO(0.58)	Os(dπ)/bpy(π)→bpy(π*)
616(0.08)	HOMO−6→LUMO(0.63)	Os(dπ)/bpy(π)→bpy(π*)
553(0.04)	HOMO−7→LUMO+1(0.60)	Os(dπ)/bpy(π)→bpy(π*)
427(0.12)	HOMO−1→LUMO+15(0.41)	bpy(π)/L_2(π)→bpy(π*)
383(0.51)	HOMO−9→LUMO+2(0.41)	L_2(π)→bpy(π*)/L_2(π*)
342(0.15)	HOMO−6→LUMO+14(0.36)	Os(dπ)/bpy(π)→L_2(π*)
	HOMO−1→LUMO+21(0.34)	bpy(π)/L_2(π)→L_2(π*)

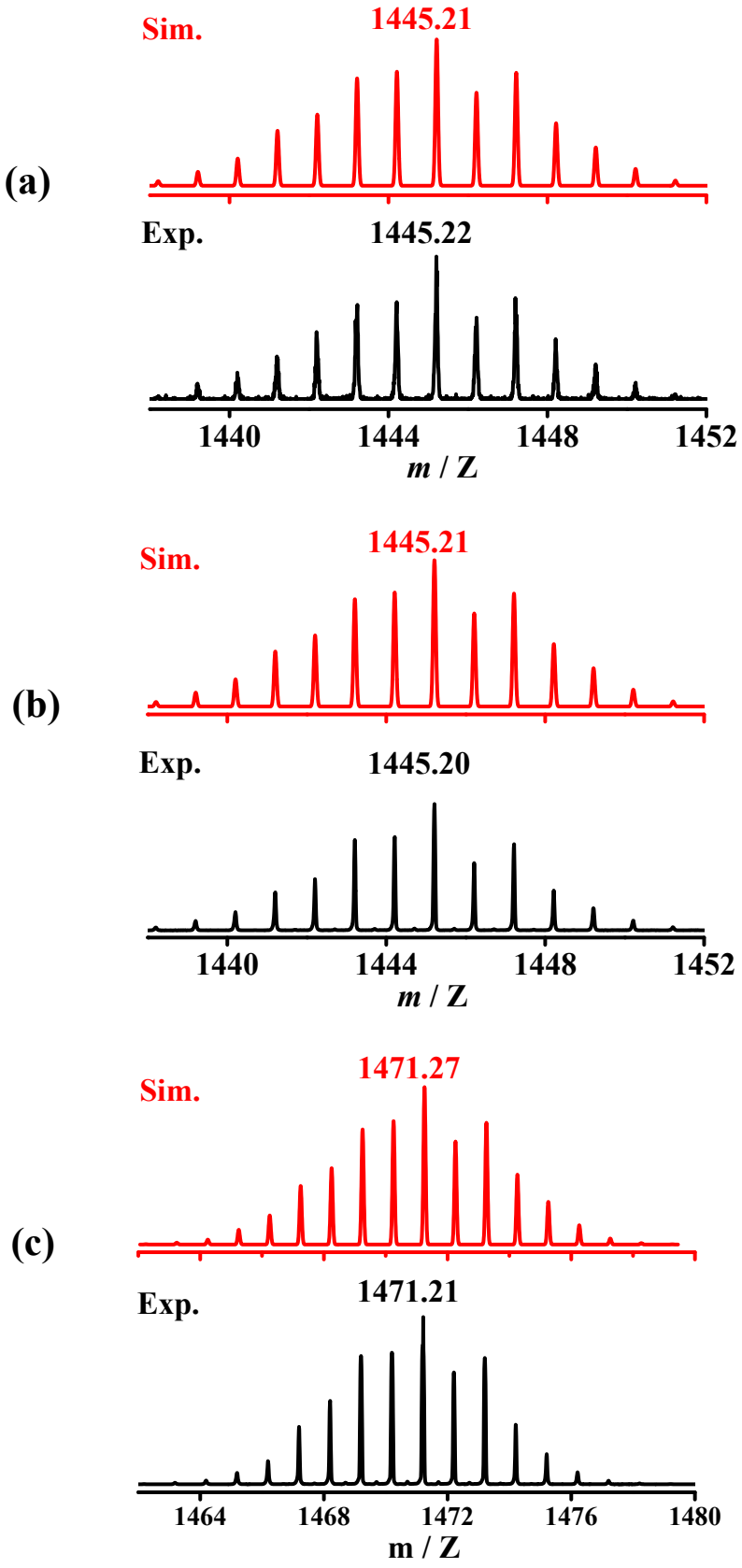


Fig. S1 ESI(+) mass spectra of (a) {[**1**](ClO$_4$)$_2$–ClO$_4$}$^+$, (b) {[**2**](ClO$_4$)$_2$–ClO$_4$}$^+$, and (c) {[**3**](ClO$_4$)$_2$–ClO$_4$}$^+$ in CH$_3$CN.

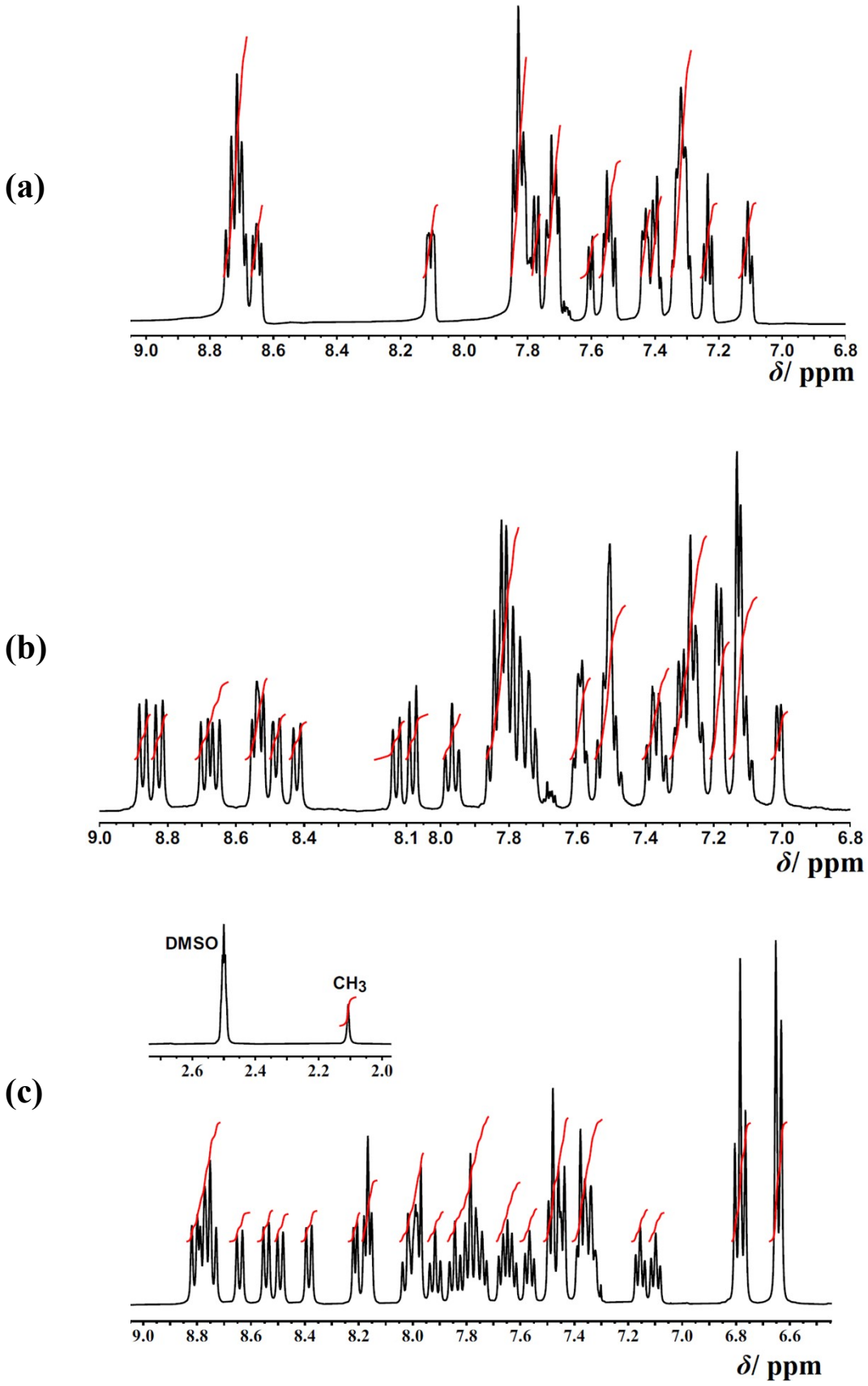


Fig. S2 ^{1}H NMR spectra of (a) [**1**]$(ClO_4)_2$, (b) [**2**]$(ClO_4)_2$ and (c) [**3**]$(ClO_4)_2$ in $(CD_3)_2SO$.

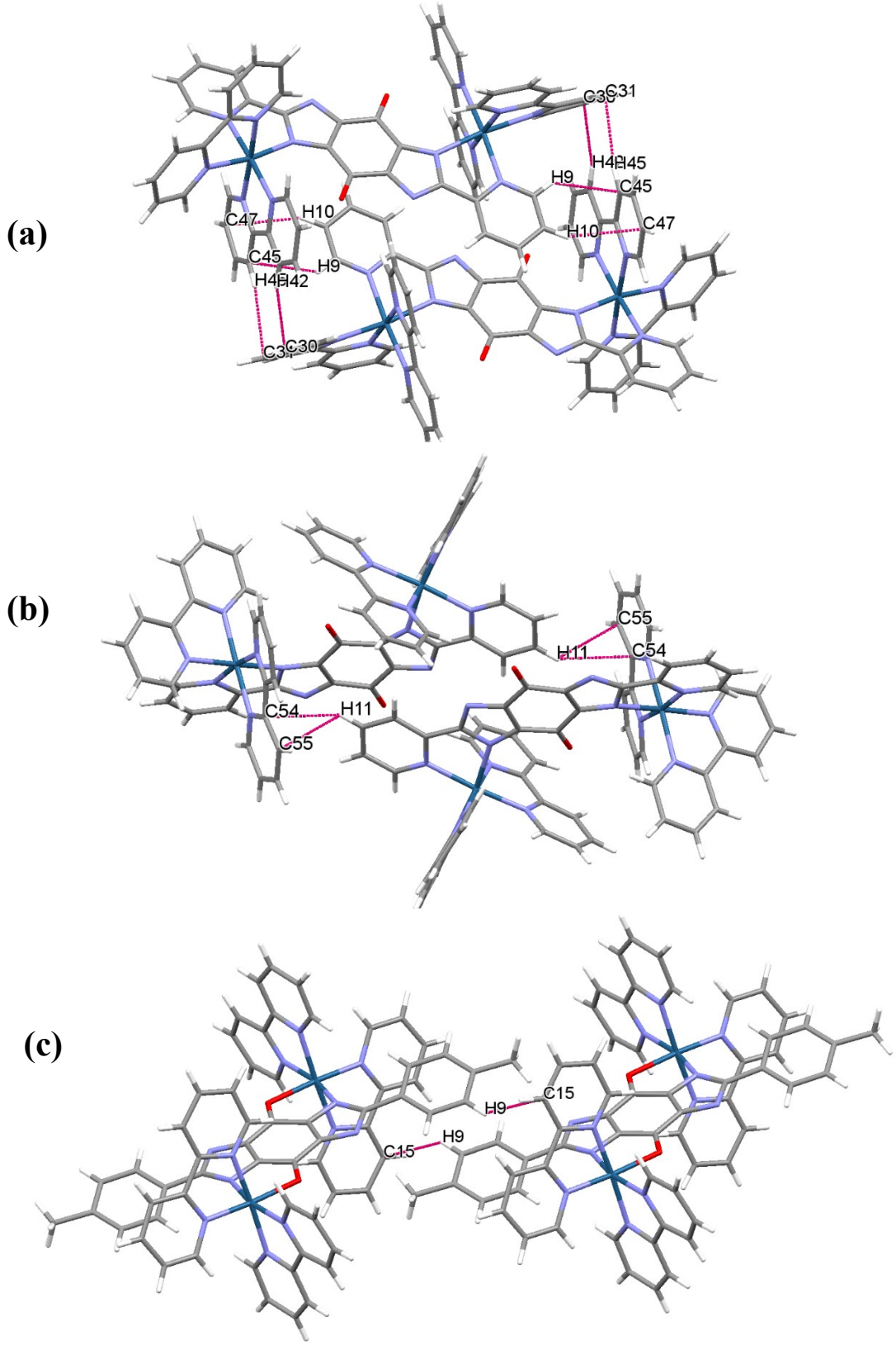


Fig. S3 Intermolecular CH---π interactions in (a) [**1**]$(ClO_4)_2$, (b) [**2**]$(ClO_4)_2$ and (c) [**3**]$(ClO_4)_2$.

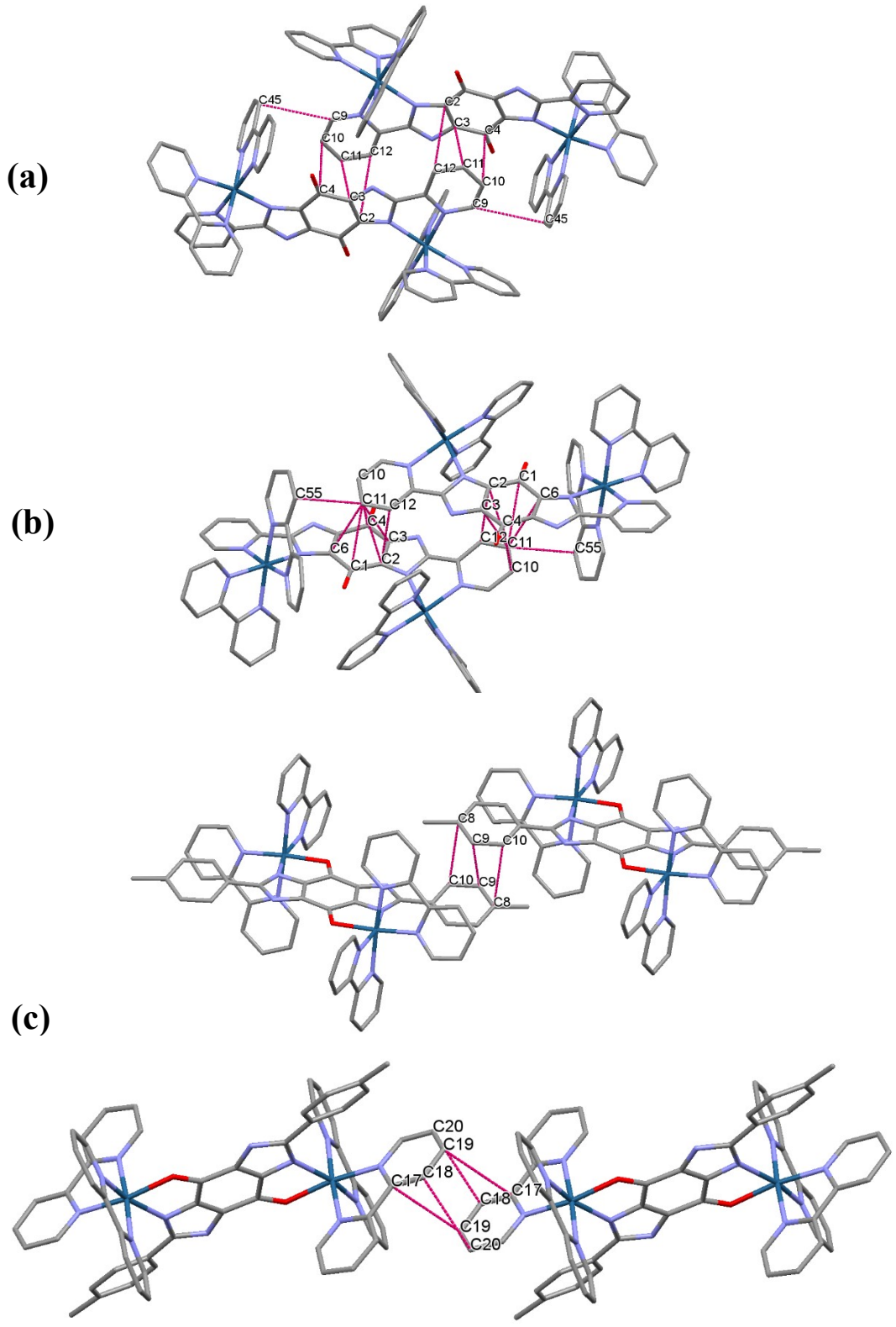


Fig. S4 Intermolecular π---π interactions in (a) [**1**]$(ClO_4)_2$, (b) [**2**]$(ClO_4)_2$ and (c) [**3**]$(ClO_4)_2$.

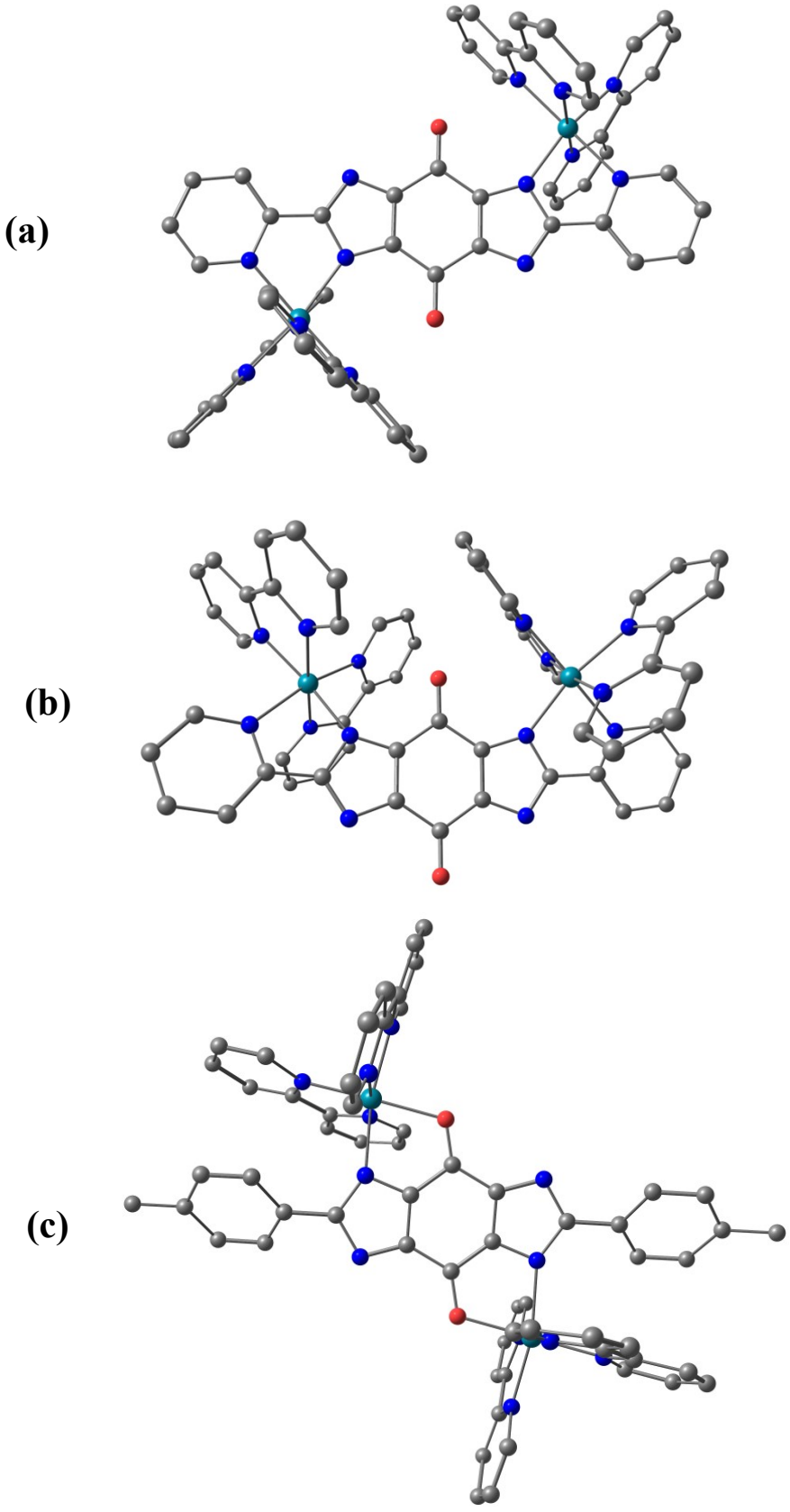
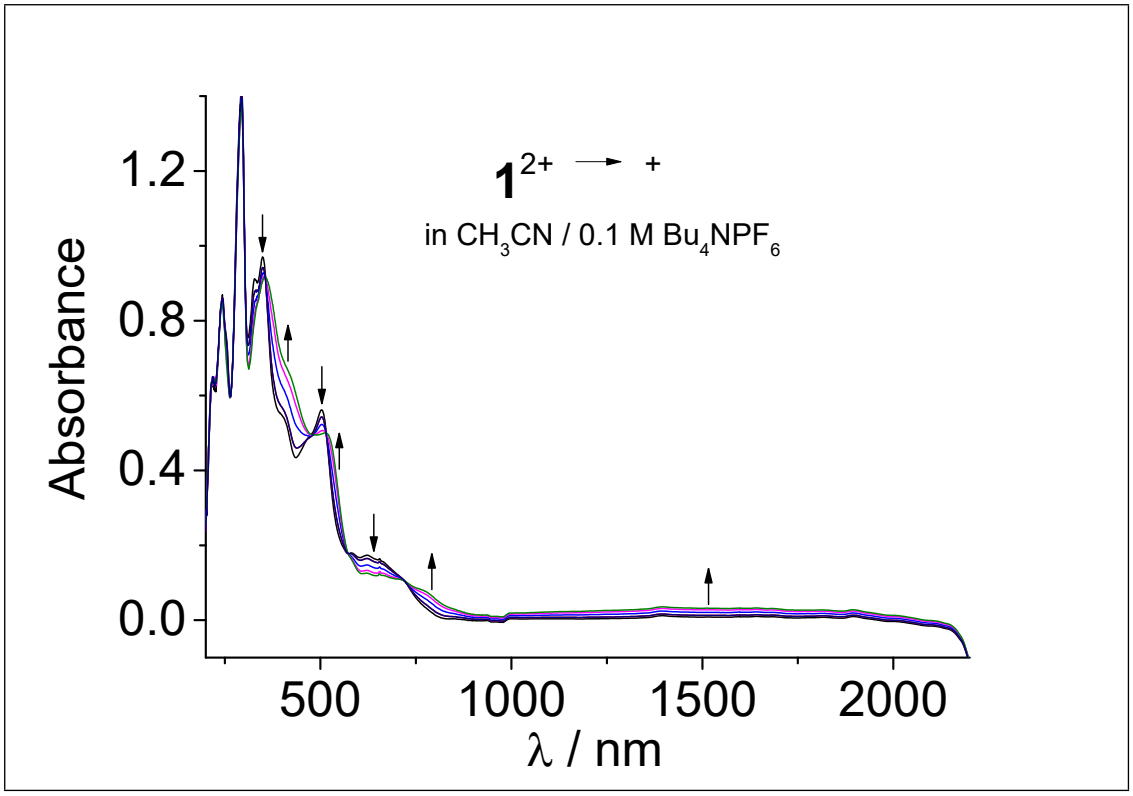


Fig. S5 DFT (M06L/LanL2DZ/6-31G**) optimized structures of (a) [$\mathbf{1}^{2+}$] (*S*=0), (b) [$\mathbf{2}^{2+}$] (*S*=0) and (c) [$\mathbf{3}^{2+}$] (*S*=0).



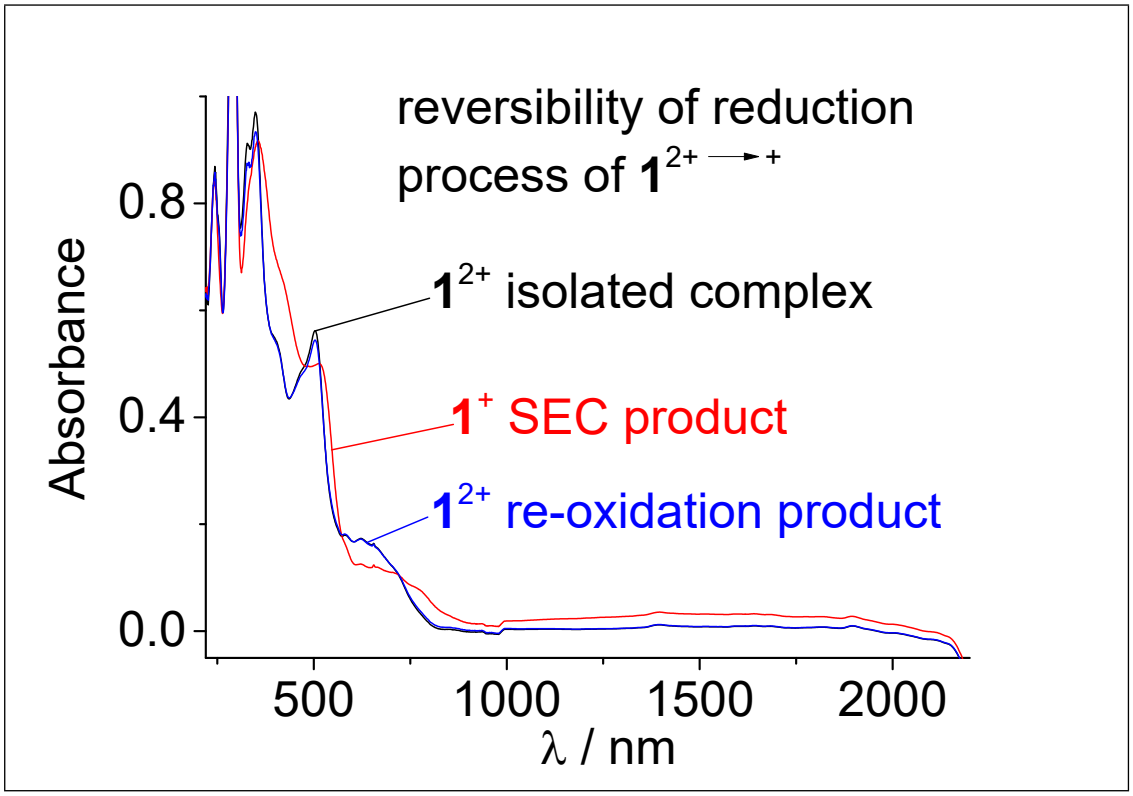


Fig. S6 UV-vis-NIR spectroelectrochemical response of [**1**]$(ClO_4)_2$ on reduction.

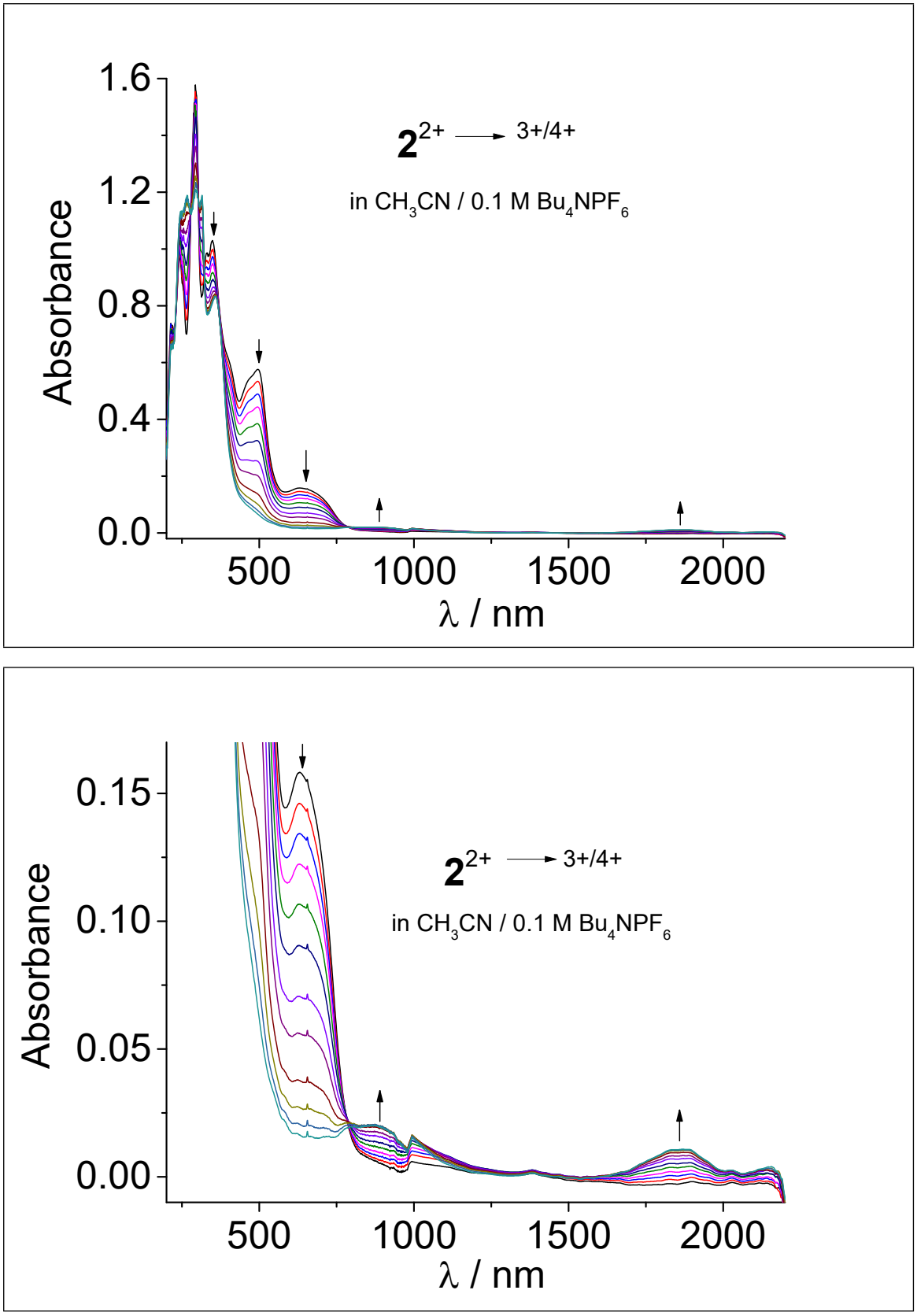


Fig. S7 UV-vis-NIR spectroelectrochemical response of [**2**]$(ClO_4)_2$ on oxidation.