

Electronic Supplementary Information

A structurally characterised redox pair involving an indigo radical: Indigo based redox activity in complexes with one or two [Ru(bpy)₂] fragments†

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Table S1 Selected crystallographic data for [1]ClO₄•0.5C₇H₈, *rac*-[2](ClO₄)₂•CH₃CN and *meso*-[2](ClO₄)₃

Complex	2x[1]ClO ₄ •C ₇ H ₈	<i>rac</i> -[2](ClO ₄) ₂ •CH ₃ CN	<i>meso</i> -[2](ClO ₄) ₃
Empirical formula	C ₈₀ H _{59.5} Cl ₂ N _{12.5} O ₁₂ Ru ₂	C ₅₈ H ₄₃ Cl ₂ N ₁₁ O ₁₀ Ru ₂	C ₅₆ H ₄₀ Cl ₃ N ₁₀ O ₁₄ Ru ₂
Formula weight	1660.94	1327.07	1385.47
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /(Å)	13.9550(2)	12.9402(5)	12.7946(3)
<i>b</i> /(Å)	14.6279(3)	15.1780(4)	18.2770(5)
<i>c</i> /(Å)	18.8595(4)	15.4382(4)	24.8597(6)
α (°)	104.432(2)	81.868(2)	90
β (°)	92.932(2)	69.543(3)	104.716(3)
γ (°)	109.944(2)	73.626(3)	90
<i>V</i> /(Å ³)	3465.32(12)	2722.61(16)	5622.7(3)
<i>Z</i>	2	2	4
μ /mm ⁻¹	0.590	0.725	0.757
<i>T</i> /K	150(2)	150(2)	150(2)
ρ_{calcd} /g cm ⁻³	1.592	1.619	1.637
<i>F</i> (000)	1690	1340	2788
θ range(°)	2.16 to 25.00	2.57 to 25.00	2.23 to 25.00
data/restraints/ parameters	12182/0/ 993	9569/0/ 749	9740/0/ 766
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0356, 0.0886	0.0571, 0.1287	0.0561, 0.1288
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0452, 0.0954	0.0775, 0.1408	0.0729, 0.1417
GOF on <i>F</i> ²	0.990	1.049	1.051
largest difference in peak / hole (e Å ⁻³)	0.942/ -0.654	1.203 /-0.872	1.191/ -0.708

Table S2 Selected experimental and DFT ((U)B3LYP) calculated bond lengths (Å) for **1ⁿ**
(Molecule A)

Bond lengths (Å)	X-ray	DFT						
	1⁺	1⁺ (S=0)	1³⁺ (S=0)	1²⁺ (S=1/2)	1 (S=1/2)	1⁻ (S=1)	1²⁻ (S=3/2)	1³⁻ (S=1)
Ru1-O1	2.0943(18)	2.106	2.127	2.115	2.102	2.111	2.147	2.137
Ru1-N2	2.105(2)	2.152	2.074	2.140	2.142	2.160	2.204	2.199
Ru1-N3	2.056(2)	2.096	2.103	2.109	2.084	2.088	2.098	2.084
Ru1-N4	2.031(2)	2.090	2.090	2.096	2.090	2.085	2.092	2.110
Ru1-N6	2.058(2)	2.098	2.137	2.117	2.083	2.076	2.106	2.102
Ru1-N5	2.067(2)	2.109	2.132	2.113	2.108	2.109	2.099	2.112
O1-C7	1.283(3)	1.280	1.248	1.260	1.293	1.303	1.294	1.324
O2-C10	1.227(3)	1.228	1.218	1.222	1.246	1.266	1.273	1.299
C9-C10	1.507(4)	1.516	1.511	1.514	1.487	1.465	1.466	1.436
C9 -C8	1.387(4)	1.386	1.396	1.393	1.397	1.407	1.408	1.416
C8-C7	1.427(4)	1.442	1.499	1.468	1.426	1.415	1.418	1.408
C10-C11	1.456(4)	1.458	1.465	1.461	1.456	1.453	1.449	1.445
C7-C6	1.444(4)	1.442	1.442	1.445	1.445	1.447	1.452	1.437
C16-C11	1.402(4)	1.416	1.418	1.416	1.423	1.431	1.436	1.455
C16-C15	1.383(4)	1.396	1.396	1.392	1.401	1.405	1.406	1.412
C6-C1	1.407(4)	1.422	1.417	1.416	1.426	1.432	1.436	1.452
C6-C5	1.411(4)	1.405	1.401	1.401	1.403	1.402	1.401	1.411
C11-C12	1.388(4)	1.392	1.383	1.387	1.393	1.396	1.397	1.402
C13-C12	1.380(4)	1.395	1.409	1.401	1.394	1.394	1.394	1.394
N2-C9	1.349(3)	1.354	1.356	1.351	1.365	1.375	1.375	1.407
N2-C16	1.428(3)	1.419	1.429	1.434	1.407	1.393	1.388	1.367
C1-C2	1.397(4)	1.400	1.383	1.389	1.400	1.400	1.401	1.395
C8-N1	1.391(3)	1.394	1.337	1.362	1.397	1.400	1.405	1.401
N1-C1	1.367(4)	1.373	1.411	1.396	1.370	1.366	1.362	1.363

Table S3 Selected experimental and DFT ((U)B3LYP) calculated bond lengths (Å) for *rac-2*ⁿ

Bond lengths (Å)	X-ray	DFT						
	<i>rac-2</i> ²⁺	<i>rac-2</i> ²⁺ (S=0)	<i>rac-2</i> ⁴⁺ (S=0)	<i>rac-2</i> ³⁺ (S=1/2)	<i>rac-2</i> ⁺ (S=1/2)	<i>rac-2</i> (S=1)	<i>rac-2</i> ⁻ (S=3/2)	<i>rac-2</i> ²⁻ (S=2)
Ru1-O2	2.036(3)	2.082	2.088	2.087	2.074	2.074	2.088	2.085
Ru1-N6	2.047(4)	2.115	2.114	2.112	2.117	2.112	2.093	2.103
Ru1-N5	2.058(4)	2.103	2.123	2.114	2.095	2.082	2.091	2.098
Ru1-N1	2.077(4)	2.152	2.150	2.161	2.125	2.131	2.155	2.176
Ru1-N4	2.031(4)	2.092	2.109	2.101	2.089	2.095	2.091	2.097
Ru1-N3	2.060(4)	2.098	2.118	2.112	2.085	2.089	2.079	2.093
Ru2-O1	2.068(3)	2.080	2.088	2.086	2.075	2.074	2.079	2.087
Ru2-N2	2.095(4)	2.150	2.152	2.159	2.127	2.134	2.135	2.172
Ru2-N8	2.060(4)	2.114	2.114	2.112	2.116	2.110	2.122	2.101
Ru2-N7	2.055(4)	2.105	2.123	2.116	2.095	2.078	2.093	2.101
Ru2-N9	2.033(4)	2.094	2.111	2.101	2.087	2.095	2.066	2.096
Ru2-N10	2.064(4)	2.097	2.120	2.112	2.084	2.091	2.085	2.092
O1-C7	1.279(6)	1.267	1.244	1.253	1.299	1.295	1.294	1.283
O2-C10	1.274(6)	1.267	1.244	1.253	1.298	1.295	1.294	1.283
N2-C9	1.378(6)	1.383	1.345	1.364	1.395	1.395	1.395	1.394
N1-C8	1.387(6)	1.383	1.346	1.364	1.394	1.395	1.397	1.394
C8-C9	1.399(7)	1.399	1.424	1.411	1.416	1.417	1.417	1.412
C8-C7	1.454(7)	1.477	1.492	1.483	1.438	1.443	1.444	1.455
C9-C10	1.449(7)	1.477	1.493	1.483	1.438	1.443	1.442	1.455
N1-C1	1.391(7)	1.396	1.440	1.421	1.386	1.384	1.382	1.380
N2-C16	1.391(7)	1.396	1.440	1.421	1.386	1.384	1.381	1.380
C11-C10	1.426(7)	1.429	1.442	1.439	1.430	1.431	1.434	1.434
C16-C11	1.401(7)	1.423	1.413	1.415	1.429	1.429	1.432	1.431
C1-C6	1.412(7)	1.423	1.413	1.415	1.430	1.429	1.432	1.431
C6-C7	1.438(7)	1.429	1.442	1.439	1.430	1.431	1.433	1.434
C1-C2	1.399(7)	1.404	1.388	1.394	1.407	1.408	1.408	1.409
C15-C16	1.408(7)	1.404	1.388	1.394	1.407	1.408	1.408	1.409
Ru···Ru	6.320	6.509	6.525	6.526	6.395	6.426	6.441	6.499

Table S4 Selected experimental and DFT ((U)B3LYP) calculated bond lengths (Å) for *meso-2*ⁿ

Bond lengths (Å)	X-ray	DFT						
	<i>meso-2</i> ³⁺	<i>meso-2</i> ³⁺ (S=1/2)	<i>meso-2</i> ⁴⁺ (S=0)	<i>meso-2</i> ²⁺ (S=0)	<i>meso-2</i> ⁺ (S=1/2)	<i>meso-2</i> (S=1)	<i>meso-2</i> ⁻ (S=3/2)	<i>meso-2</i> ²⁻ (S=2)
Ru1-O2	2.063(4)	2.087	2.091	2.082	2.074	2.078	2.081	2.082
Ru1-N5	2.065(4)	2.114	2.125	2.101	2.085	2.090	2.091	2.101
Ru1-N3	2.065(4)	2.112	2.115	2.098	2.089	2.089	2.076	2.095
Ru1-N4	2.046(4)	2.102	2.107	2.094	2.090	2.078	2.084	2.098
Ru1-N6	2.068(4)	2.111	2.116	2.114	2.085	2.106	2.090	2.103
Ru1-N1	2.053(4)	2.163	2.148	2.154	2.130	2.143	2.163	2.177
Ru2-O1	2.051(4)	2.087	2.091	2.082	2.074	2.078	2.081	2.082
Ru2-N2	2.095(5)	2.163	2.148	2.154	2.130	2.143	2.163	2.177
Ru2-N9	2.051(4)	2.102	2.107	2.094	2.090	2.078	2.084	2.097
Ru2-N8	2.060(4)	2.111	2.116	2.115	2.116	2.106	2.090	2.102
Ru2-N7	2.075(4)	2.114	2.125	2.101	2.085	2.090	2.091	2.101
Ru2-N10	2.053(4)	2.112	2.115	2.098	2.089	2.089	2.076	2.095
O1-C7	1.233(6)	1.253	1.244	1.267	1.298	1.293	1.294	1.279
O2-C10	1.242(6)	1.253	1.244	1.267	1.298	1.293	1.294	1.279
N1-C1	1.355(7)	1.421	1.440	1.396	1.387	1.384	1.381	1.382
N1-C8	1.425(7)	1.364	1.346	1.384	1.397	1.396	1.397	1.394
N2-C9	1.405(6)	1.364	1.346	1.384	1.397	1.396	1.397	1.394
N2-C16	1.390(7)	1.421	1.440	1.396	1.387	1.384	1.381	1.382
C1-C2	1.398(7)	1.394	1.387	1.404	1.407	1.407	1.409	1.409
C1-C6	1.464(8)	1.415	1.413	1.422	1.428	1.429	1.432	1.429
C6-C7	1.444(7)	1.439	1.442	1.429	1.431	1.432	1.432	1.435
C7-C8	1.428(8)	1.482	1.493	1.476	1.438	1.442	1.443	1.458
C9-C10	1.453(7)	1.482	1.493	1.476	1.438	1.442	1.443	1.458
C10-C11	1.448(7)	1.439	1.442	1.429	1.431	1.432	1.431	1.435
C8-C9	1.397(7)	1.411	1.424	1.400	1.416	1.414	1.415	1.411
C11-C16	1.400(7)	1.415	1.413	1.422	1.428	1.429	1.432	1.429
Ru···Ru	6.267	6.537	6.522	6.523	6.438	6.470	6.485	6.553

Table S5 Selected experimental bond angles (deg) for [1]ClO₄•0.5C₇H₈

1⁺ (Molecule A)		1⁺ (Molecule B)	
Bond angles (deg)	X-ray	Bond angles (deg)	X-ray
O1-Ru1-N2	92.30(8)	O4-Ru2-N7	92.72(8)
N6-Ru1-O1	90.94(8)	N9-Ru2-O4	90.03(8)
N6-Ru1-N2	95.48(8)	N9-Ru2-N7	95.58(8)
N6-Ru1-N5	78.30(8)	N9-Ru2-N10	78.47(9)
N3-Ru1-O1	93.38(8)	N12-Ru2-O4	93.09(8)
N3-Ru1-N6	174.64(8)	N9-Ru2-N12	175.32(9)
N3-Ru1-N2	87.51(8)	N12-Ru2-N7	87.77(8)
N3-Ru1-N5	98.95(8)	N12-Ru2-N10	98.25(8)
N4-Ru1-O1	170.45(8)	N11-Ru2-O4	170.39(8)
N4-Ru1-N6	96.24(8)	N11-Ru2-N9	97.17(9)
N4-Ru1-N3	79.13(9)	N11-Ru2-N12	79.36(9)
N4-Ru1-N2	93.29(8)	N11-Ru2-N7	92.91(9)
N4- Ru1- N5	90.68(8)	N11- Ru2-N10	89.16(9)
N5- Ru1- O1	84.59(8)	N10- Ru2- O4	86.03(8)
N5-Ru1-N2	172.96(8)	N10-Ru2-N9	78.47(9)
N1-H1 ^{...} O2	122.91	N8-H8 ^{...} O3	123.36

Table S6 Selected experimental and DFT ((U)B3LYP) calculated bond angles (deg) for **1ⁿ**
(Molecule A)

Bond angles (deg)	X-ray	DFT						
	1⁺	1⁺ (S=0)	1³⁺ (S=0)	1²⁺ (S=1/2)	1 (S=1/2)	1⁻ (S=1)	1²⁻ (S=3/2)	1³⁻ (S=1)
O1-Ru1-N2	92.30(8)	91.719	89.794	90.587	92.962	92.819	91.732	91.888
N6-Ru1-O1	90.94(8)	86.371	87.686	87.085	87.923	88.084	89.345	92.817
N6-Ru1-N2	95.48(8)	94.664	96.000	96.014	93.578	94.034	94.339	92.394
N6-Ru1-N5	78.30(8)	78.007	77.384	77.817	78.294	78.374	78.678	78.555
N3-Ru1-O1	93.38(8)	95.134	97.048	96.406	93.139	93.146	93.838	90.839
N3-Ru1-N6	174.64(8)	177.088	168.782	173.440	177.516	177.739	174.121	172.717
N3-Ru1-N2	87.51(8)	87.789	94.188	89.518	88.612	87.803	90.509	93.780
N3-Ru1-N5	98.95(8)	99.721	92.947	97.060	99.630	99.884	96.719	95.494
N4-Ru1-O1	170.45(8)	167.981	170.062	168.574	166.987	167.407	168.440	166.796
N4-Ru1-N6	96.24(8)	100.141	95.298	97.568	100.503	100.390	97.220	96.757
N4-Ru1-N3	79.13(9)	77.941	78.396	78.004	78.067	78.091	78.841	78.685
N4-Ru1-N2	93.29(8)	97.753	99.294	99.250	96.356	95.828	97.221	96.759
N4- Ru1- N5	90.68(8)	89.670	87.403	87.896	90.262	89.559	87.894	87.839
N5- Ru1- O1	84.59(8)	81.763	83.996	82.876	81.692	82.997	84.064	85.165
N5-Ru1-N2	172.96(8)	170.428	171.065	171.184	170.369	171.408	171.854	170.305

Table S7 Selected experimental and DFT ((U)B3LYP) calculated bond angles (deg) for *rac-2*ⁿ

Bond angles (deg)	X-ray	DFT						
	<i>rac-2</i> ²⁺	<i>rac-2</i> ²⁺ (S=0)	<i>rac-2</i> ⁴⁺ (S=0)	<i>rac-2</i> ³⁺ (S=1/2)	<i>rac-2</i> ⁺ (S=1/2)	<i>rac-2</i> (S=1)	<i>rac-2</i> ⁻ (S=3/2)	<i>rac-2</i> ²⁻ (S=2)
O2-Ru1-N6	85.66(15)	84.017	85.320	84.901	82.912	83.249	84.202	85.694
O2-Ru1-N5	87.15(15)	87.459	88.813	87.974	86.608	86.971	89.937	90.729
O2-Ru1-N1	90.13(15)	88.398	86.654	87.421	89.691	90.103	89.378	88.240
O2-Ru1-N3	96.23(15)	95.621	97.416	96.562	94.766	94.399	94.606	93.748
N6-Ru1-N5	78.80(17)	77.809	77.733	77.835	77.729	78.080	78.365	78.645
N6-Ru1-N1	172.25(16)	169.52	170.733	170.406	169.257	169.876	170.239	170.205
N6-Ru1-N3	99.66(17)	99.044	94.666	97.179	99.459	100.021	97.367	95.970
N5-Ru1-N1	94.52(16)	94.684	97.489	96.177	94.121	94.001	89.937	93.770
N5-Ru1-N3	176.19(16)	175.376	169.801	172.980	176.714	177.528	173.444	172.732
N4-Ru1-O2	167.92(16)	169.009	169.558	169.366	169.170	167.931	167.668	168.628
N4-Ru1-N6	84.20(17)	88.242	85.846	86.866	90.431	88.914	86.548	86.636
N4-Ru1-N5	97.28(17)	98.543	94.738	96.865	100.362	100.414	96.175	95.978
N4-Ru1-N1	100.67(17)	100.205	102.571	101.402	97.991	98.810	100.788	100.431
N4-Ru1-N3	79.06(17)	77.870	77.770	77.792	77.853	77.895	78.495	78.714
N3-Ru1-N1	87.25(16)	88.860	90.955	89.397	88.876	88.059	90.456	92.090
O1-Ru2-N2	89.27(15)	88.398	86.622	87.421	89.713	90.060	89.151	88.183
N8-Ru2-O1	87.31(15)	83.975	85.483	84.981	82.862	83.056	85.787	86.141
N8-Ru2-N2	173.67(16)	169.50	170.788	170.515	169.144	169.635	171.349	170.438
N8-Ru2-N10	95.02(18)	99.182	94.583	97.006	99.646	100.196	99.950	95.622
N7-Ru2-O1	88.19(15)	87.264	88.888	87.901	86.812	87.091	88.037	90.843
N7-Ru2-N2	95.15(17)	94.530	97.450	96.078	94.003	93.811	94.732	93.728
N7-Ru2-N8	79.43(18)	77.828	77.671	77.812	77.742	78.162	78.107	78.682
N7-Ru2-N10	173.58(17)	175.74	169.714	172.898	176.780	177.698	176.856	172.468
N9-Ru2-O1	170.61(16)	168.79	169.600	169.317	169.269	168.016	169.734	169.018
N9-Ru2-N2	97.89(17)	100.24	102.482	101.342	97.845	98.631	97.330	100.005
N9-Ru2-N8	86.11(17)	88.163	85.824	86.708	90.621	89.356	88.695	86.667
N9-Ru2-N7	97.16(17)	98.880	94.819	96.898	100.174	100.459	99.298	95.870
N9-Ru2-N10	79.12(17)	77.891	77.706	77.813	77.875	77.847	78.118	78.755
N10-Ru2-O1	94.82(16)	95.467	97.317	96.543	94.761	94.329	94.304	93.705
N10-Ru2-N2	90.57(16)	88.805	91.122	89.661	88.818	88.003	87.408	92.415

Table S8 Selected experimental and DFT ((U)B3LYP) calculated bond angles (deg) for *meso-2*ⁿ

Bond angles (deg)	X-ray	DFT						
	<i>meso-2</i> ³⁺	<i>meso-2</i> ³⁺ (S=1/2)	<i>meso-2</i> ⁴⁺ (S=0)	<i>meso-2</i> ²⁺ (S=0)	<i>meso-2</i> ⁺ (S=1/2)	<i>meso-2</i> (S=1)	<i>meso-2</i> ⁻ (S=3/2)	<i>meso-2</i> ²⁻ (S=2)
O2-Ru1-N5	87.89(15)	88.296	88.560	87.863	87.914	89.737	90.804	89.865
O2-Ru1-N3	96.43(16)	96.475	97.732	95.447	94.119	94.221	93.829	94.448
O2-Ru1-N6	84.40(16)	84.961	85.526	83.976	82.661	83.859	85.684	85.829
N5-Ru1-N6	78.67(17)	77.811	77.632	77.828	77.842	78.135	78.579	78.640
N3-Ru1-N5	173.00(16)	172.681	169.261	175.269	177.045	175.244	172.514	173.048
N3-Ru1-N6	96.22(18)	97.027	94.118	99.120	100.272	99.646	95.895	96.214
N4-Ru1-O2	173.38(16)	169.352	169.997	168.843	168.550	168.453	169.029	168.763
N4-Ru1-N5	96.25(16)	96.604	94.534	98.342	99.933	97.631	95.840	96.154
N4-Ru1-N3	78.96(16)	77.792	77.847	77.851	77.747	78.054	78.715	78.712
N4-Ru1-N1	94.40(18)	101.466	102.452	100.345	97.880	98.939	99.805	100.646
N4-Ru1-N6	91.34(17)	86.838	85.850	88.262	90.799	88.949	87.082	86.066
N1-Ru1-O2	90.15(17)	87.307	86.575	88.284	89.779	89.290	88.434	88.350
N1-Ru1-N5	97.59(17)	96.452	96.957	94.848	94.197	94.433	93.696	93.975
N1-Ru1-N3	87.93(17)	89.334	92.120	88.641	87.961	88.259	92.306	91.600
O2-Ru1-N5	87.89(15)	88.296	88.560	87.863	87.914	89.737	90.804	89.865
O1-Ru2-N2	88.37(16)	87.311	86.575	88.283	89.789	89.290	88.422	88.349
O1-Ru2-N9	170.31(16)	169.347	169.997	168.847	168.531	168.471	169.038	168.764
O1-Ru2-N8	81.00(15)	84.966	85.526	83.979	82.644	83.871	85.698	85.831
O1-Ru2-N7	88.05(15)	88.306	88.560	87.853	87.917	89.728	90.808	89.866
O1-Ru2-N10	88.05(15)	96.463	97.732	95.452	94.119	94.226	93.828	94.446
N9-Ru2-N2	100.51(17)	101.464	102.452	100.345	97.897	98.926	99.804	100.643
N9-Ru2-N10	79.45(17)	77.796	77.847	77.852	77.747	78.053	78.715	78.712
N8-Ru2-N2	168.04(17)	170.493	170.526	169.510	169.155	169.881	170.207	170.588
N8-Ru2-N9	90.49(16)	86.832	85.850	88.258	90.791	88.957	87.081	86.068
N8-Ru2-N7	79.17(16)	77.809	77.632	77.828	77.843	78.133	78.579	78.641
N8-Ru2-N10	93.96(16)	97.024	94.118	99.117	100.274	99.647	95.885	96.212
N7-Ru2-N2	95.09(16)	96.452	96.957	94.855	94.193	94.439	93.701	93.973
N7-Ru2-N9	94.94(17)	96.600	94.534	98.346	99.929	97.637	95.837	96.154
N10-Ru2-N2	92.66(16)	89.339	92.120	88.637	87.964	88.252	92.311	91.603
N7-Ru2-N10	171.16(15)	172.678	169.261	175.270	177.044	175.249	172.506	173.047

Table S9 Selected experimental and DFT ((U)B3LYP) calculated N1-C8-C9-N2 torsional angles (deg) for [2](ClO₄)₂•CH₃CN and [2](ClO₄)₃

Complex	N1-C8-C9-N2 torsional angle (deg)	
	exp.	DFT
<i>rac</i> - 2 ²⁺	-177.37	-179.053
<i>rac</i> - 2 ³⁺	-	-178.752
<i>meso</i> - 2 ²⁺	-	179.978
<i>meso</i> - 2 ³⁺	-179.84	-179.996

Table S10 Electrochemical data^a for *rac*-[2](ClO₄)₂ and *meso*-[2](ClO₄)₃ at 298 K

	$E^{\circ}_{298}/V (\Delta E/mV)^{a,b}$						
complex	O2	O1	R1	R2	R3	R4	R5
[2](ClO ₄) ₂	0.59 (60)	0.14 (70)	-0.71 (60)	-1.28 (60)	-1.76 (100)	-2.14 (140)	-
[2](ClO ₄) ₃	-	0.56(60)	0.10(80)	-0.77(60)	-1.33(60)	-1.82(100)	-2.2(140)
$K_c^{c,d}$							
	K_{c1}	K_{c2}	K_{c3}	K_{c4}	K_{c5}	K_{c6}	
[2](ClO ₄) ₂	4.2x10 ⁷	4.6x10 ⁹	1.4x10 ⁸	2.7x10 ⁶	-	2.5x10 ¹⁴	
[2](ClO ₄) ₃	-	2.27x10 ¹¹	3.10x10 ⁹	2.02x10 ⁸	2.76x10 ⁶	6.26 x10 ⁷	

^aFrom cyclic voltammetry in CH₃CN/0.1 M Et₄NClO₄ at 100 mV s⁻¹. ^bPotential in V *versus* SCE; peak potential differences ΔE_p /[mV] (in parentheses). ^cComproportionation constant from $RT \ln K_c = nF(\Delta E)$. ^d K_{c1} between O2 and O1; K_{c2} between R1 and R2; K_{c3} between R2 and R3; K_{c4} between R3 and R4; K_{c5} between R4 and R5; K_{c6} between R1 and O1

Table S11 DFT (B3LYP) calculated MO compositions for **1⁺** in $S = 0$ State (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
LUMO+5	-3.703	0.03	0.96	0.01
LUMO+4	-3.792	0.06	0.92	0.01
LUMO+3	-4.046	0.03	0.95	0.02
LUMO+2	-4.679	0.07	0.71	0.22
LUMO+1	-4.733	0.06	0.75	0.18
LUMO	-4.841	0.05	0.45	0.50
HOMO	-6.887	0.13	0.06	0.81
HOMO-1	-7.765	0.29	0.05	0.67
HOMO-2	-8.012	0.68	0.14	0.19
HOMO-3	-8.219	0.68	0.16	0.15
HOMO-4	-8.536	0.61	0.14	0.25
HOMO-5	-8.879	0.03	0.03	0.94

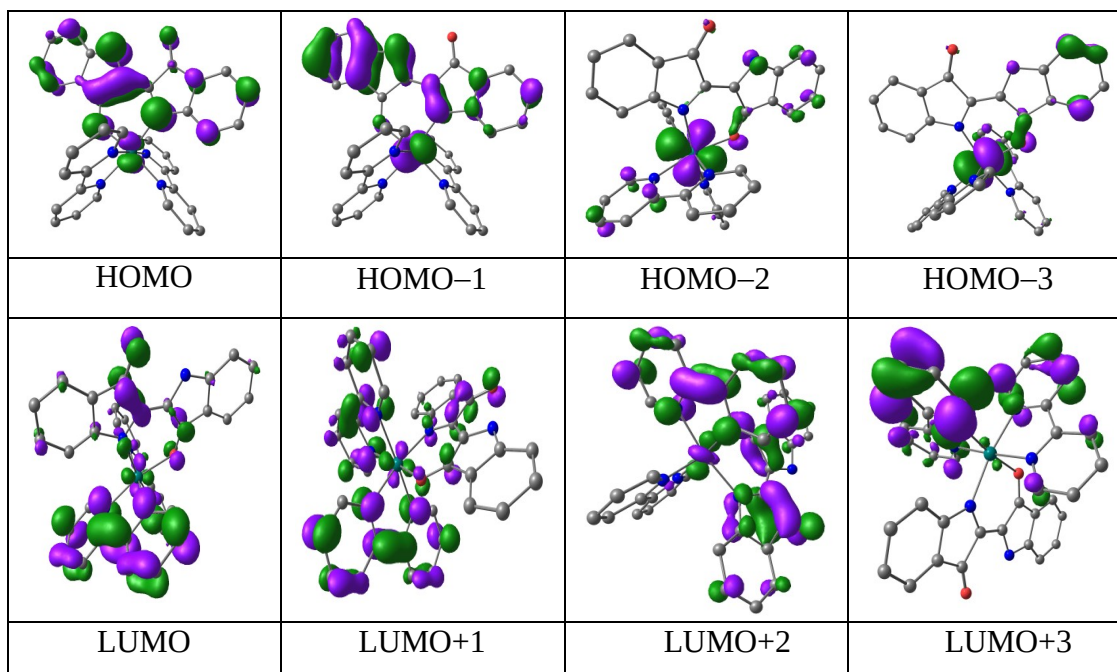
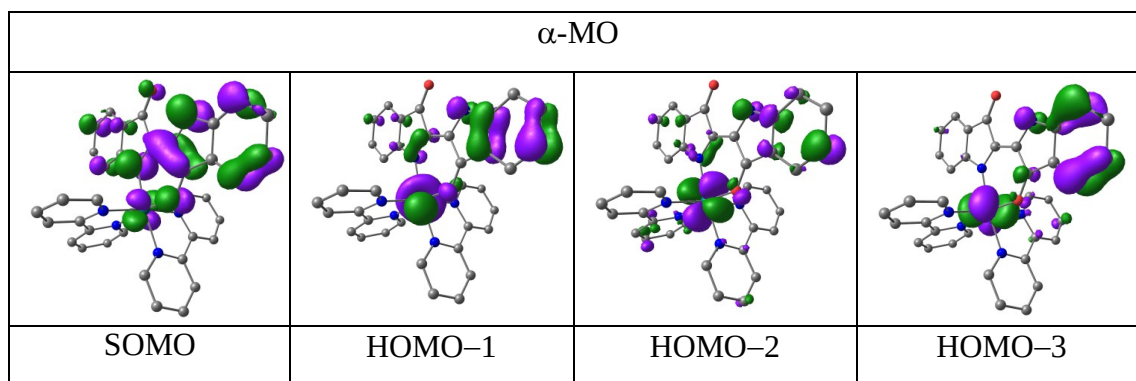


Table S12 DFT (UB3LYP) calculated MO compositions for **1**²⁺ in S = 1/2 state (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
α -MO				
LUMO+5	-6.306	0.02	0.94	0.04
LUMO+4	-6.344	0.04	0.93	0.02
LUMO+3	-6.546	0.03	0.93	0.04
LUMO+2	-7.330	0.04	0.95	0.01
LUMO+1	-7.433	0.05	0.93	0.01
LUMO	-8.246	0.03	0.02	0.95
SOMO	-10.661	0.15	0.03	0.81
HOMO-1	-11.106	0.51	0.07	0.42
HOMO-2	-11.292	0.65	0.12	0.23
HOMO-3	-11.505	0.65	0.12	0.23
HOMO-4	-11.795	0.56	0.14	0.29
HOMO-5	-12.147	0.04	0.19	0.77
β -MO				
LUMO+5	-6.342	0.04	0.94	0.02
LUMO+4	-6.539	0.03	0.94	0.03
LUMO+3	-7.316	0.05	0.94	0.01
LUMO+2	-7.420	0.06	0.92	0.02
LUMO+1	-8.009	0.04	0.03	0.93
LUMO	-9.160	0.19	0.05	0.76
HOMO	-10.890	0.26	0.04	0.70
HOMO-1	-11.080	0.73	0.12	0.15
HOMO-2	-11.259	0.72	0.12	0.16
HOMO-3	-11.491	0.61	0.13	0.26
HOMO-4	-12.081	0.05	0.06	0.89
HOMO-5	-12.154	0.01	0.68	0.31



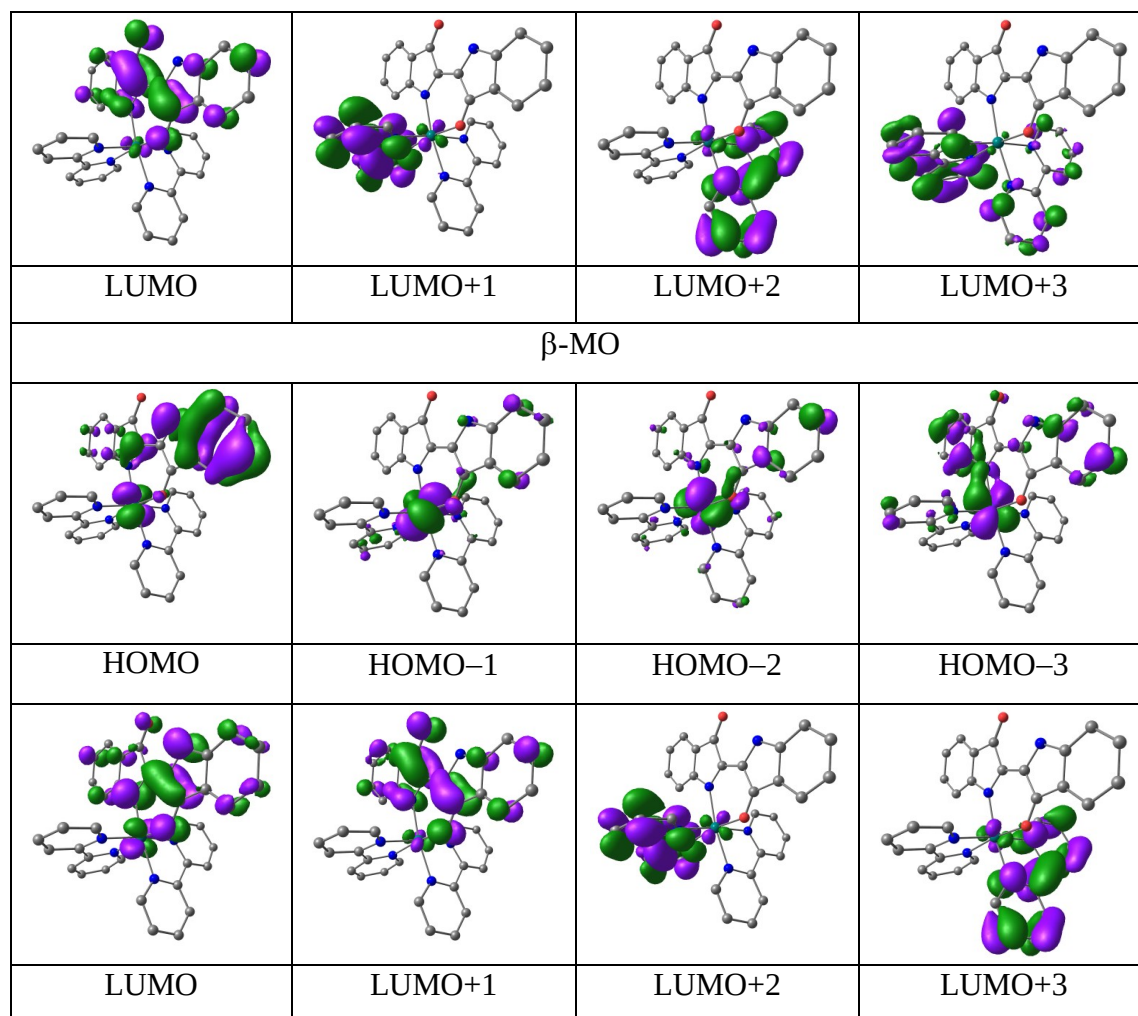


Table S13 DFT (UB3LYP) calculated MO compositions for $\mathbf{1}^{3+}$ in $S = 0$ State (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
LUMO+5	-9.098	0.04	0.91	0.05
LUMO+4	-9.431	0.02	0.04	0.94
LUMO+3	-9.927	0.04	0.95	0.01
LUMO+2	-10.052	0.05	0.93	0.02
LUMO+1	-11.388	0.04	0.02	0.95
LUMO	-12.804	0.21	0.04	0.75
HOMO	-14.346	0.36	0.07	0.58
HOMO-1	-14.459	0.64	0.23	0.13
HOMO-2	-14.583	0.67	0.17	0.16
HOMO-3	-14.727	0.12	0.83	0.05
HOMO-4	-14.796	0.32	0.44	0.24
HOMO-5	-14.906	0.28	0.55	0.17

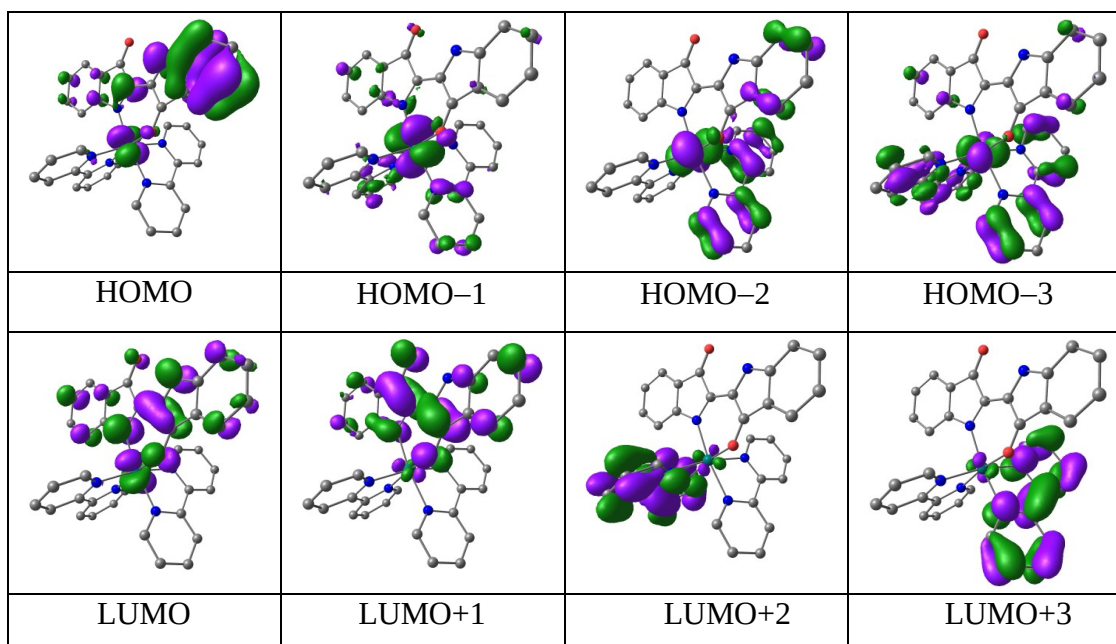
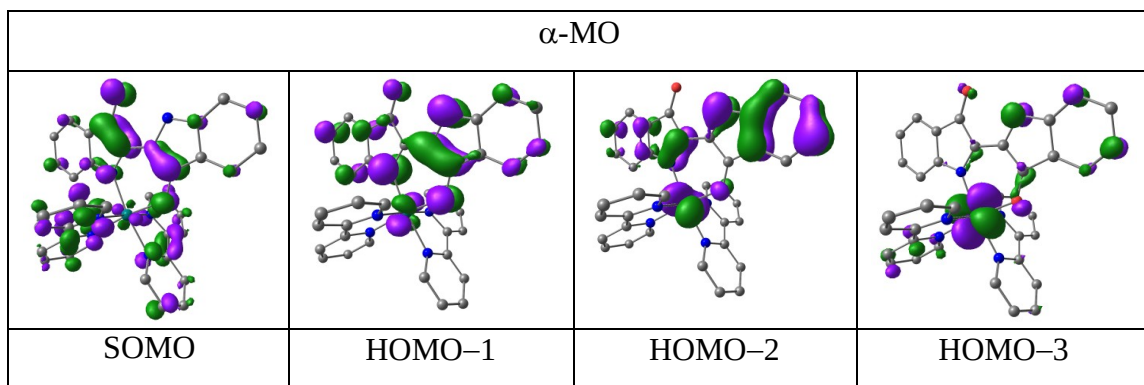


Table S14 DFT (UB3LYP) calculated MO compositions for **1** in $S = 1/2$ state (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
α -MO				
LUMO+5	-0.815	0.02	0.97	0.01
LUMO+4	-0.827	0.03	0.96	0.01
LUMO+3	-0.928	0.07	0.92	0.01
LUMO+2	-2.008	0.04	0.94	0.02
LUMO+1	-2.008	0.07	0.44	0.49
LUMO	-2.068	0.06	0.90	0.03
SOMO	-2.657	0.04	0.58	0.38
HOMO-1	-4.009	0.15	0.06	0.80
HOMO-2	-4.875	0.53	0.07	0.40
HOMO-3	-5.098	0.64	0.25	0.11
HOMO-4	-5.267	0.69	0.13	0.19
HOMO-5	-5.524	0.53	0.12	0.36
β -MO				
LUMO+5	-0.753	0.03	0.96	0.01
LUMO+4	-0.896	0.07	0.92	0.01
LUMO+3	-1.116	0.04	0.94	0.02
LUMO+2	-1.599	0.04	0.13	0.83
LUMO+1	-1.748	0.06	0.90	0.04
LUMO	-1.770	0.05	0.88	0.06
HOMO	-3.914	0.13	0.05	0.82
HOMO-1	-4.846	0.58	0.08	0.34
HOMO-2	-5.038	0.58	0.11	0.30
HOMO-3	-5.268	0.69	0.12	0.18
HOMO-4	-5.515	0.55	0.12	0.33
HOMO-5	-5.743	0.05	0.02	0.93



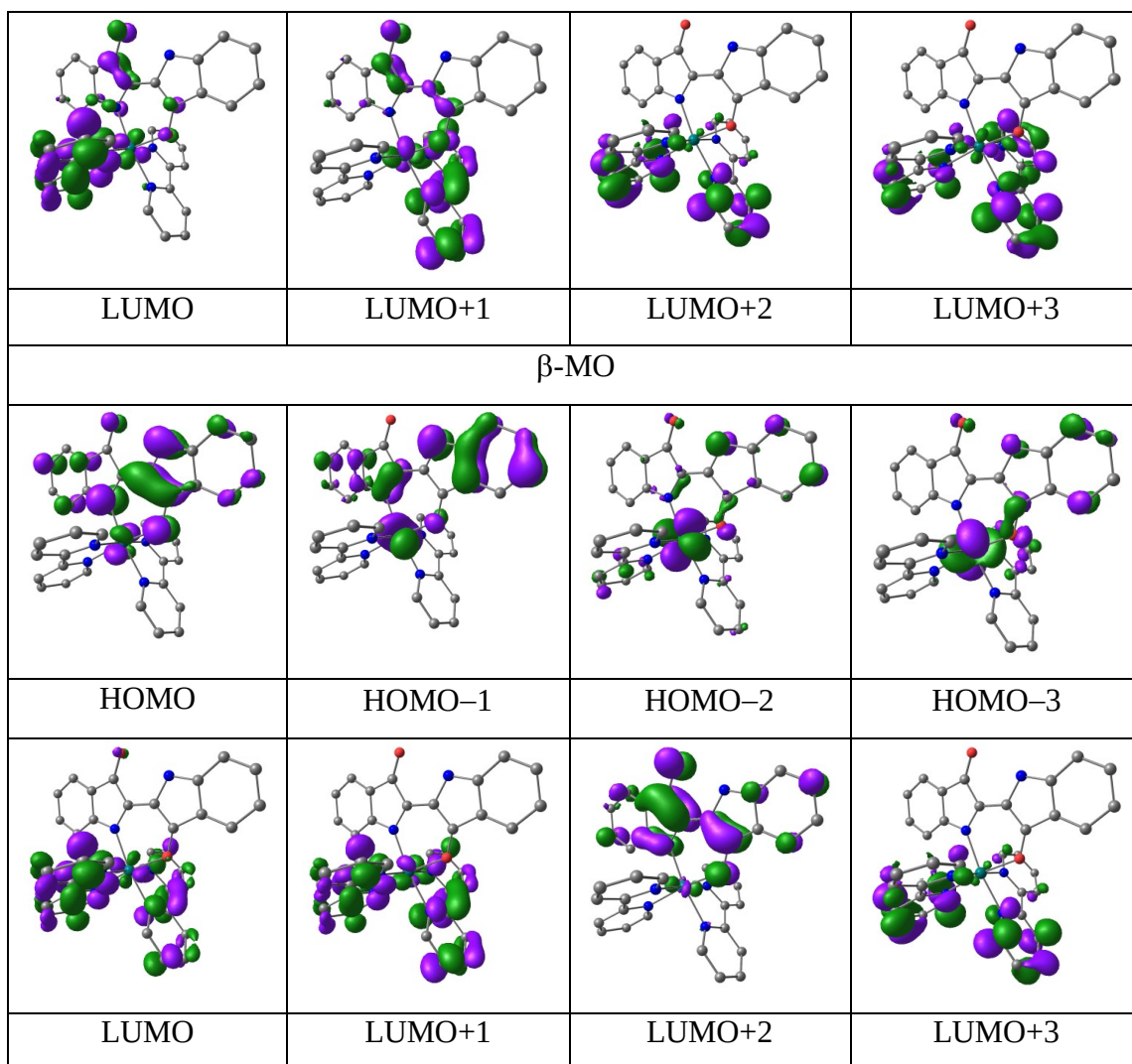
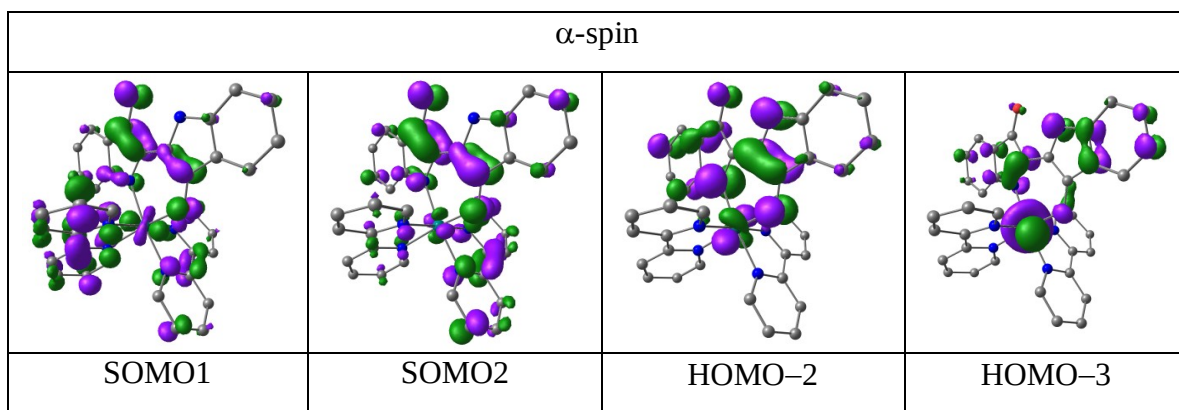


Table S15 DFT (UB3LYP) calculated MO compositions for **1⁻** in *S* = 1 State (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
α -MO				
LUMO+5	2.545	0.03	0.04	0.93
LUMO+4	2.019	0.03	0.96	0.01
LUMO+3	1.972	0.04	0.95	0.01
LUMO+2	1.882	0.08	0.91	0.01
LUMO+1	1.680	0.04	0.93	0.02
LUMO	0.602	0.10	0.83	0.07
SOMO1	0.007	0.08	0.48	0.45
SOMO2	-0.121	0.04	0.57	0.38
HOMO-2	-1.164	0.17	0.10	0.73
HOMO-3	-1.958	0.67	0.09	0.24
HOMO-4	-2.214	0.46	0.10	0.44
HOMO-5	-2.322	0.64	0.15	0.21
β -MO				
LUMO+5	2.087	0.03	0.95	0.01
LUMO+4	1.948	0.09	0.90	0.01
LUMO+3	1.721	0.04	0.93	0.02
LUMO+2	1.472	0.04	0.07	0.89
LUMO+1	1.162	0.07	0.91	0.02
LUMO	1.054	0.06	0.91	0.03
HOMO	-0.938	0.13	0.06	0.81
HOMO-1	-1.861	0.65	0.09	0.26
HOMO-2	-2.024	0.63	0.13	0.24
HOMO-3	-2.303	0.62	0.14	0.24
HOMO-4	-2.527	0.22	0.07	0.72
HOMO-5	-2.576	0.22	0.05	0.73



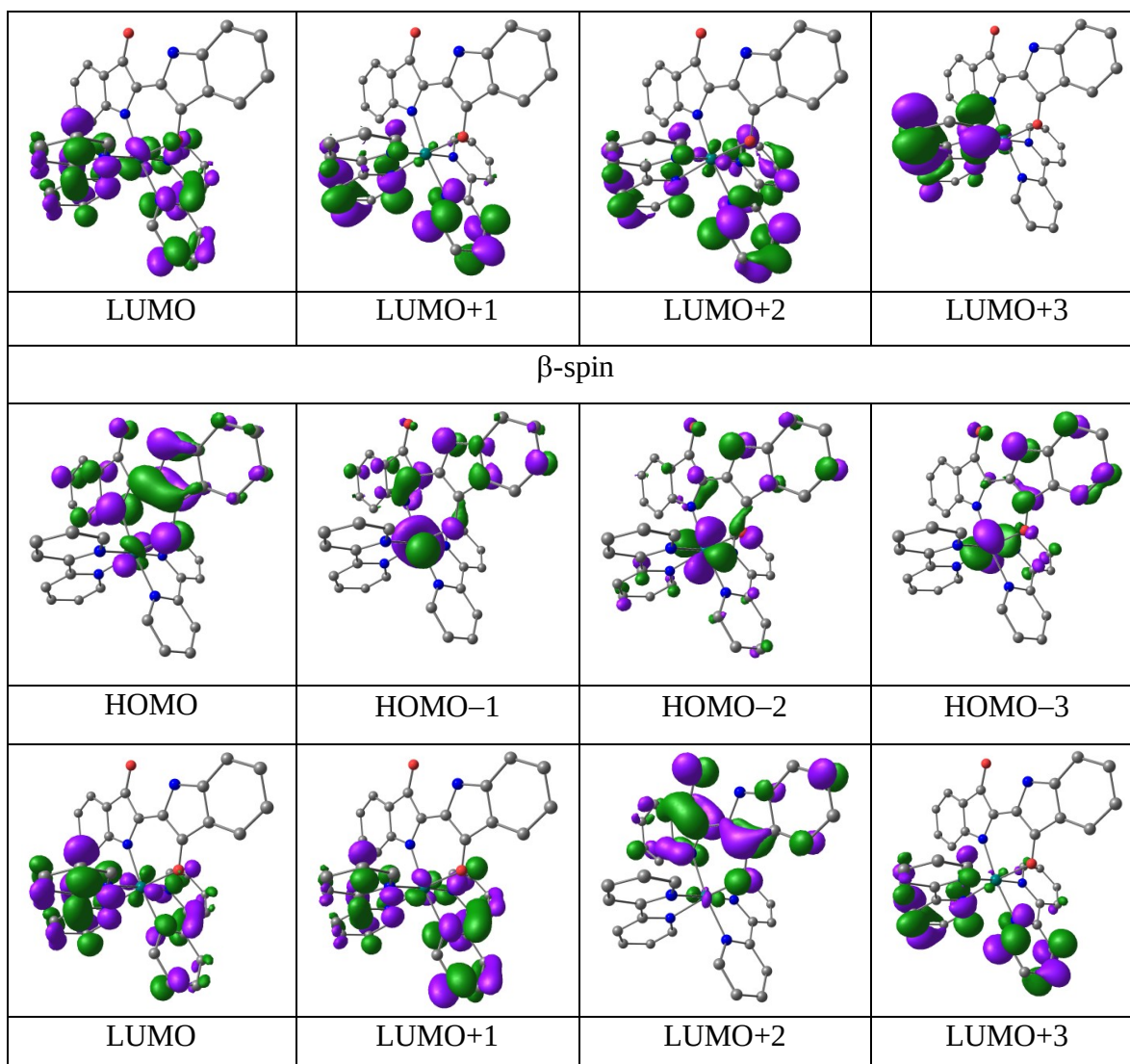
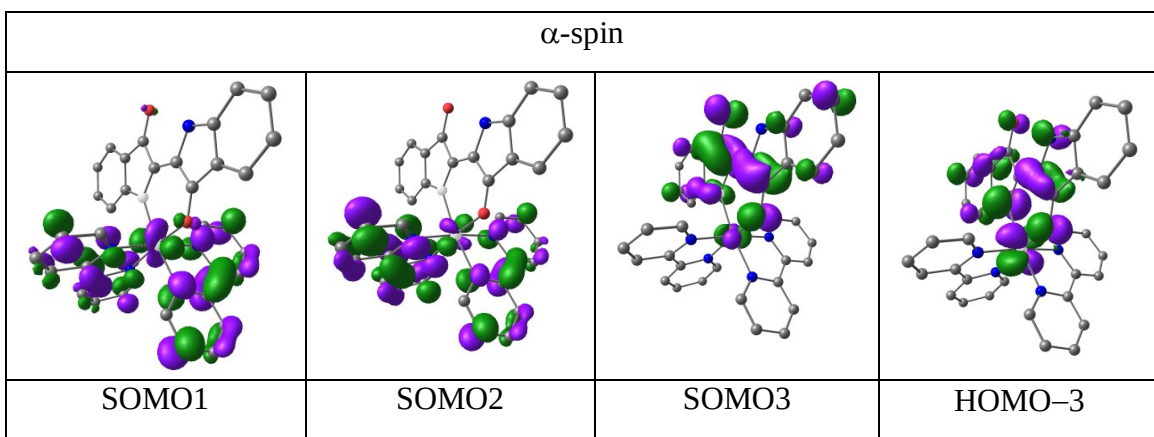


Table S16 DFT (UB3LYP) calculated MO compositions for **1**²⁻ in S = 3/2 State (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
α -MO				
LUMO+5	5.854	0.01	0.04	0.95
LUMO+4	5.103	0.04	0.95	0.01
LUMO+3	5.083	0.03	0.96	0.01
LUMO+2	4.989	0.11	0.87	0.01
LUMO+1	4.884	0.02	0.09	0.89
LUMO	4.816	0.08	0.83	0.09
SOMO1	2.797	0.10	0.88	0.02
SOMO2	2.716	0.09	0.88	0.03
SOMO3	2.303	0.08	0.06	0.86
HOMO-3	1.452	0.31	0.12	0.58
HOMO-4	1.070	0.75	0.11	0.13
HOMO-5	0.732	0.72	0.14	0.13
β -MO				
LUMO+5	5.133	0.02	0.04	0.94
LUMO+4	5.087	0.11	0.87	0.02
LUMO+3	4.906	0.09	0.88	0.04
LUMO+2	4.407	0.07	0.91	0.02
LUMO+1	4.327	0.08	0.89	0.03
LUMO	3.839	0.05	0.06	0.89
HOMO	1.808	0.33	0.10	0.57
HOMO-1	1.288	0.76	0.12	0.12
HOMO-2	1.072	0.74	0.15	0.11
HOMO-3	0.773	0.51	0.14	0.35
HOMO-4	0.081	0.08	0.05	0.88
HOMO-5	-0.096	0.02	0.02	0.96



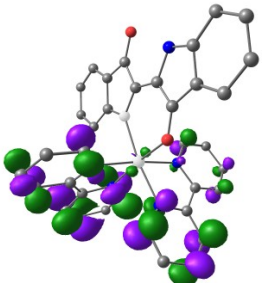
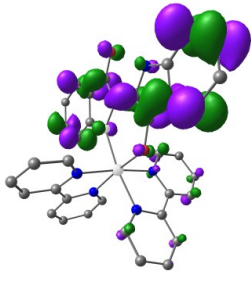
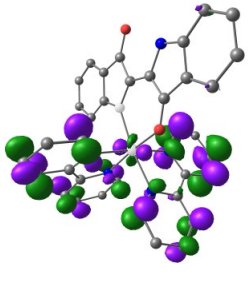
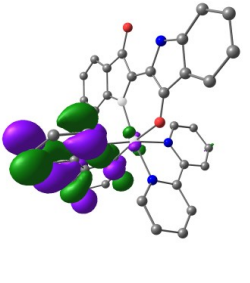
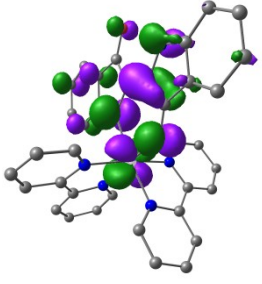
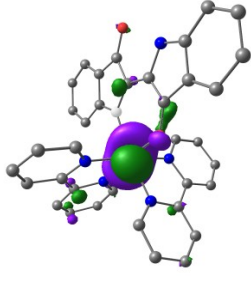
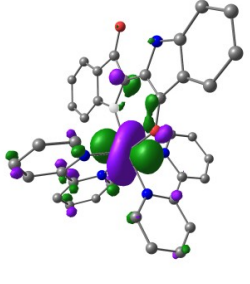
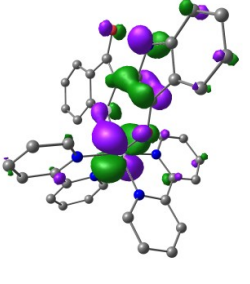
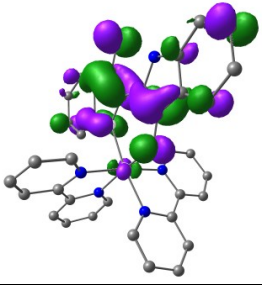
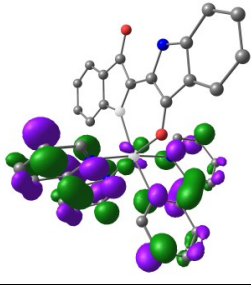
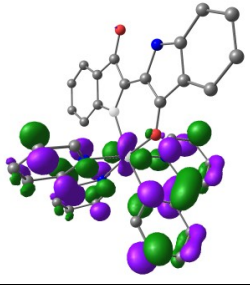
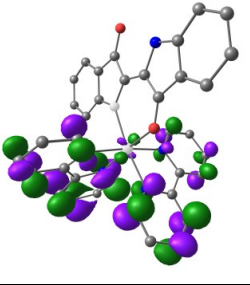
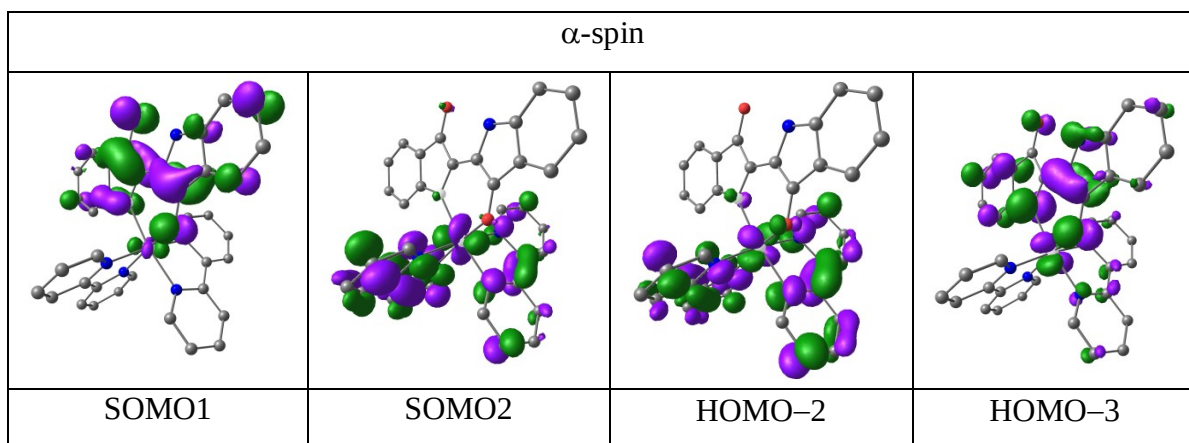
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β -spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17. DFT (UB3LYP) calculated MO compositions for $\mathbf{1}^{3-}$ in $S = 1$ State (Molecule A)

MO	Energy (eV)	Composition		
		Ru	bpy	HInd
α -MO				
LUMO+5	1.366	0.57	0.29	0.14
LUMO+4	0.474	0.06	0.22	0.72
LUMO+3	0.430	0.04	0.92	0.03
LUMO+2	0.415	0.03	0.87	0.11
LUMO+1	0.312	0.13	0.80	0.07
LUMO	0.127	0.12	0.84	0.04
SOMO1	-1.980	0.10	0.29	0.61
SOMO2	-2.142	0.07	0.68	0.25
HOMO-2	-2.202	0.07	0.89	0.04
HOMO-3	-3.011	0.27	0.10	0.63
HOMO-4	-3.577	0.77	0.11	0.11
HOMO-5	-3.901	0.57	0.16	0.27
β -MO				
LUMO+5	7.781	0.04	0.96	0.01
LUMO+4	7.753	0.03	0.97	0.01
LUMO+3	7.636	0.13	0.85	0.02
LUMO+2	7.398	0.08	0.88	0.04
LUMO+1	6.732	0.11	0.65	0.24
LUMO	6.576	0.06	0.93	0.01
HOMO	6.048	0.03	0.30	0.67
HOMO-1	4.715	0.20	0.07	0.72
HOMO-2	3.973	0.75	0.12	0.12
HOMO-3	3.845	0.65	0.19	0.16
HOMO-4	3.548	0.62	0.13	0.25
HOMO-5	3.381	0.04	0.02	0.94



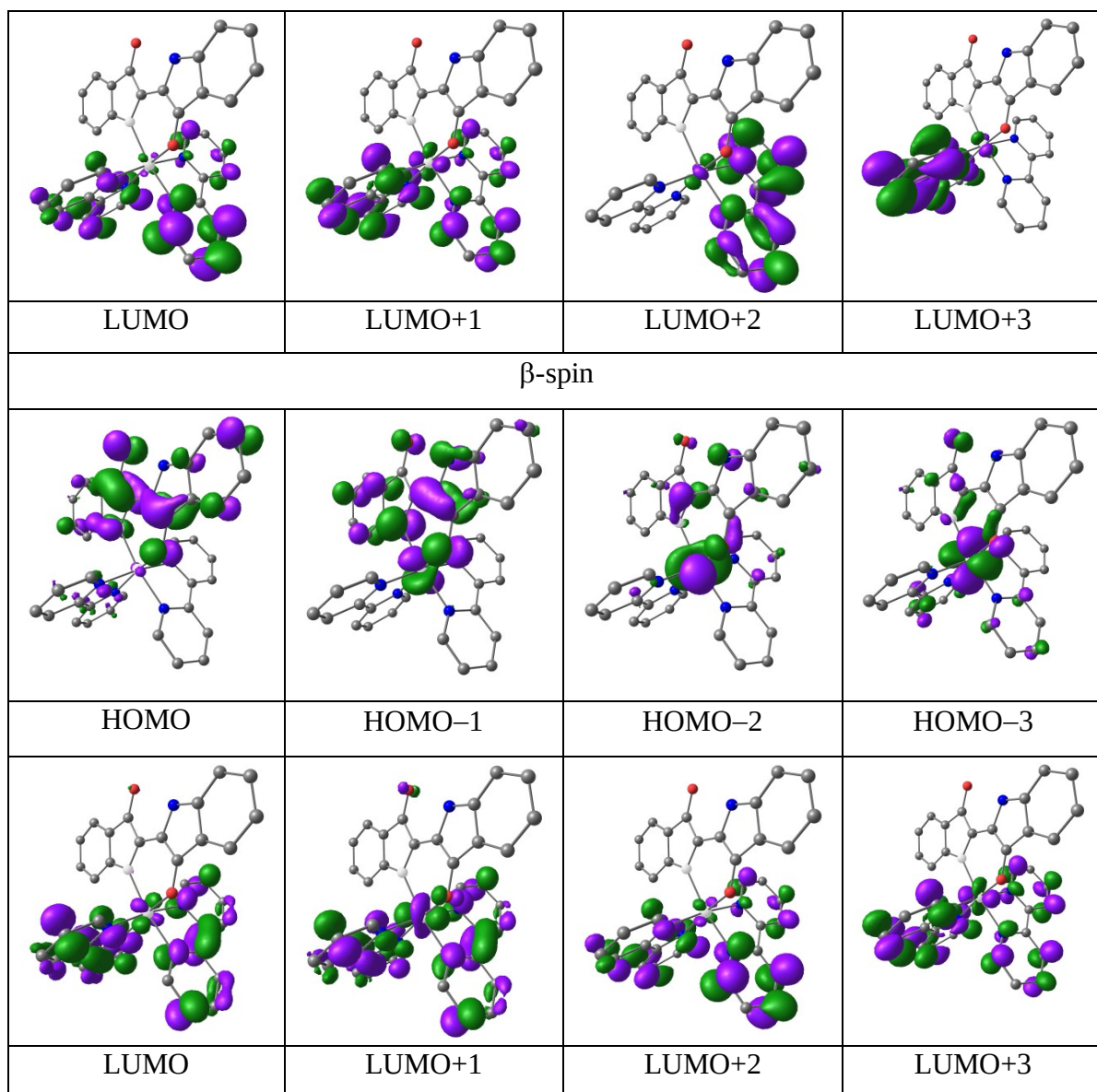
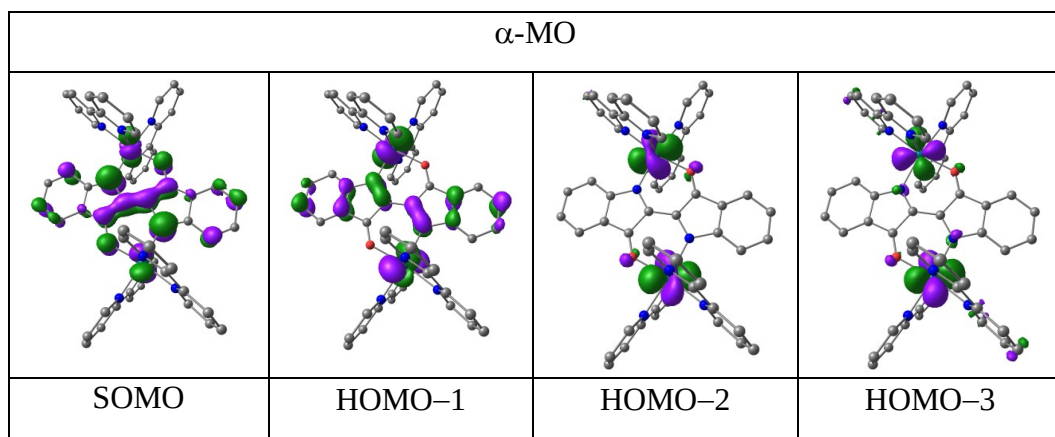


Table S18 DFT (UB3LYP) calculated MO compositions for *rac-2*³⁺ in *S* = 1/2 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	-7.823	0.03	0.95	0.02
LUMO+4	-8.360	0.05	0.94	0.01
LUMO+3	-8.457	0.06	0.93	0.01
LUMO+2	-8.502	0.06	0.92	0.02
LUMO+1	-8.773	0.07	0.91	0.02
LUMO	-9.867	0.09	0.05	0.86
SOMO	-11.513	0.29	0.08	0.63
HOMO-1	-12.095	0.45	0.08	0.46
HOMO-2	-12.221	0.77	0.14	0.09
HOMO-3	-12.298	0.76	0.15	0.09
HOMO-4	-12.415	0.76	0.16	0.08
HOMO-5	-12.515	0.75	0.15	0.10
β -MO				
LUMO+5	-8.356	0.05	0.94	0.01
LUMO+4	-8.453	0.07	0.92	0.01
LUMO+3	-8.485	0.07	0.91	0.02
LUMO+2	-8.747	0.08	0.89	0.03
LUMO+1	-9.587	0.10	0.06	0.84
LUMO	-10.158	0.24	0.09	0.67
HOMO	-11.714	0.48	0.11	0.42
HOMO-1	-12.132	0.74	0.13	0.13
HOMO-2	-12.157	0.69	0.12	0.19
HOMO-3	-12.343	0.75	0.16	0.09
HOMO-4	-12.391	0.76	0.15	0.09
HOMO-5	-12.638	0.65	0.15	0.20



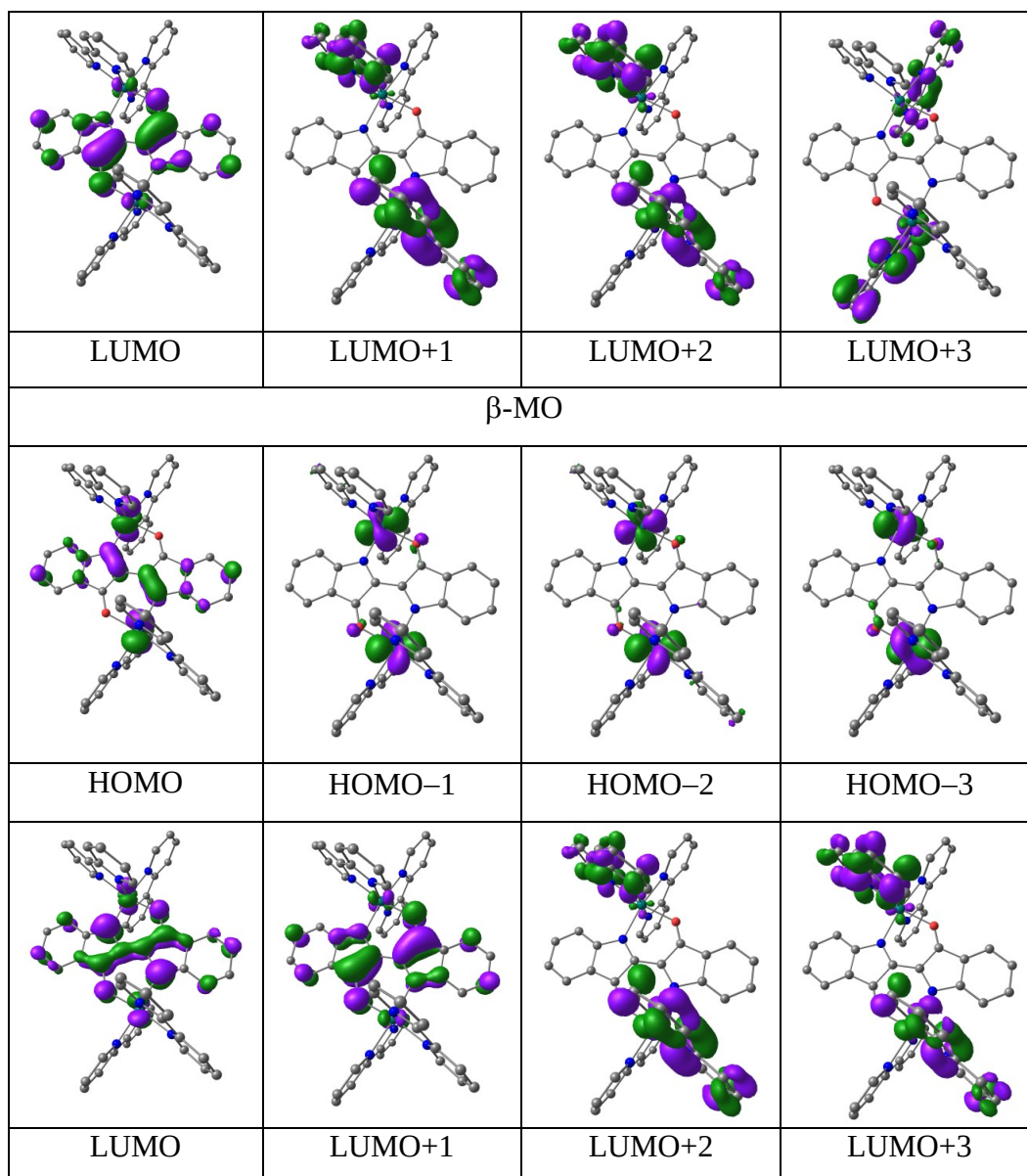


Table S19 DFT (UB3LYP) calculated MO compositions for *rac-2*⁴⁺ in *S* = 0 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
LUMO+5	-10.657	0.04	0.95	0.01
LUMO+4	-10.663	0.04	0.94	0.02
LUMO+3	-10.802	0.05	0.94	0.01
LUMO+2	-10.814	0.05	0.93	0.02
LUMO+1	-12.409	0.09	0.03	0.88
LUMO	-13.267	0.27	0.06	0.67
HOMO	-14.767	0.62	0.10	0.28
HOMO-1	-14.934	0.78	0.15	0.07
HOMO-2	-14.964	0.74	0.16	0.10
HOMO-3	-15.115	0.78	0.15	0.07
HOMO-4	-15.137	0.72	0.14	0.14
HOMO-5	-15.398	0.41	0.42	0.17

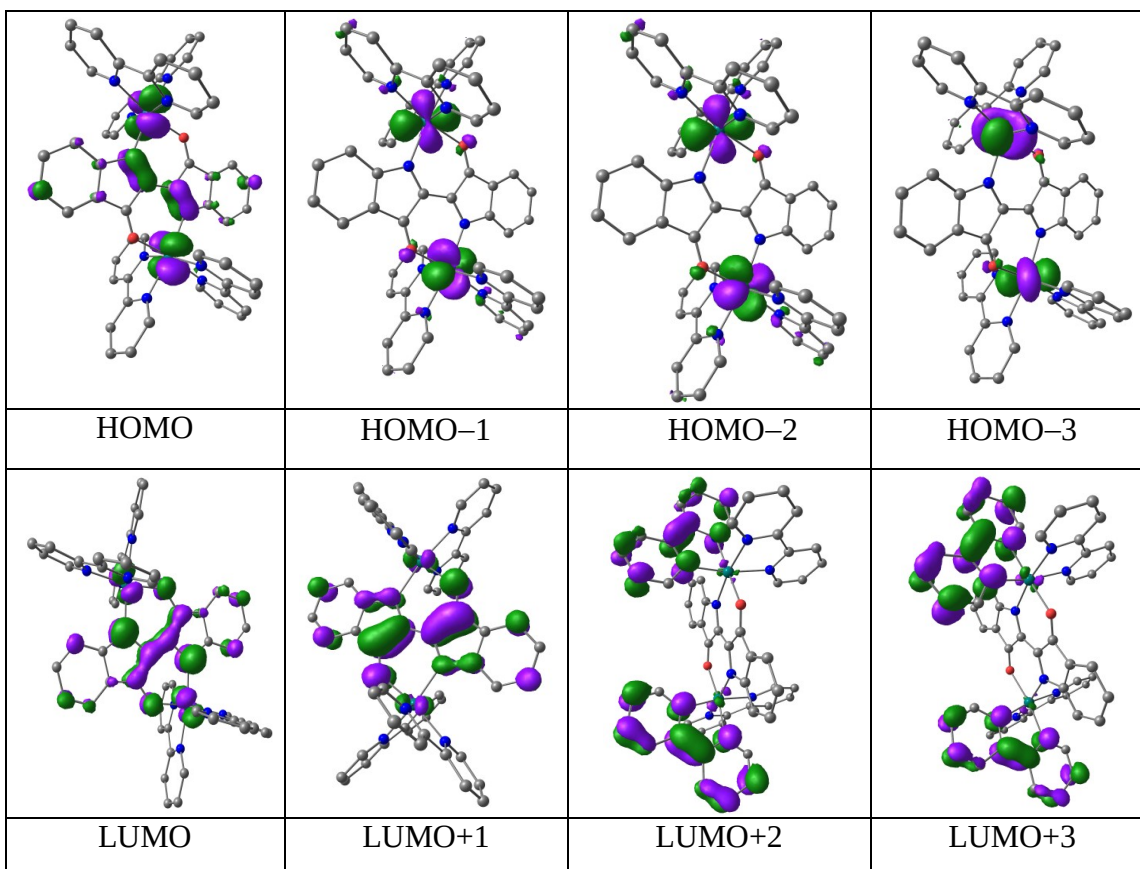


Table S20 DFT (B3LYP) calculated MO compositions for *rac-2*²⁺ in *S* = 0 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
LUMO+5	-5.498	0.04	0.95	0.01
LUMO+4	-6.078	0.07	0.91	0.02
LUMO+3	-6.101	0.08	0.90	0.01
LUMO+2	-6.165	0.05	0.93	0.01
LUMO+1	-6.344	0.08	0.90	0.02
LUMO	-6.735	0.07	0.08	0.85
HOMO	-8.213	0.20	0.09	0.71
HOMO-1	-9.025	0.31	0.08	0.61
HOMO-2	-9.424	0.77	0.13	0.10
HOMO-3	-9.472	0.76	0.14	0.10
HOMO-4	-9.645	0.73	0.16	0.10
HOMO-5	-9.711	0.76	0.15	0.09

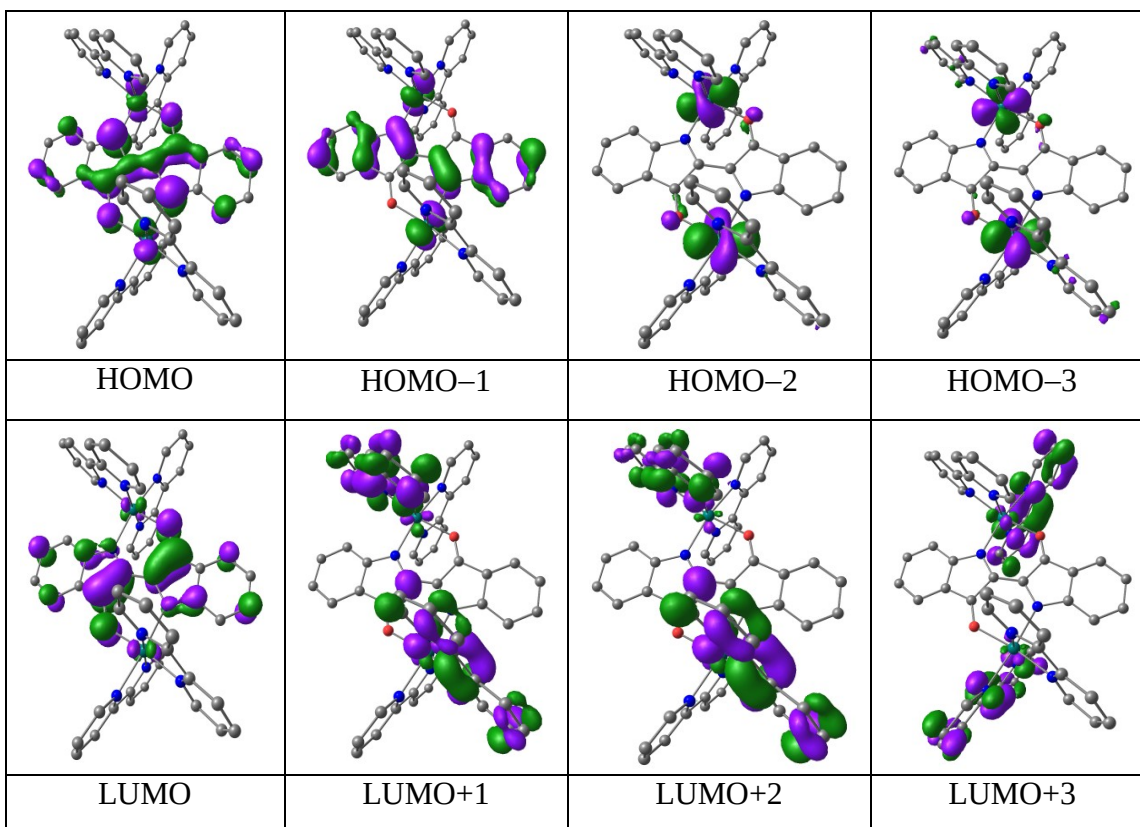
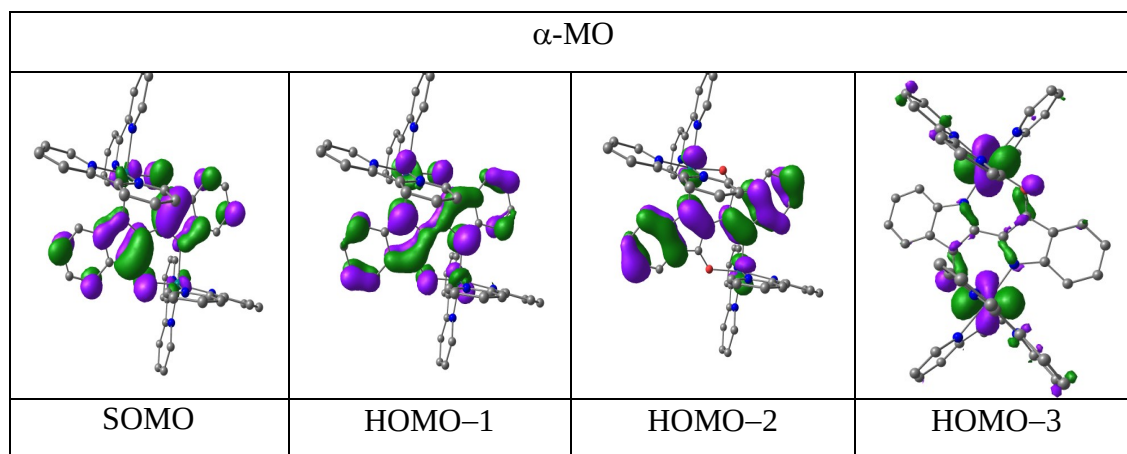


Table S21 DFT (UB3LYP) calculated MO compositions for *rac-2*⁺ in *S* = 1/2 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	-3.136	0.03	0.95	0.02
LUMO+4	-3.148	0.04	0.94	0.02
LUMO+3	-3.847	0.09	0.80	0.12
LUMO+2	-3.910	0.07	0.92	0.01
LUMO+1	-3.936	0.06	0.92	0.01
LUMO	-3.946	0.08	0.90	0.02
SOMO	-4.596	0.04	0.19	0.76
HOMO-1	-5.428	0.14	0.09	0.77
HOMO-2	-6.211	0.21	0.05	0.74
HOMO-3	-6.871	0.77	0.11	0.12
HOMO-4	-6.936	0.77	0.13	0.10
HOMO-5	-7.093	0.71	0.14	0.15
β -MO				
LUMO+5	-3.145	0.04	0.94	0.02
LUMO+4	-3.190	0.05	0.17	0.78
LUMO+3	-3.819	0.06	0.93	0.01
LUMO+2	-3.830	0.06	0.93	0.02
LUMO+1	-3.930	0.07	0.92	0.01
LUMO	-3.941	0.08	0.89	0.03
HOMO	-5.176	0.12	0.09	0.79
HOMO-1	-6.208	0.22	0.05	0.74
HOMO-2	-6.815	0.76	0.11	0.13
HOMO-3	-6.882	0.74	0.13	0.12
HOMO-4	-7.051	0.66	0.13	0.21
HOMO-5	-7.081	0.72	0.13	0.15



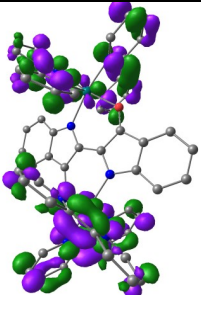
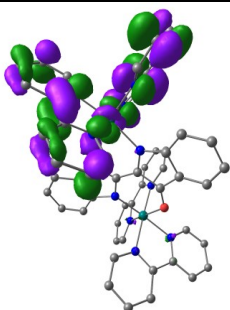
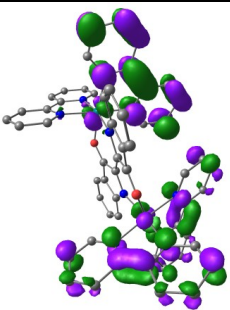
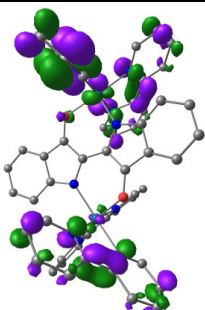
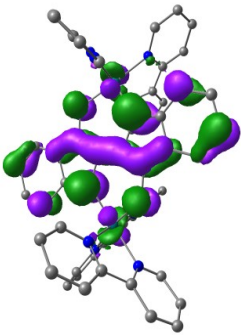
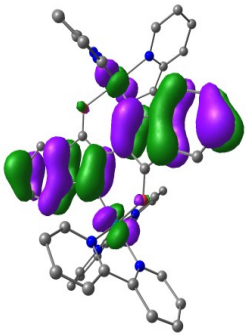
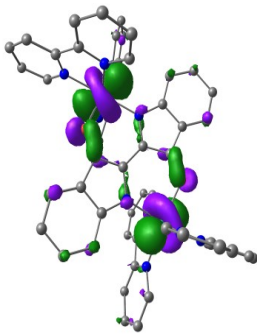
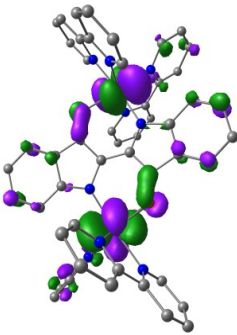
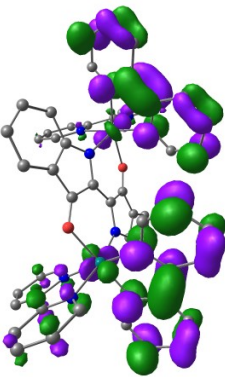
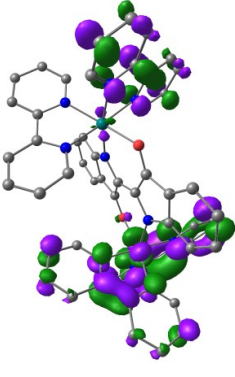
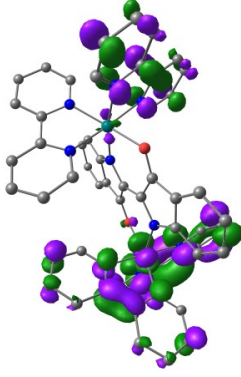
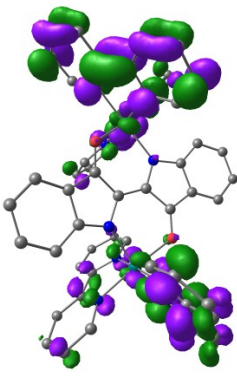
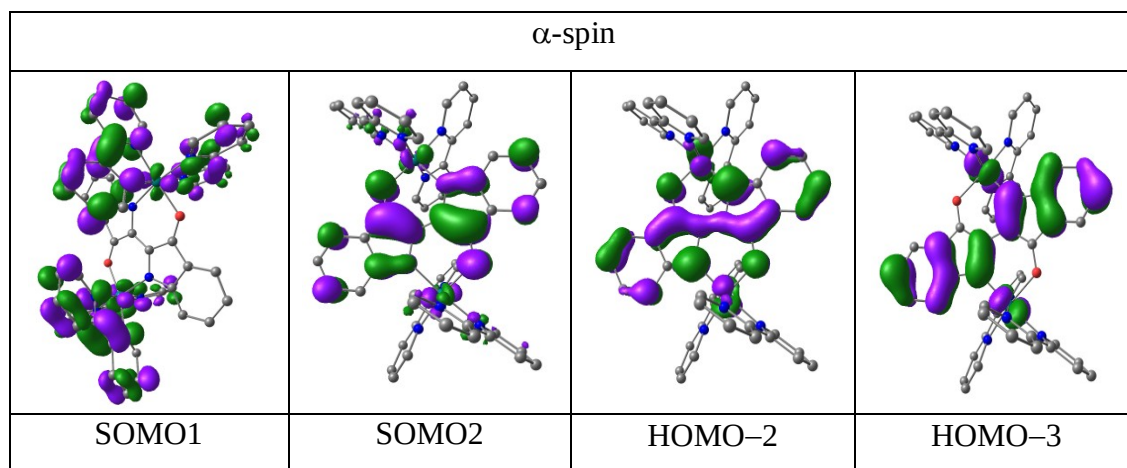
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β -MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

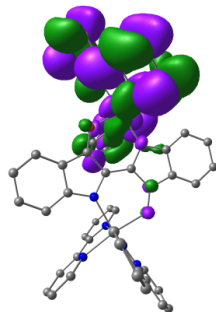
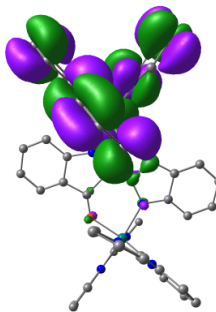
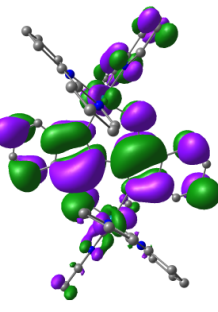
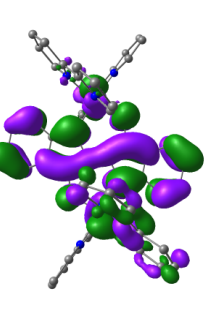
Table S22. DFT (UB3LYP) calculated MO compositions for *rac-2* in $S = 1$ state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	-0.576	0.07	0.92	0.01
LUMO+4	-0.750	0.03	0.95	0.02
LUMO+3	-0.776	0.04	0.94	0.01
LUMO+2	-1.635	0.08	0.90	0.02
LUMO+1	-1.656	0.09	0.89	0.03
LUMO	-1.783	0.08	0.88	0.03
SOMO1	-2.128	0.08	0.91	0.02
SOMO2	-2.674	0.08	0.10	0.82
HOMO-2	-3.285	0.18	0.13	0.70
HOMO-3	-3.954	0.27	0.08	0.65
HOMO-4	-4.485	0.78	0.11	0.11
HOMO-5	-4.529	0.75	0.13	0.12
β -MO				
LUMO+5	-0.757	0.04	0.94	0.01
LUMO+4	-1.173	0.08	0.20	0.72
LUMO+3	-1.381	0.07	0.92	0.02
LUMO+2	-1.386	0.08	0.90	0.02
LUMO+1	-1.392	0.09	0.88	0.03
LUMO	-1.418	0.05	0.84	0.11
HOMO	-2.989	0.15	0.12	0.73
HOMO-1	-3.934	0.29	0.08	0.63
HOMO-2	-4.370	0.76	0.11	0.13
HOMO-3	-4.406	0.74	0.14	0.12
HOMO-4	-4.614	0.74	0.14	0.12
HOMO-5	-4.670	0.76	0.14	0.10



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

Table S23 DFT (UB3LYP) calculated MO compositions for *rac-2⁻* in $S = 3/2$ State

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	1.821	0.11	0.87	0.01
LUMO+4	1.766	0.10	0.89	0.01
LUMO+3	1.621	0.04	0.93	0.02
LUMO+2	1.575	0.05	0.93	0.02
LUMO+1	0.516	0.11	0.87	0.02
LUMO	0.501	0.11	0.83	0.06
SOMO1	-0.072	0.07	0.91	0.02
SOMO2	-0.151	0.08	0.87	0.04
SOMO3	-0.402	0.08	0.16	0.76
HOMO-3	-1.049	0.18	0.13	0.69
HOMO-4	-1.701	0.32	0.08	0.59
HOMO-5	-2.080	0.79	0.12	0.09
β -MO				
LUMO+5	1.614	0.05	0.93	0.02
LUMO+4	1.142	0.09	0.49	0.42
LUMO+3	1.063	0.08	0.85	0.08
LUMO+2	1.031	0.07	0.89	0.04
LUMO+1	0.963	0.08	0.87	0.05
LUMO	0.935	0.05	0.66	0.28
HOMO	-0.739	0.17	0.10	0.74
HOMO-1	-1.670	0.37	0.08	0.56
HOMO-2	-1.971	0.78	0.12	0.10
HOMO-3	-2.032	0.76	0.14	0.09
HOMO-4	-2.236	0.74	0.15	0.11
HOMO-5	-2.275	0.75	0.14	0.10
α -spin				
				
SOMO1	SOMO2	SOMO3	HOMO-3	

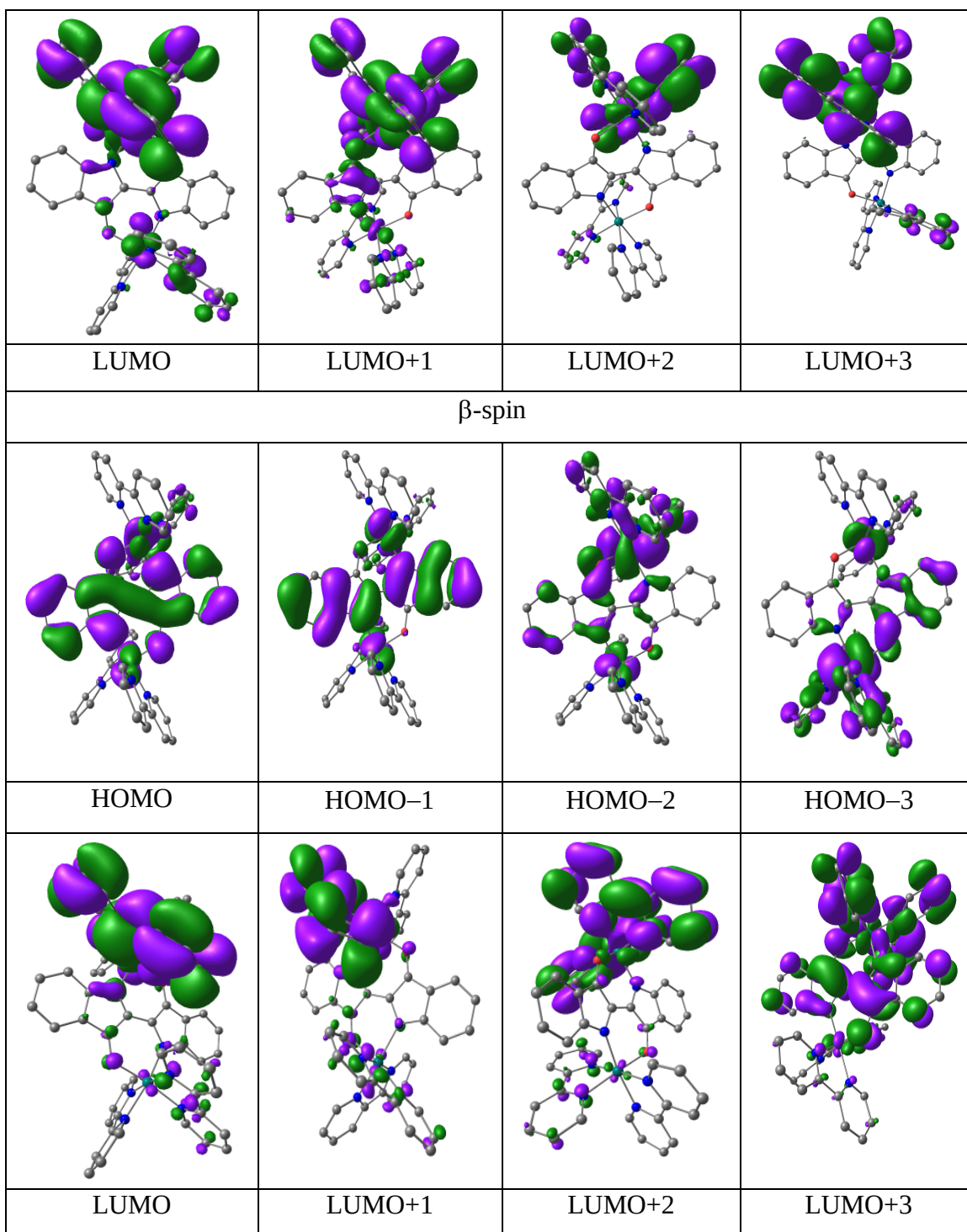
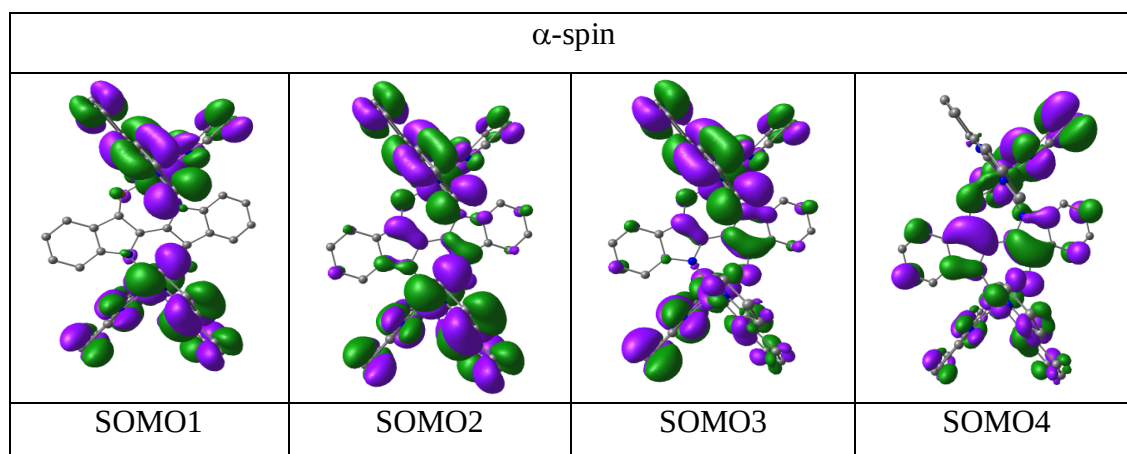


Table S24 DFT (UB3LYP) calculated MO compositions for *rac*-2²⁻ in *S* = 2 State

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	4.199	0.06	0.93	0.01
LUMO+4	4.133	0.10	0.89	0.02
LUMO+3	4.057	0.04	0.94	0.02
LUMO+2	3.917	0.05	0.93	0.02
LUMO+1	3.826	0.07	0.91	0.02
LUMO	2.594	0.13	0.82	0.04
SOMO1	2.213	0.13	0.82	0.05
SOMO2	2.007	0.08	0.87	0.05
SOMO3	1.891	0.05	0.87	0.08
SOMO4	1.798	0.07	0.25	0.68
HOMO-4	1.197	0.20	0.14	0.66
HOMO-5	0.530	0.38	0.09	0.53
β -MO				
LUMO+5	3.876	0.08	0.90	0.02
LUMO+4	3.639	0.07	0.90	0.04
LUMO+3	3.496	0.10	0.84	0.06
LUMO+2	3.284	0.07	0.43	0.50
LUMO+1	3.259	0.05	0.76	0.19
LUMO	3.167	0.11	0.80	0.10
HOMO	1.549	0.19	0.12	0.69
HOMO-1	0.601	0.44	0.11	0.45
HOMO-2	0.421	0.76	0.13	0.12
HOMO-3	0.365	0.76	0.15	0.10
HOMO-4	0.192	0.75	0.16	0.09
HOMO-5	0.136	0.75	0.16	0.09



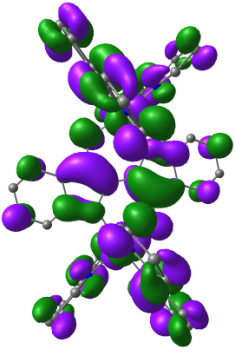
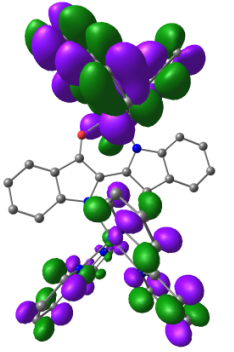
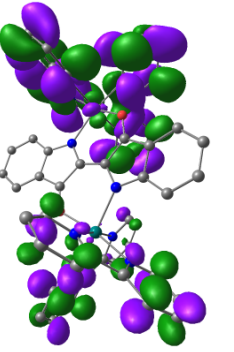
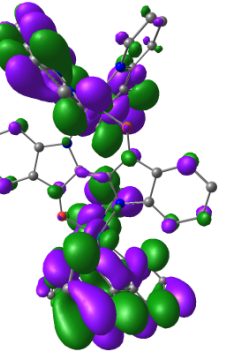
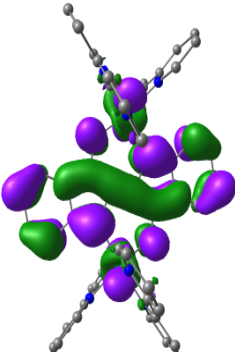
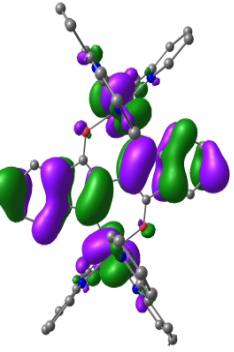
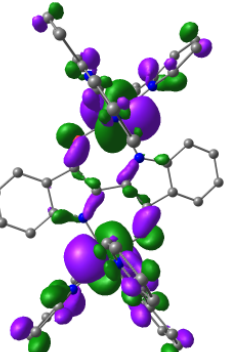
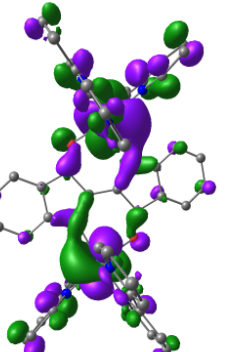
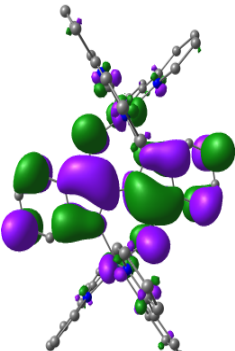
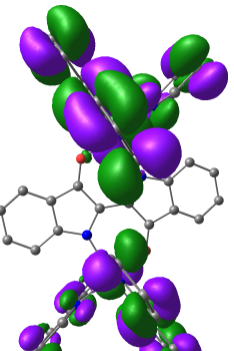
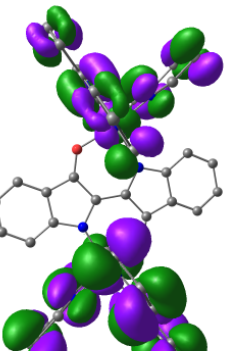
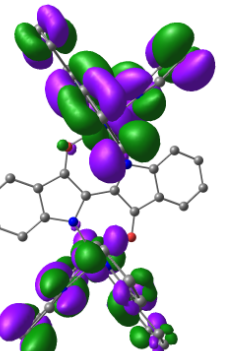
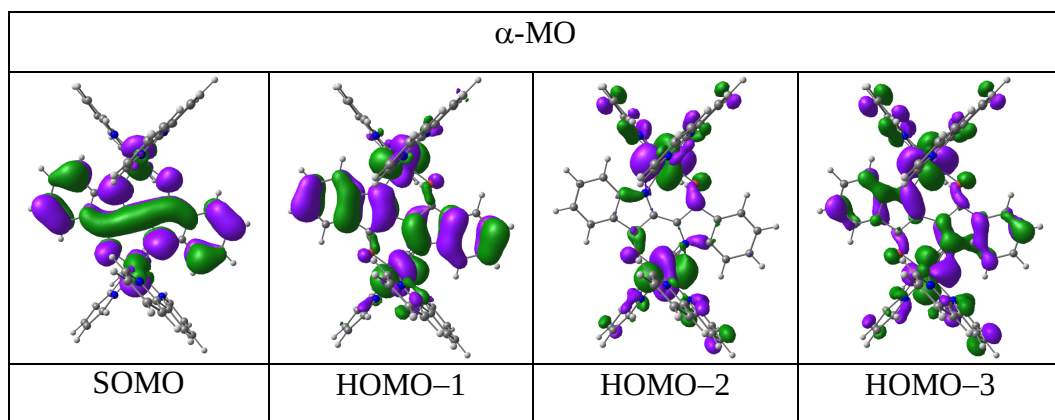
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β -spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25 DFT (UB3LYP) calculated MO compositions for *meso-2*³⁺ in *S* = 1/2 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	-1.791	0.03	0.52	0.45
LUMO+4	-2.560	0.06	0.93	0.01
LUMO+3	-2.560	0.06	0.93	0.01
LUMO+2	-2.601	0.04	0.94	0.01
LUMO+1	-2.601	0.04	0.94	0.01
LUMO	-3.743	0.08	0.04	0.88
SOMO	-5.507	0.27	0.06	0.68
HOMO-1	-6.224	0.67	0.08	0.24
HOMO-2	-6.283	0.82	0.12	0.06
HOMO-3	-6.333	0.71	0.13	0.16
HOMO-4	-6.473	0.80	0.14	0.06
HOMO-5	-6.542	0.77	0.13	0.10
β -MO				
LUMO+5	-2.555	0.06	0.93	0.01
LUMO+4	-2.557	0.06	0.93	0.01
LUMO+3	-2.591	0.05	0.94	0.01
LUMO+2	-2.593	0.05	0.94	0.01
LUMO+1	-3.431	0.08	0.05	0.87
LUMO	-4.116	0.21	0.06	0.73
HOMO	-5.899	0.59	0.09	0.32
HOMO-1	-6.230	0.78	0.12	0.10
HOMO-2	-6.240	0.82	0.12	0.07
HOMO-3	-6.424	0.79	0.14	0.07
HOMO-4	-6.435	0.72	0.12	0.16
HOMO-5	-6.624	0.70	0.13	0.18



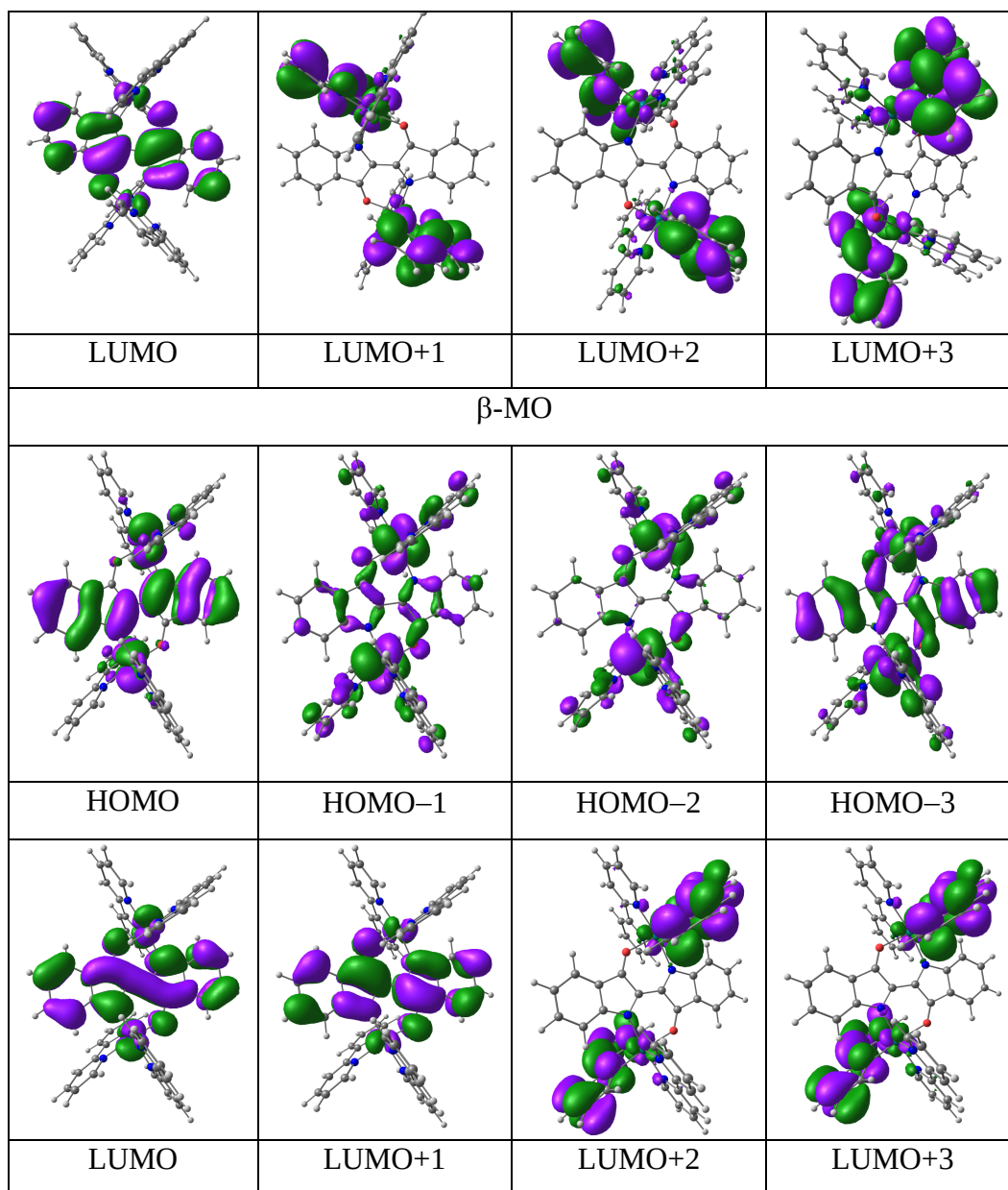


Table S26 DFT (UB3LYP) calculated MO compositions for *meso-2*⁴⁺ in *S* = 0 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
LUMO+5	-10.677	0.05	0.95	0.01
LUMO+4	-10.679	0.04	0.94	0.01
LUMO+3	-10.797	0.05	0.94	0.01
LUMO+2	-10.799	0.05	0.93	0.02
LUMO+1	-12.406	0.09	0.03	0.88
LUMO	-13.268	0.27	0.06	0.67
HOMO	-14.766	0.62	0.10	0.28
HOMO-1	-14.936	0.75	0.16	0.09
HOMO-2	-14.955	0.78	0.16	0.06
HOMO-3	-15.115	0.78	0.15	0.07
HOMO-4	-15.131	0.71	0.15	0.14
HOMO-5	-15.401	0.44	0.37	0.18

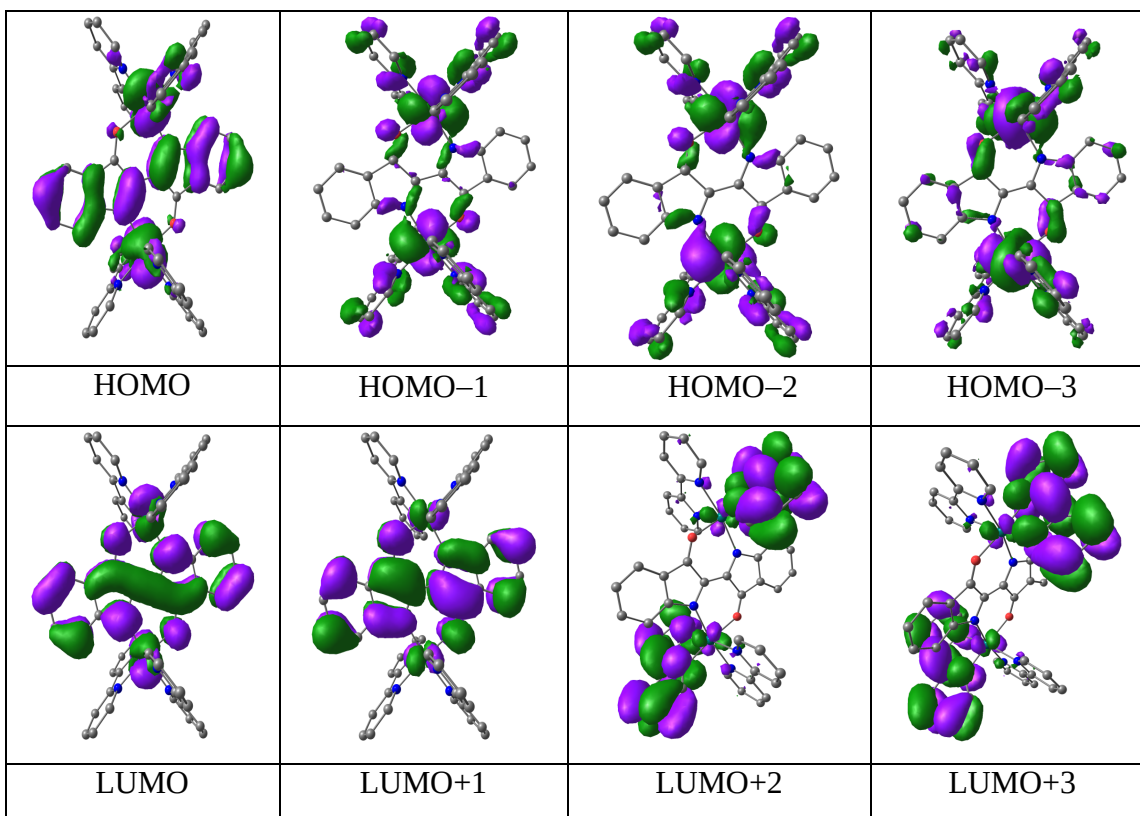


Table S27 DFT (B3LYP) calculated MO compositions for *meso*-2²⁺ in *S* = 0 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
LUMO+5	-1.521	0.04	0.93	0.03
LUMO+4	-2.319	0.07	0.91	0.02
LUMO+3	-2.321	0.07	0.93	0.01
LUMO+2	-2.340	0.05	0.94	0.01
LUMO+1	-2.341	0.06	0.93	0.01
LUMO	-3.043	0.08	0.06	0.86
HOMO	-4.617	0.22	0.07	0.71
HOMO-1	-5.432	0.47	0.07	0.46
HOMO-2	-5.694	0.82	0.11	0.06
HOMO-3	-5.698	0.78	0.13	0.09
HOMO-4	-5.907	0.78	0.14	0.07
HOMO-5	-5.933	0.76	0.13	0.12

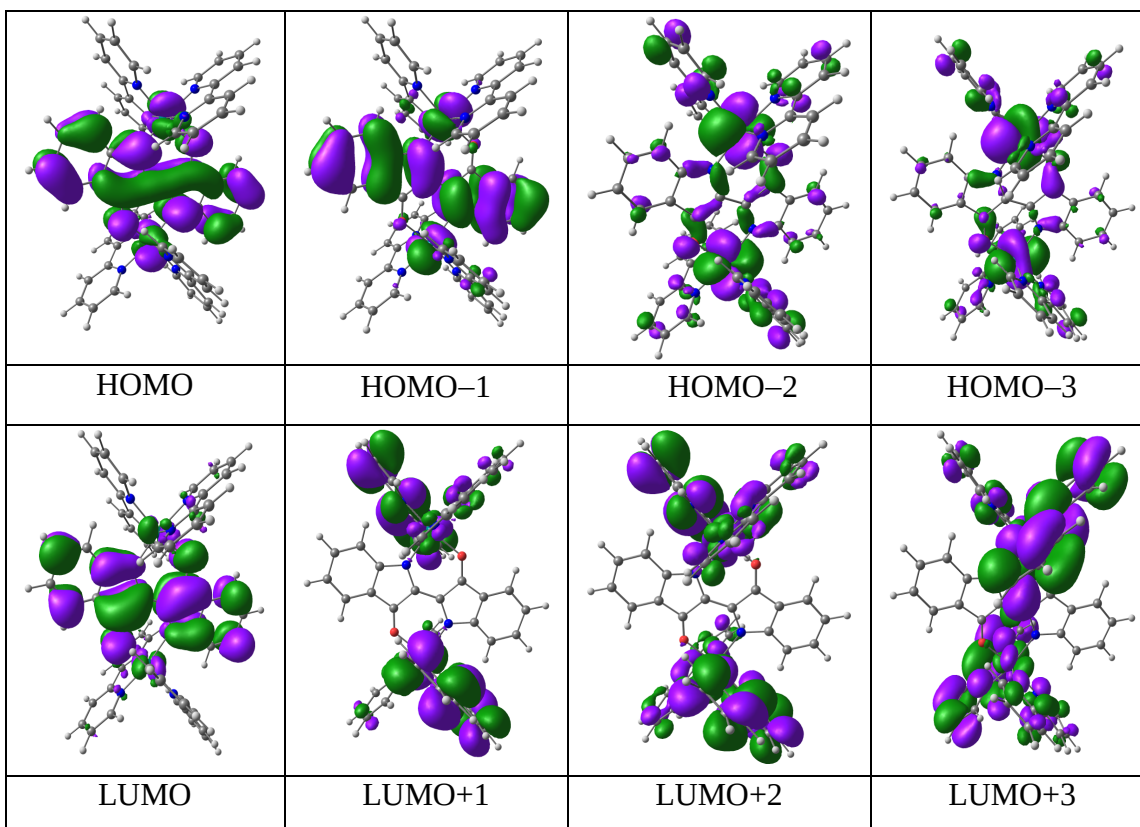
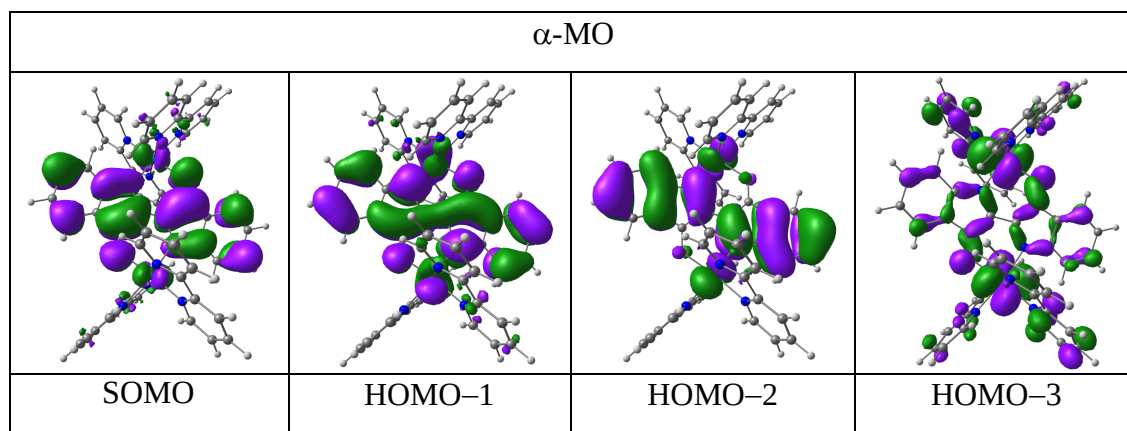


Table S28 DFT calculated MO compositions for *meso-2⁺* in *S* = 1/2 state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	-3.134	0.03	0.95	0.02
LUMO+4	-3.136	0.04	0.94	0.02
LUMO+3	-3.847	0.09	0.77	0.14
LUMO+2	-3.909	0.08	0.91	0.01
LUMO+1	-3.932	0.06	0.92	0.02
LUMO	-3.935	0.06	0.92	0.01
SOMO	-4.594	0.04	0.22	0.74
HOMO-1	-5.434	0.14	0.08	0.77
HOMO-2	-6.213	0.22	0.05	0.73
HOMO-3	-6.884	0.75	0.13	0.13
HOMO-4	-6.924	0.80	0.11	0.08
HOMO-5	-7.075	0.70	0.14	0.17
β -MO				
LUMO+5	-3.133	0.04	0.93	0.03
LUMO+4	-3.203	0.05	0.14	0.81
LUMO+3	-3.811	0.06	0.93	0.01
LUMO+2	-3.828	0.06	0.92	0.02
LUMO+1	-3.916	0.08	0.91	0.02
LUMO	-3.928	0.07	0.91	0.01
HOMO	-5.191	0.12	0.08	0.79
HOMO-1	-6.212	0.22	0.05	0.73
HOMO-2	-6.843	0.73	0.13	0.14
HOMO-3	-6.865	0.78	0.11	0.11
HOMO-4	-7.038	0.68	0.13	0.19
HOMO-5	-7.076	0.69	0.14	0.17



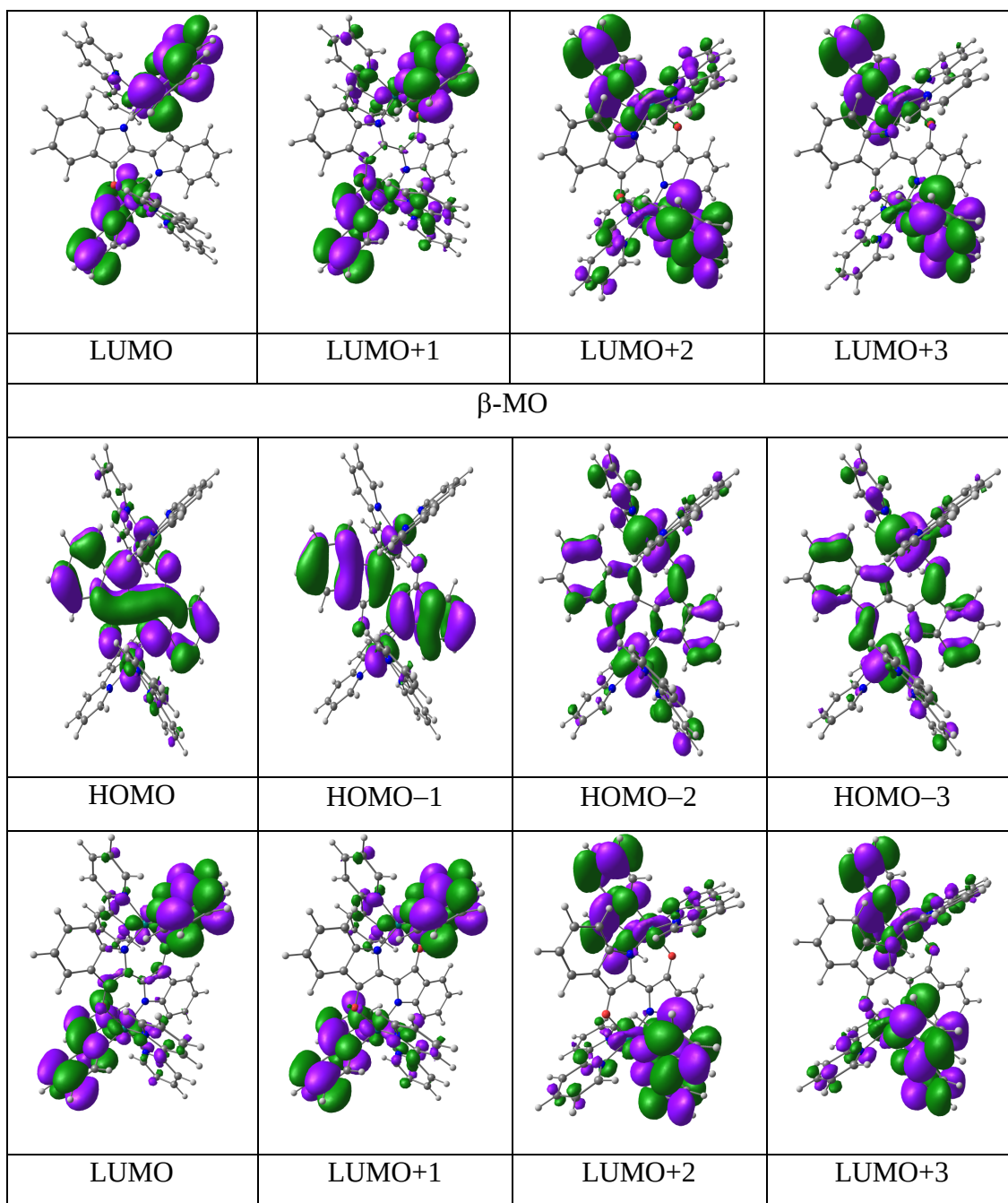
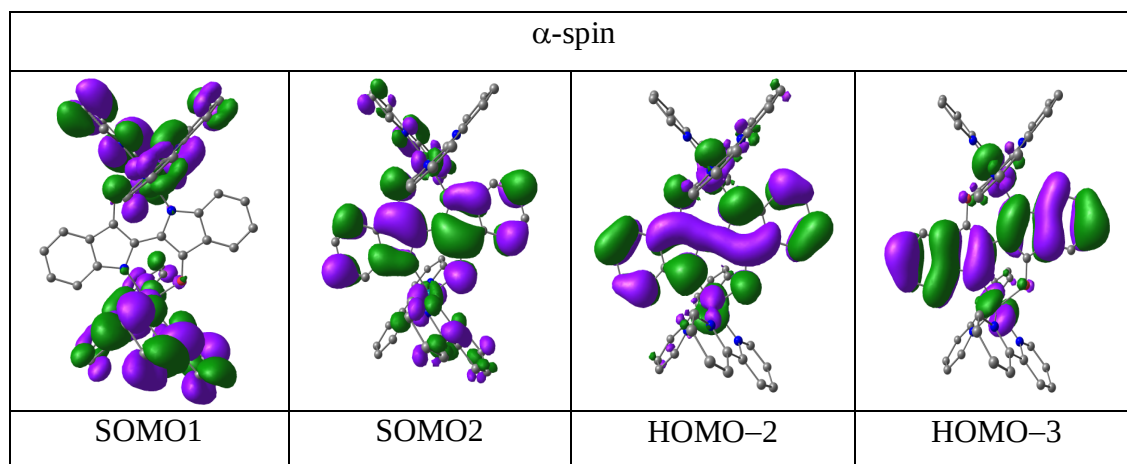


Table S29. DFT (UB3LYP) calculated MO compositions for *meso-2* in $S = 1$ state

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	-0.557	0.07	0.92	0.01
LUMO+4	-0.792	0.04	0.94	0.02
LUMO+3	-0.796	0.05	0.93	0.02
LUMO+2	-1.643	0.10	0.77	0.12
LUMO+1	-1.677	0.09	0.90	0.01
LUMO	-1.843	0.07	0.82	0.12
SOMO1	-2.184	0.06	0.92	0.02
SOMO2	-2.416	0.04	0.33	0.63
HOMO-2	-3.268	0.17	0.08	0.75
HOMO-3	-4.069	0.32	0.06	0.63
HOMO-4	-4.514	0.75	0.14	0.11
HOMO-5	-4.538	0.81	0.12	0.07
β -MO				
LUMO+5	-0.765	0.05	0.92	0.02
LUMO+4	-1.111	0.07	0.20	0.73
LUMO+3	-1.296	0.06	0.93	0.01
LUMO+2	-1.331	0.04	0.84	0.12
LUMO+1	-1.428	0.07	0.91	0.01
LUMO	-1.436	0.07	0.91	0.02
HOMO	-3.038	0.16	0.07	0.77
HOMO-1	-4.048	0.34	0.06	0.60
HOMO-2	-4.484	0.75	0.13	0.12
HOMO-3	-4.492	0.81	0.11	0.08
HOMO-4	-4.698	0.72	0.13	0.15
HOMO-5	-4.735	0.75	0.15	0.11



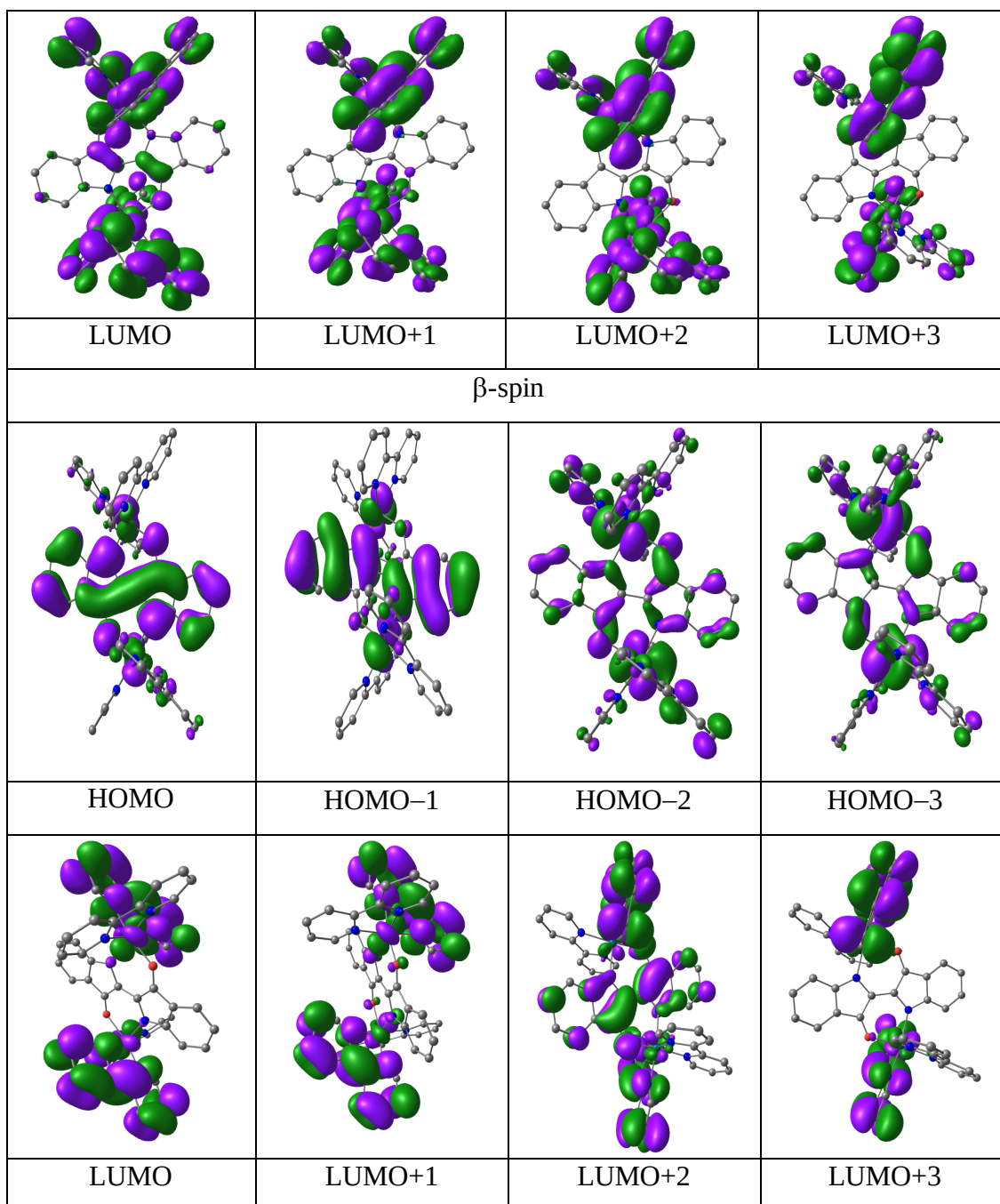
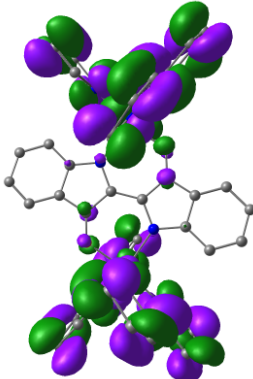
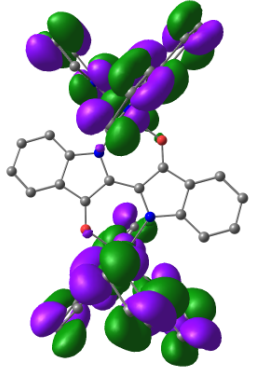
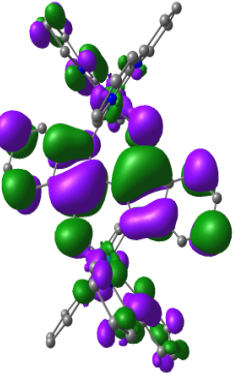
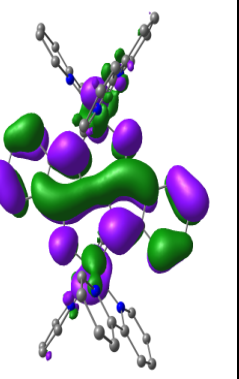


Table S30 DFT (UB3LYP) calculated MO compositions for *meso-2*⁻ in *S* = 3/2 State

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	1.717	0.04	0.95	0.01
LUMO+4	1.716	0.04	0.95	0.02
LUMO+3	1.501	0.05	0.93	0.02
LUMO+2	1.494	0.06	0.92	0.02
LUMO+1	0.519	0.13	0.83	0.04
LUMO	0.512	0.12	0.86	0.02
SOMO1	-0.171	0.06	0.88	0.05
SOMO2	-0.180	0.06	0.92	0.02
SOMO3	-0.436	0.07	0.15	0.78
HOMO-3	-1.070	0.19	0.11	0.70
HOMO-4	-1.732	0.32	0.08	0.61
HOMO-5	-2.132	0.73	0.16	0.11
β -MO				
LUMO+5	1.532	0.06	0.92	0.02
LUMO+4	1.193	0.08	0.71	0.21
LUMO+3	1.144	0.06	0.93	0.01
LUMO+2	1.000	0.04	0.33	0.62
LUMO+1	0.837	0.09	0.89	0.02
LUMO	0.815	0.08	0.90	0.02
HOMO	-0.749	0.17	0.10	0.73
HOMO-1	-1.717	0.34	0.07	0.59
HOMO-2	-2.065	0.74	0.15	0.12
HOMO-3	-2.089	0.78	0.12	0.10
HOMO-4	-2.304	0.72	0.14	0.14
HOMO-5	-2.353	0.75	0.15	0.10
α -spin				
				
SOMO1	SOMO2	SOMO3	HOMO-3	

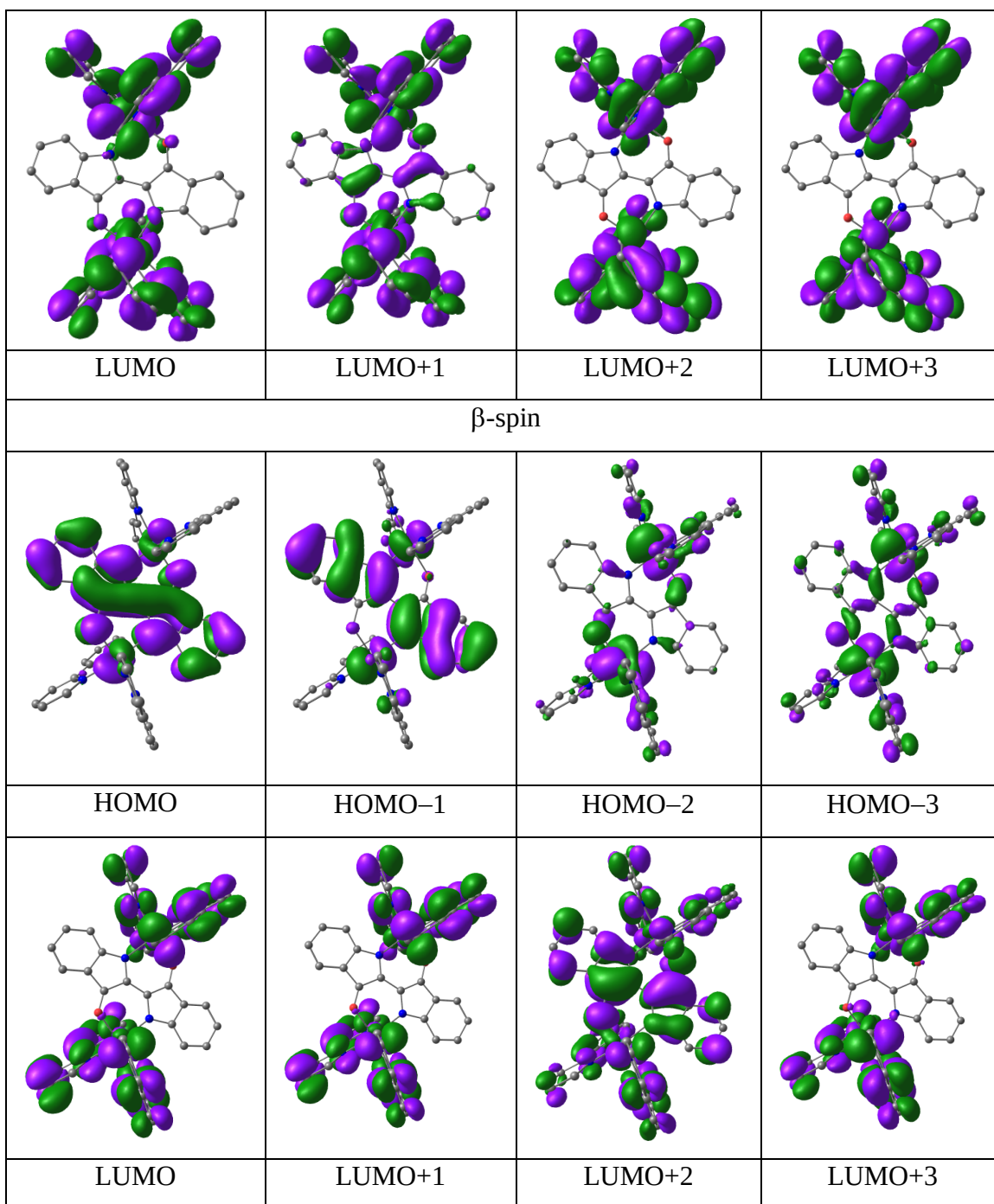
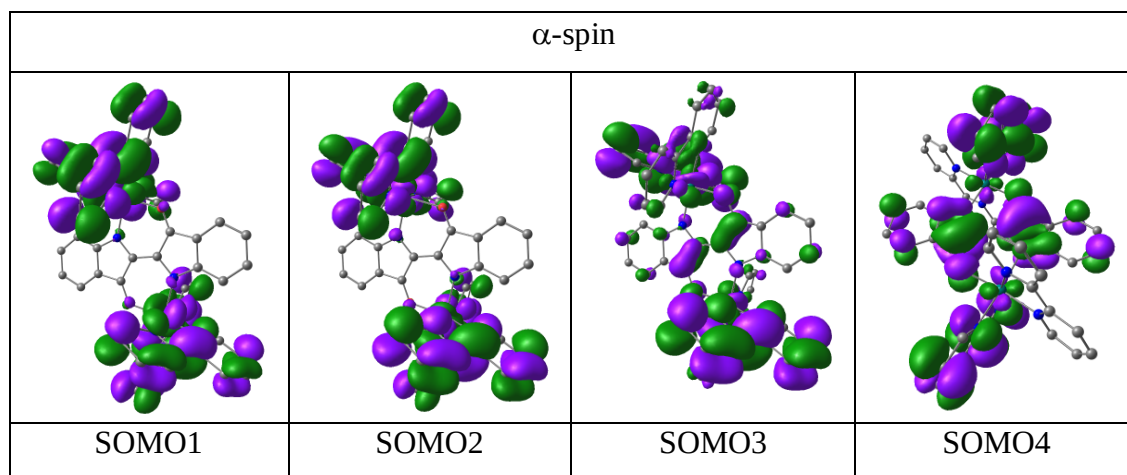


Table S31 DFT (UB3LYP) calculated MO compositions for *meso-2*²⁻ in *S* = 2 State

MO	Energy (eV)	Composition		
		Ru	bpy	Ind
α -MO				
LUMO+5	4.199	0.03	0.96	0.01
LUMO+4	4.180	0.10	0.89	0.02
LUMO+3	4.171	0.13	0.84	0.03
LUMO+2	3.957	0.07	0.90	0.03
LUMO+1	3.951	0.06	0.91	0.03
LUMO	2.640	0.18	0.65	0.17
SOMO1	2.223	0.15	0.84	0.02
SOMO2	1.858	0.04	0.94	0.02
SOMO3	1.849	0.03	0.93	0.04
SOMO4	1.730	0.05	0.32	0.64
HOMO-4	1.205	0.25	0.10	0.65
HOMO-5	0.545	0.49	0.08	0.43
β -MO				
LUMO+5	4.019	0.07	0.91	0.02
LUMO+4	3.533	0.12	0.81	0.07
LUMO+3	3.508	0.10	0.88	0.01
LUMO+2	3.294	0.04	0.95	0.02
LUMO+1	3.292	0.04	0.95	0.02
LUMO	3.059	0.04	0.16	0.79
HOMO	1.465	0.23	0.07	0.69
HOMO-1	0.579	0.53	0.09	0.38
HOMO-2	0.321	0.81	0.13	0.06
HOMO-3	0.305	0.73	0.15	0.13
HOMO-4	0.155	0.71	0.15	0.14
HOMO-5	0.143	0.72	0.19	0.08



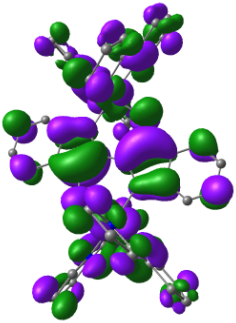
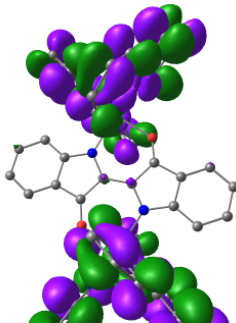
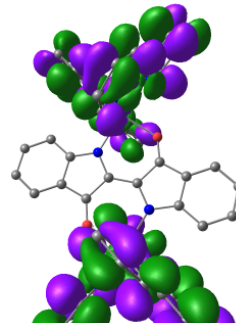
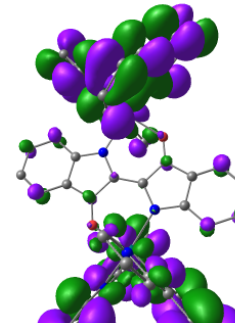
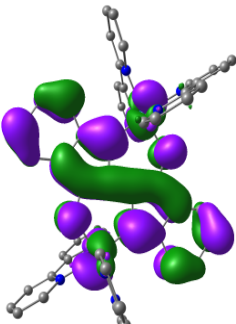
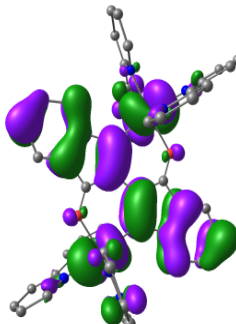
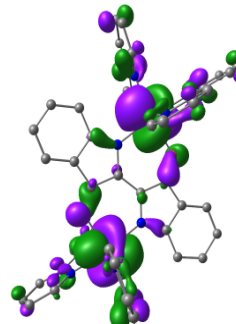
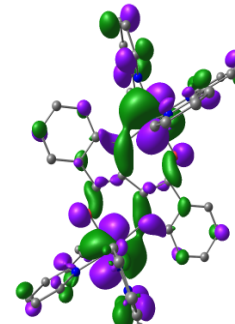
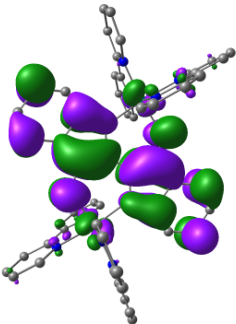
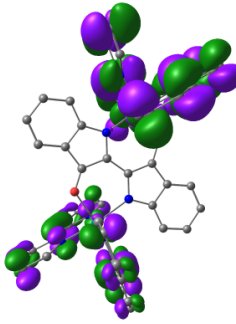
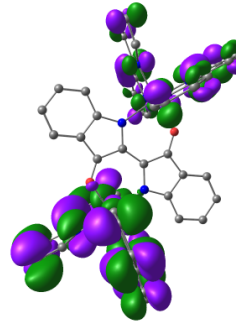
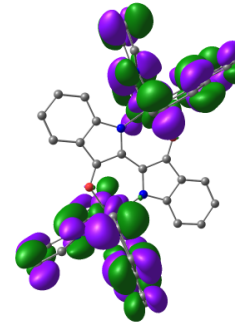
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β -spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S32 Energies of DFT (U)B3LYP/LANL2DZ/6-31G* optimized **1ⁿ** and **2ⁿ**

Complex	<i>E</i> (Hartrees)					$\Delta E_{(\text{HE-LE})}^a$
	<i>S</i> = 0	<i>S</i> = 1/2	<i>S</i> = 1	<i>S</i> = 3/2	<i>S</i> = 2	
1³⁺	−1958.9616712		−1958.9501241			0.0115471 Hartrees 2534.2955 cm ^{−1} 30.31691336 kJ/mol
1[−]	−1959.8506501		−1959.8602668			0.009616 Hartrees 2110.46804 cm ^{−1} 25.2468099 kJ/mol
1^{2−}		−1959.7914091		−1959.8056776		0.014268 Hartrees 3131.46402cm ^{−1} 37.4606369 kJ/mol
1^{3−}			−1959.6279196		−1959.5935525	0.034367 Hartrees 7542.68461 cm ^{−1} 90.2305654 kJ/mol
<i>rac</i> - 2⁴⁺	−3042.8372352		−3042.8296368			0.007599 Hartrees 1667.78771 cm ^{−1} 19.951176 kJ/mol
<i>meso</i> - 2⁴⁺	−3042.8971430		−3042.8894285			0.007715 Hartrees 1693.24677 cm ^{−1} 20.255734 kJ/mol
<i>rac</i> - 2	−3044.0009325		−3044.0042116			0.003279 Hartrees 719.657312 cm ^{−1} 8.60901516 kJ/mol
<i>meso</i> - 2	−3043.9385763		−3043.9445347			0.005962 Hartrees 1308.50774 cm ^{−1} 15.6532322 kJ/mol
<i>rac</i> - 2[−]		−3043.9828591		−3044.0469966		0.0064137 Hartrees 1407.644434cm ^{−1} 16.83917063 kJ/mol
<i>meso</i> - 2[−]		−3044.0458142		−3044.0485244		0.0027102 Hartrees 594.82014223 cm ^{−1} 7.115630642 kJ/mol
<i>rac</i> - 2^{2−}			−3043.9961642		−3044.0049150	0.0087508 Hartrees 1920.5785922 cm ^{−1} 22.97522715 kJ/mol
<i>meso</i> - 2^{2−}			−3043.9809805		−3044.0026433	0.021663 Hartrees 4754.47891 cm ^{−1} 56.8762108 kJ/mol

^aHE = Spin state in higher in energy and LE = Spin state in lower in energy.

Table S33 DFT calculated (UB3LYP/LanL2DZ/6-31G*) solvent dependent Mulliken spin densities for **1ⁿ**

Complex	Ru	bpy	HInd
1²⁺ (S=1/2)	0.151	-0.007	0.853
1²⁺ (S=1/2).CH ₃ CN	0.263	-0.004	0.741
1 (S=1/2)	-0.019	0.524	0.498
1 (S=1/2).CH ₃ CN	0.012	0.002	0.986
1⁻ (S=1)	0.017	1.043	0.943
1⁻ (S=1) .CH ₃ CN	0.039	0.982	0.979
1²⁻ (S=3/2)	0.148	1.875	0.975
1²⁻ (S=3/2) .CH ₃ CN	0.141	1.889	0.969
1³⁻ (S=1)	0.200	1.708	0.104
1³⁻ (S=1) .CH ₃ CN	0.143	1.851	0.007

Table S34 DFT calculated (UB3LYP/LanL2DZ/6-31G*) Mulliken spin densities for **2ⁿ**

Complex	Ru	bpy	HInd
<i>rac</i> - 2 ⁻ (S=3/2)	-0.013	2.104	0.908
<i>meso</i> - 2 ⁻ (S=3/2)	-0.154	2.276	0.868
<i>rac</i> - 2 ²⁻ (S=2)	0.079	3.329	0.595
<i>meso</i> - 2 ²⁻ (S=2)	0.082	3.539	0.380

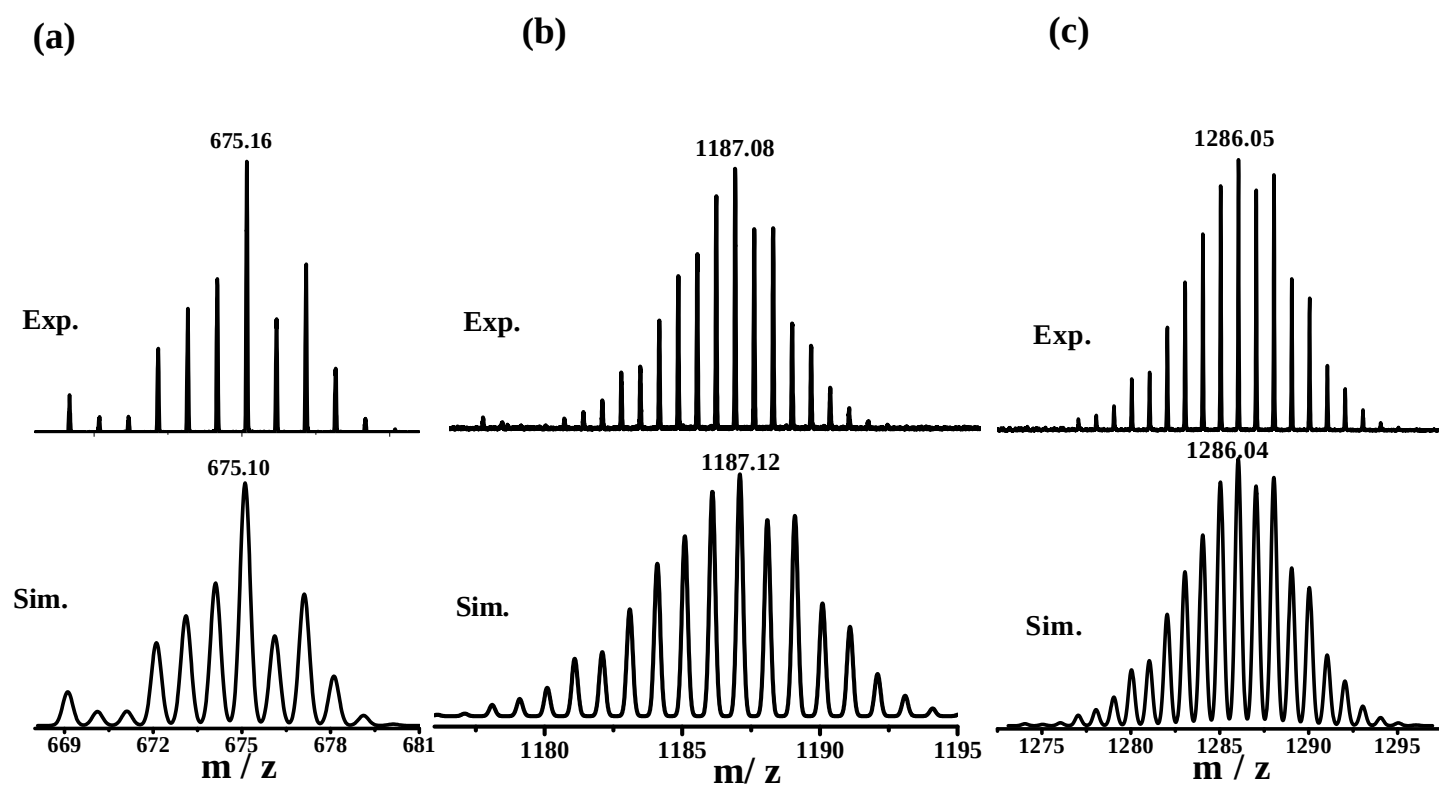


Fig. S1 Experimental and simulated ESI-MS(+) spectra of (a) $[1]ClO_4$, (b) $rac\text{-}[2](ClO_4)_2$ and (c) $meso\text{-}[2](ClO_4)_3$ in CH_3CN .

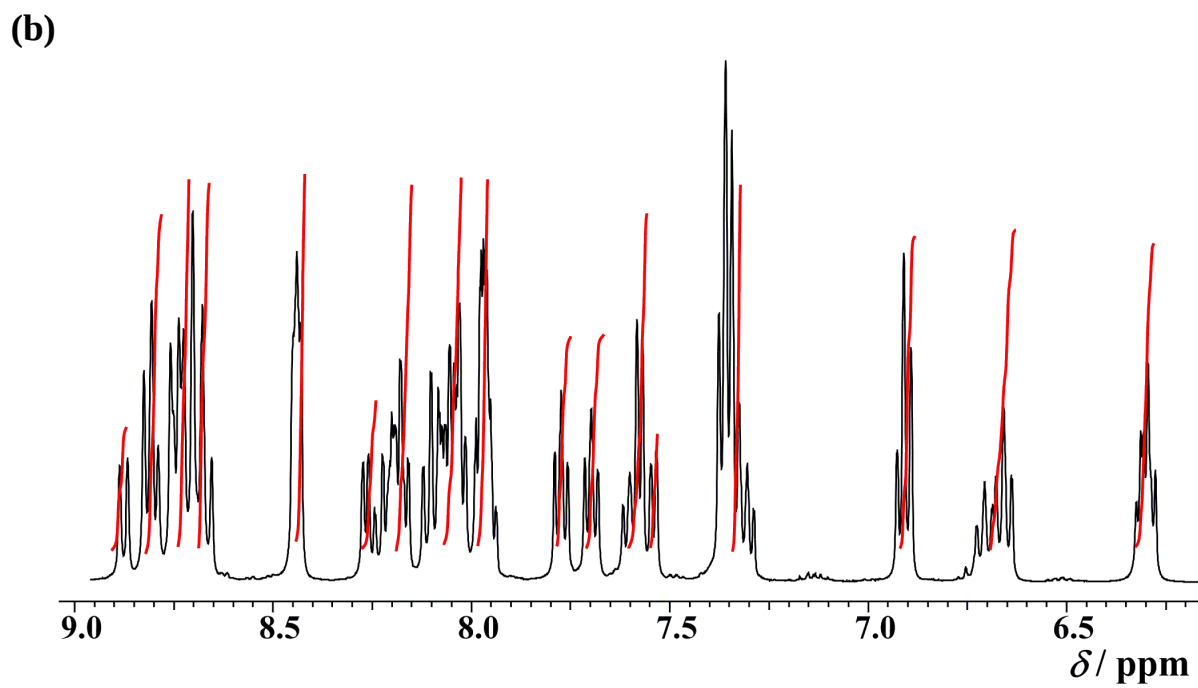
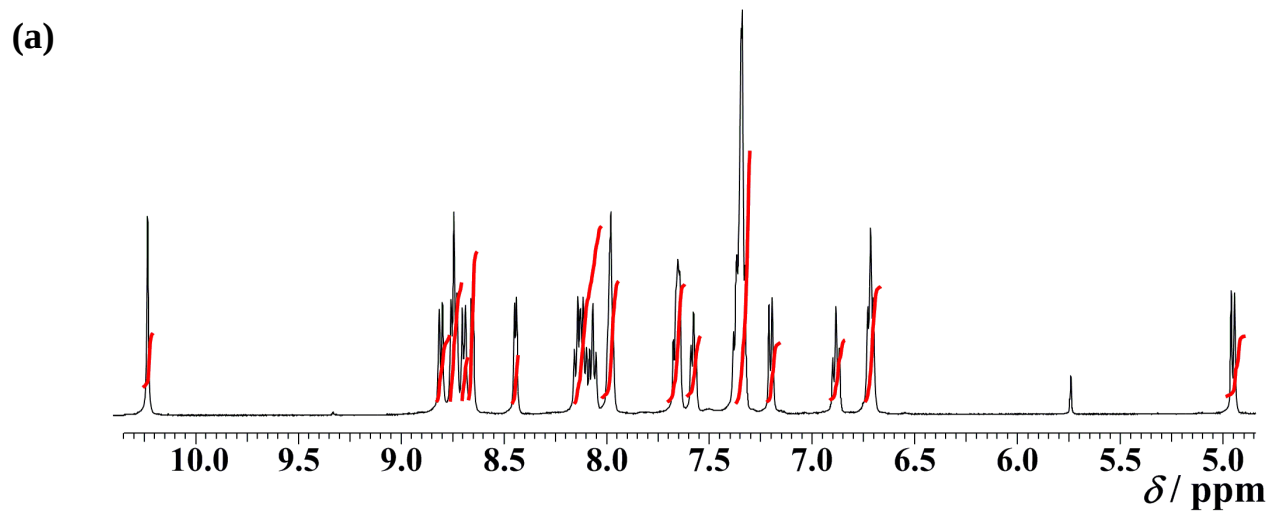


Fig. S2 ^1H NMR spectra of (a) $[1]\text{ClO}_4$ and (b) $\text{rac-[2](ClO}_4)_2$ in $(\text{CD}_3)_2\text{SO}$.

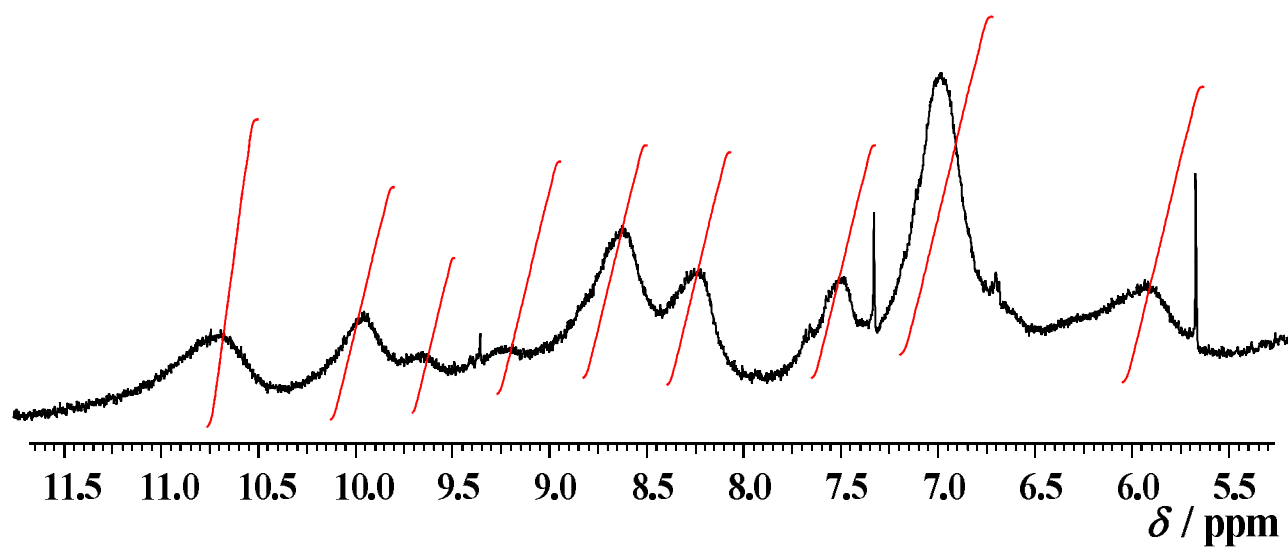


Fig. S3 ^1H NMR spectrum of *meso*-[2](ClO₄)₃ in (CD₃)₂SO.

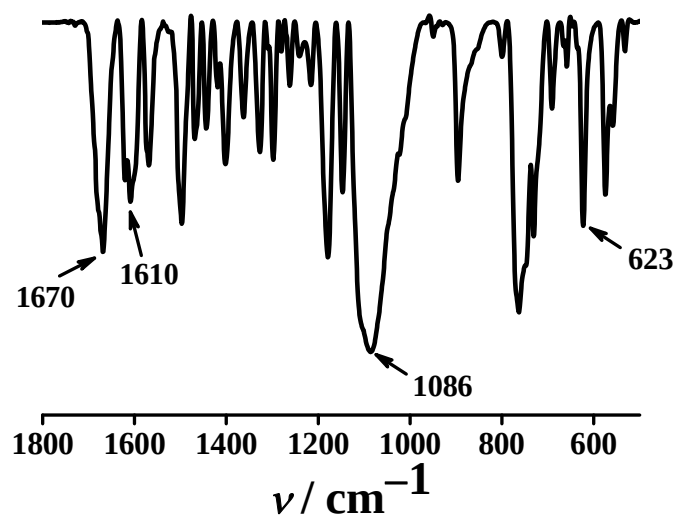


Fig. S4 IR spectrum of [1] ClO_4 on KBr disk (region: 500 to 1800 cm^{-1}).

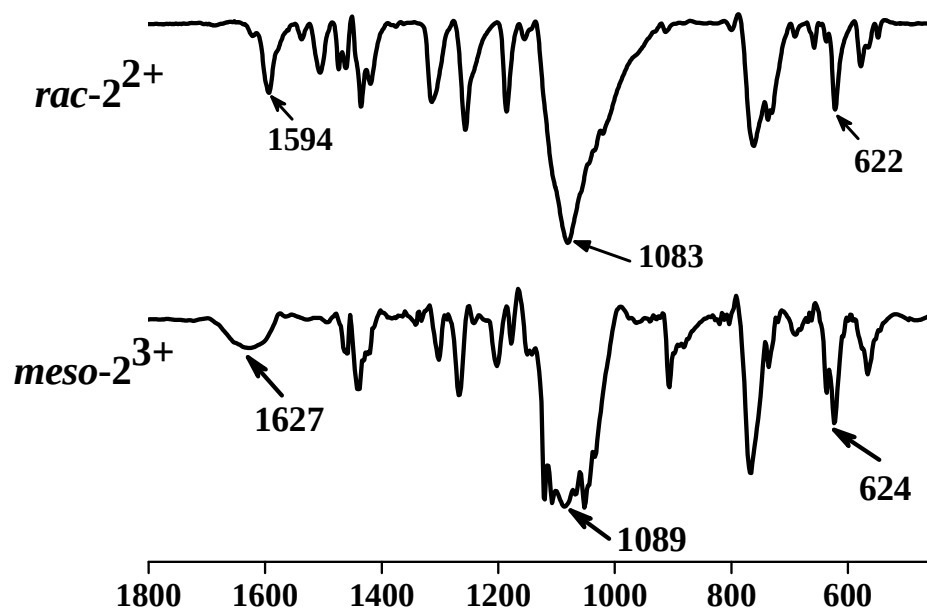


Fig. S5 IR spectra of *meso*-[2](ClO₄)₃ and *rac*-[2](ClO₄)₂ on KBr disk (region: 500 to 1800 cm⁻¹).

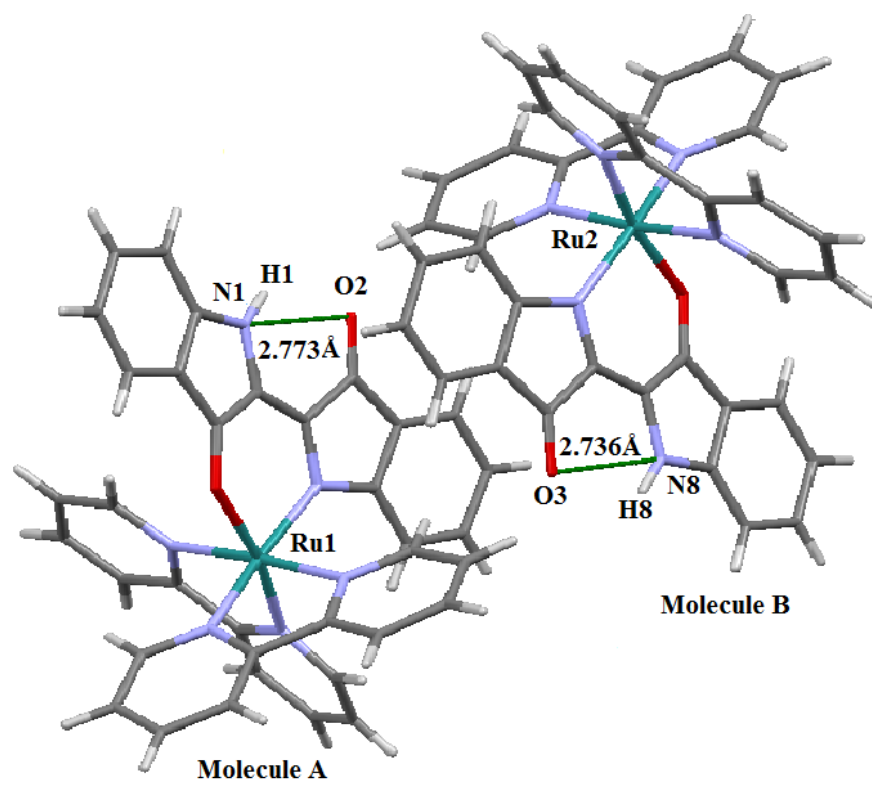


Fig. S6 Perspective view of hydrogen bonding interactions in crystalline $[1]\text{ClO}_4 \cdot 0.5\text{C}_7\text{H}_8$.

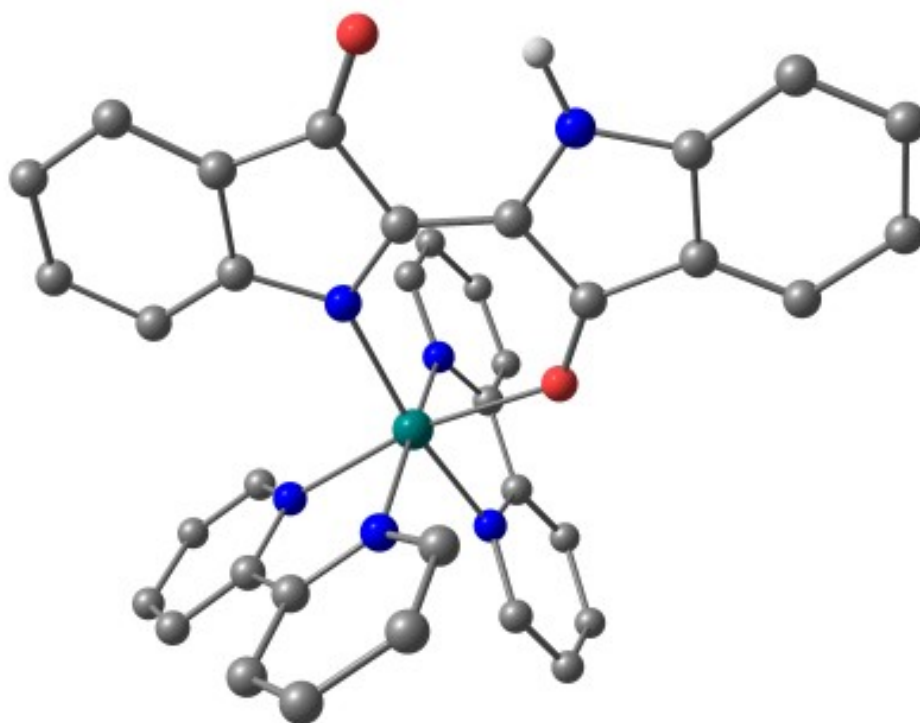
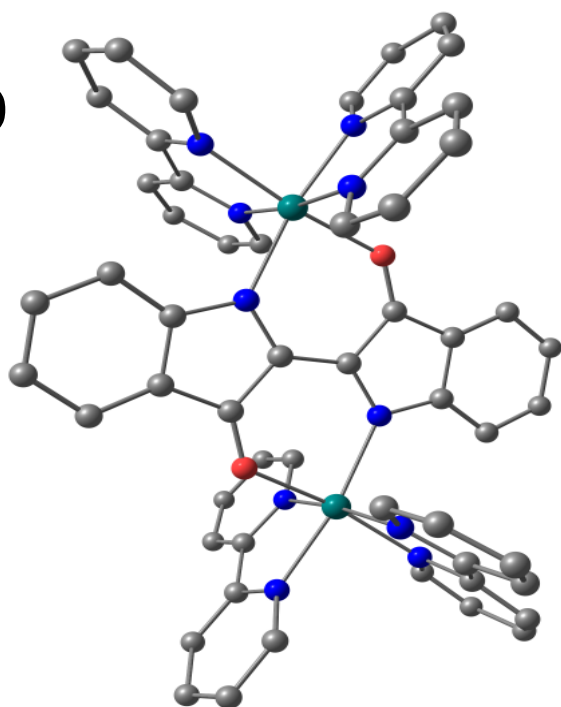


Fig. S7 DFT (B3LYP/LANL2DZ/6-31G*) optimised structure of **1⁺** ($S = 0$) (Molecule A).

(a)



(b)

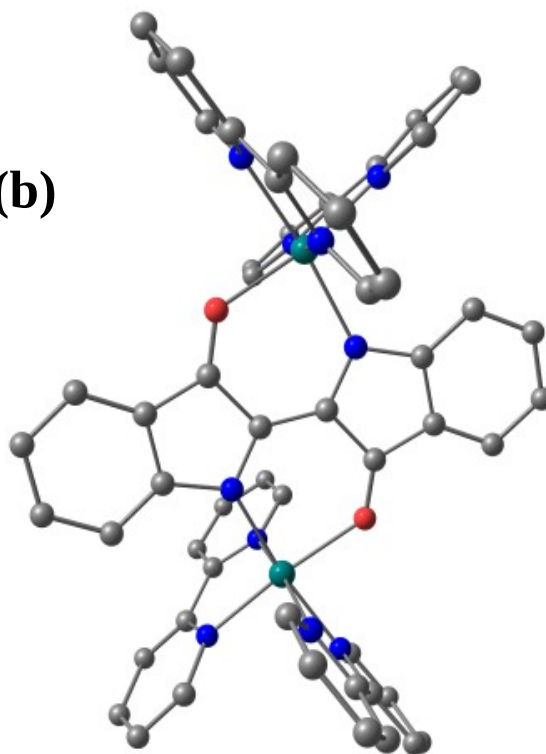
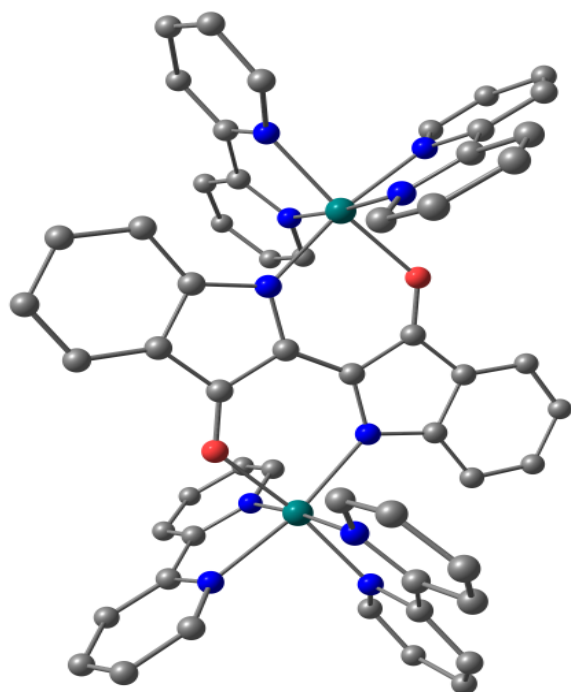


Fig. S8 DFT (UB3LYP/LANL2DZ/6-31G*) optimised structures of (a) *meso*-**2**³⁺ (*S*=1/2) and (b) *rac*-**2**³⁺ (*S* =1/2).

(a)



(b)

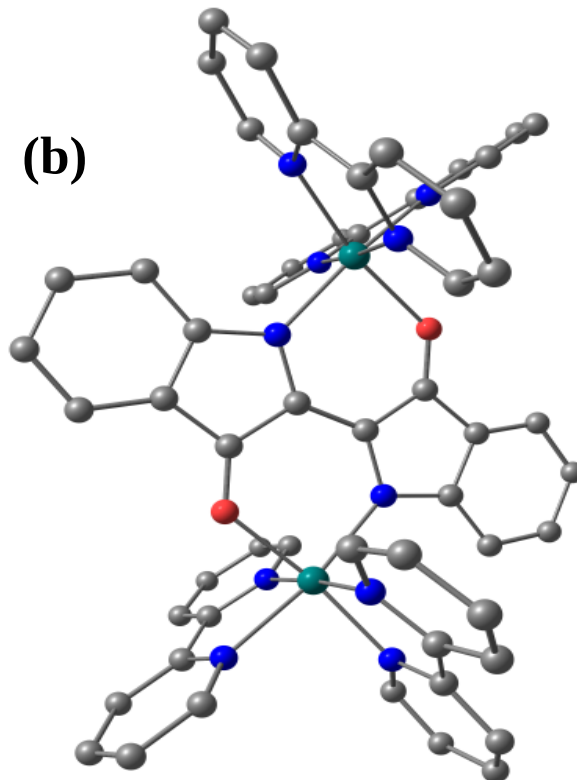


Fig. S9 DFT (UB3LYP/LANL2DZ/6-31G*) optimised structures of (a) *meso*- 2^{2+} ($S=0$) and (b) *rac*- 2^{2+} ($S=0$).

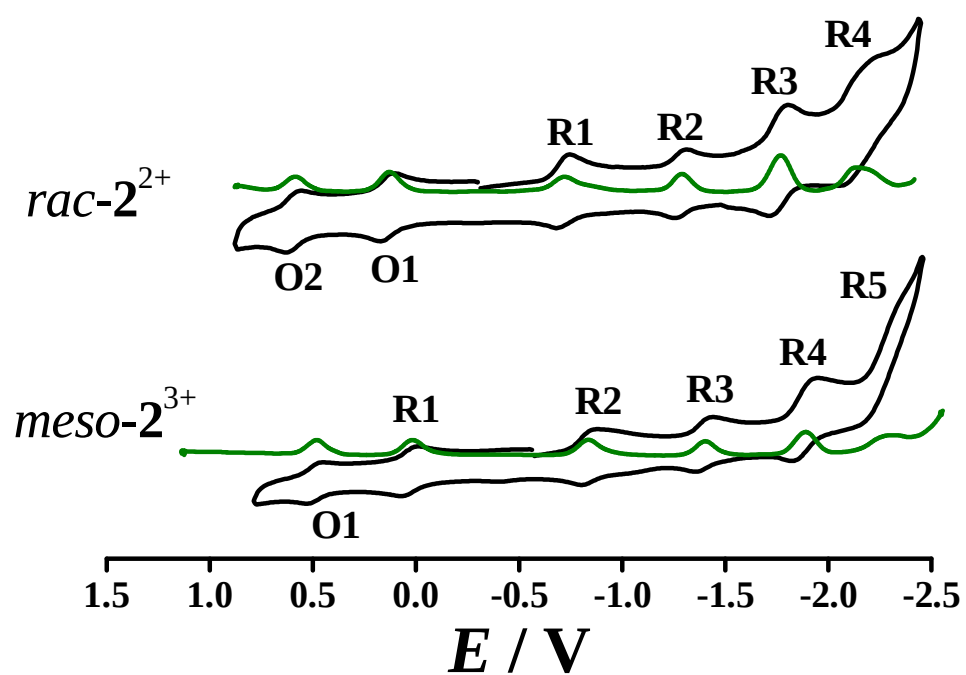


Fig. S10 Cyclic (black) and differential pulse (green) voltammograms in CH_3CN for $rac-[2](ClO_4)_2$ and $meso-[2](ClO_4)_3$ at 298 K.

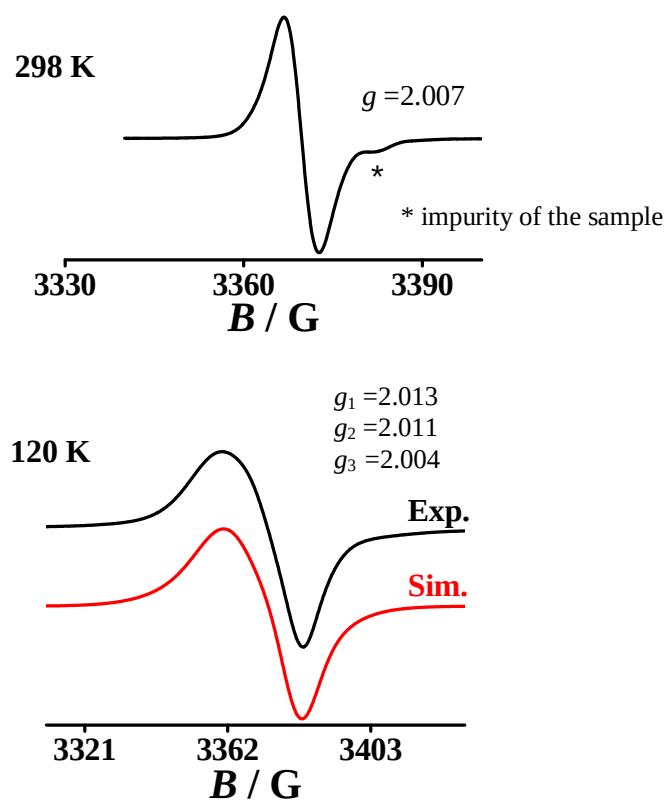


Fig. S11 EPR spectra of *rac*-[2](ClO₄)₂ after in situ reduction at 298 K and 120 K in CH₃CN/ 0.1 M Bu₄NPF₆.

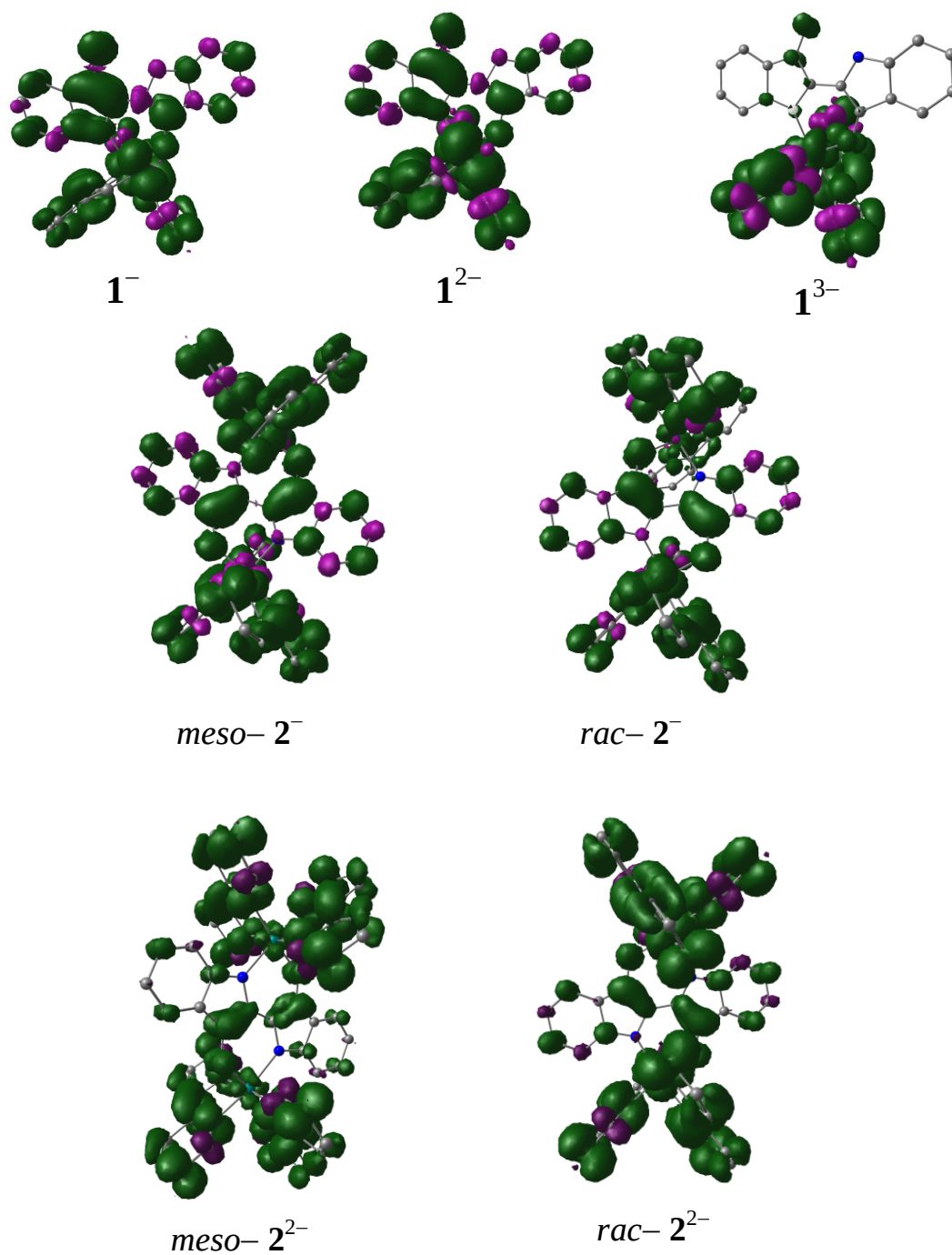


Fig. S12 DFT calculated Mulliken spin density plots for 1^n , *rac*- 2^n and *meso*- 2^n .

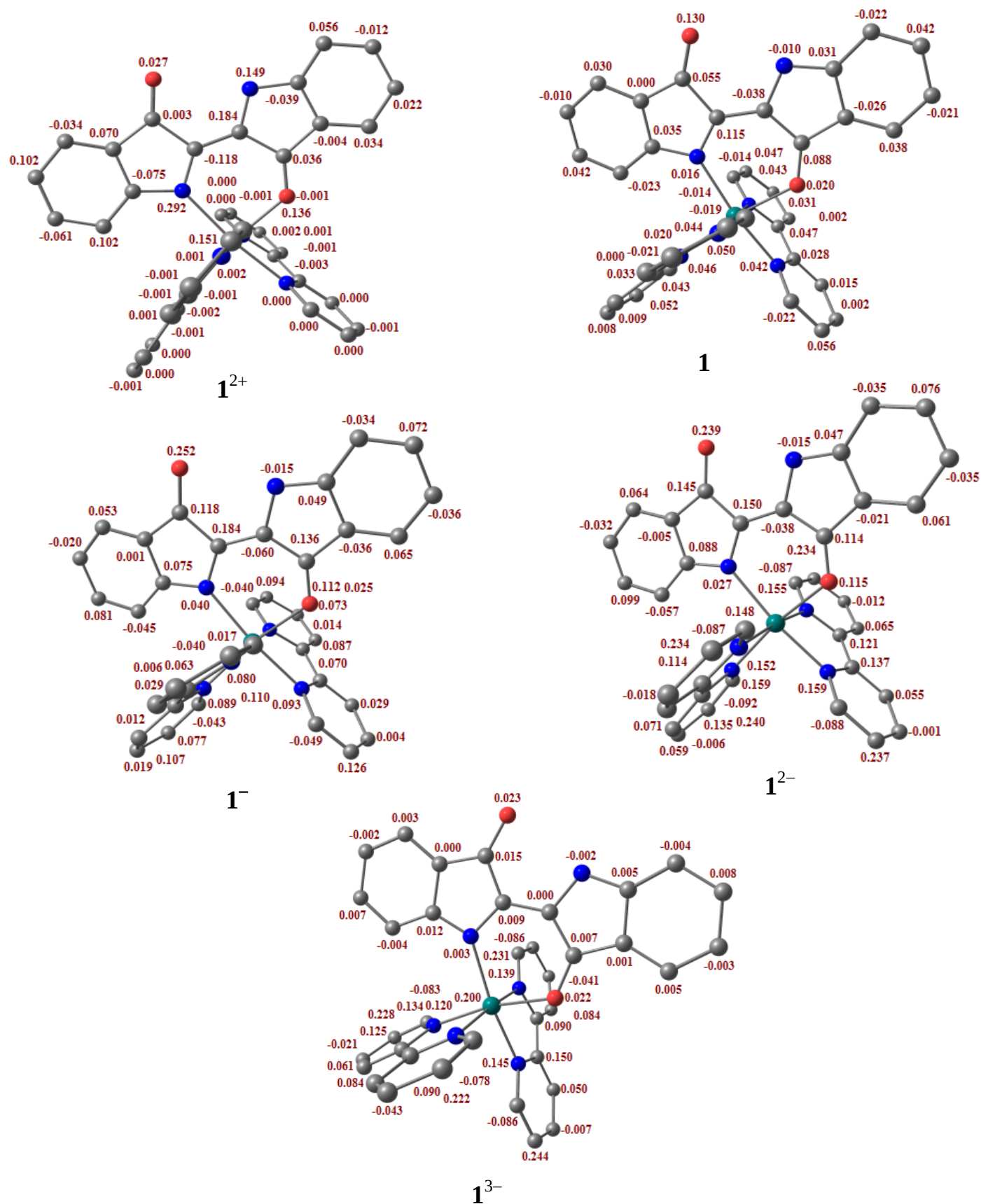


Fig. S13 DFT calculated Mulliken spin density values on each atoms of 1^n ($n = 2, 0, -, 2-, 3-$).

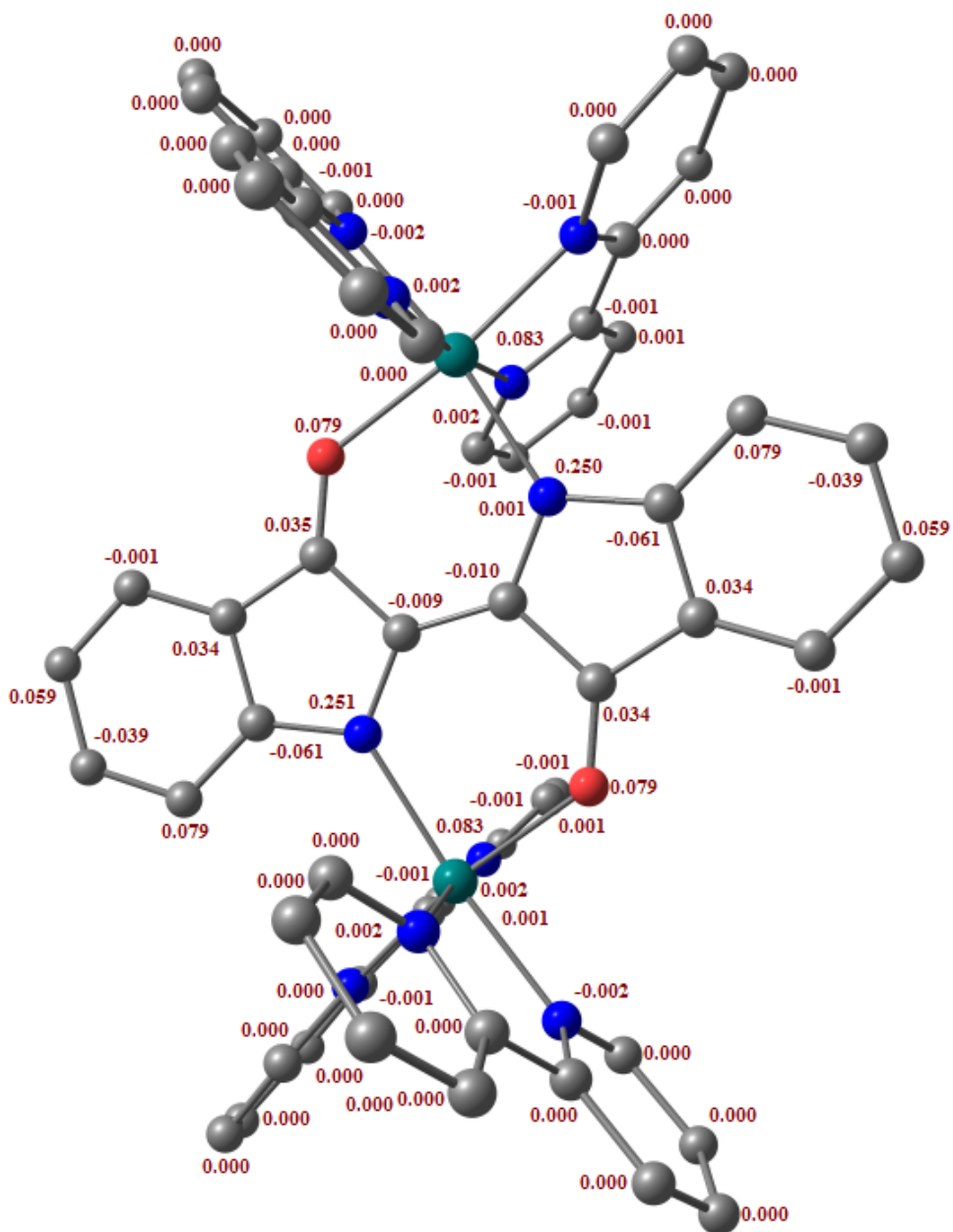


Fig. S14 DFT calculated Mulliken spin density values on each atoms of *rac*-2³⁺ ($S = 1/2$).

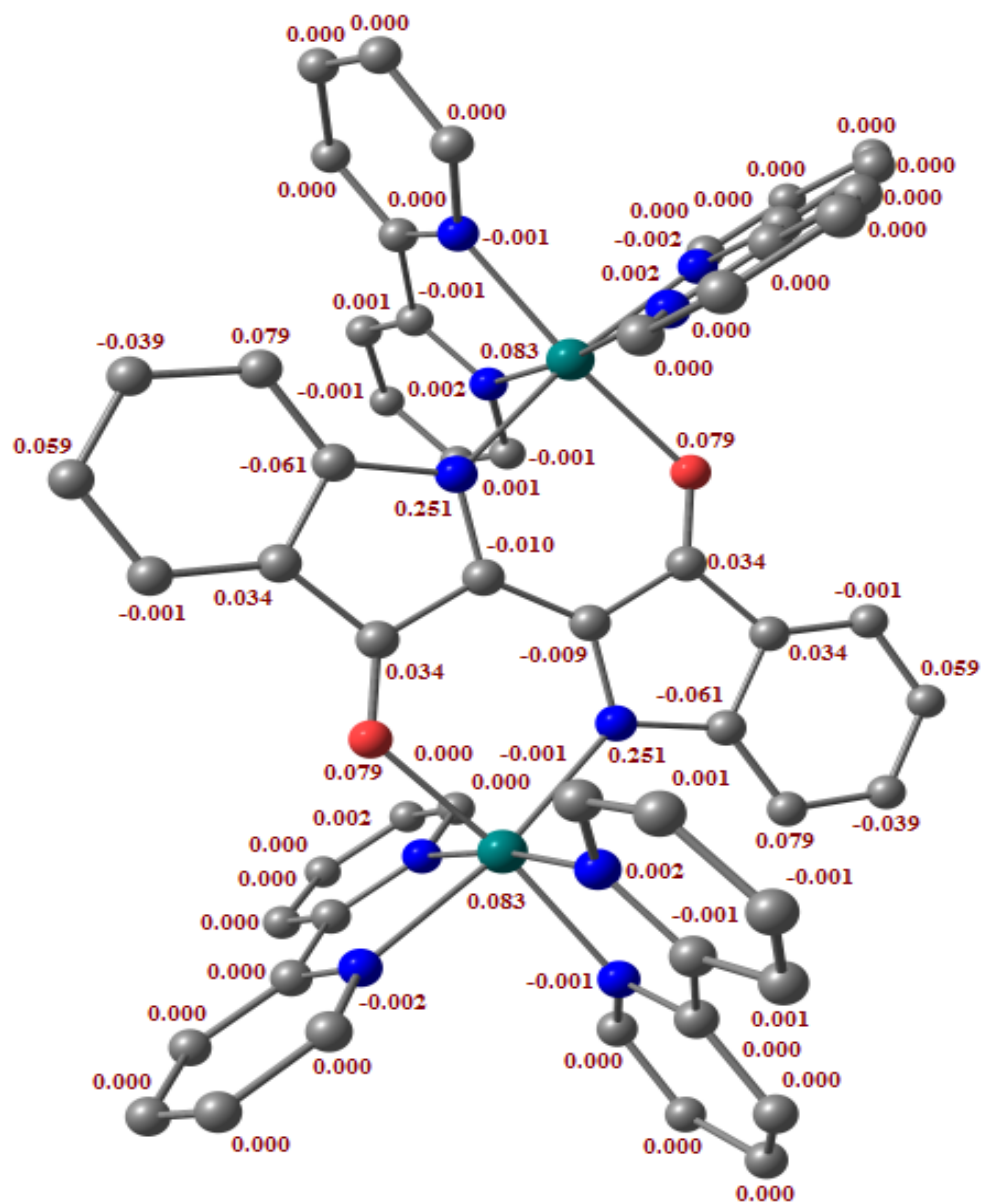


Fig. S15 DFT calculated Mulliken spin density value on each atoms of *meso*-2³⁺ ($S = 1/2$).

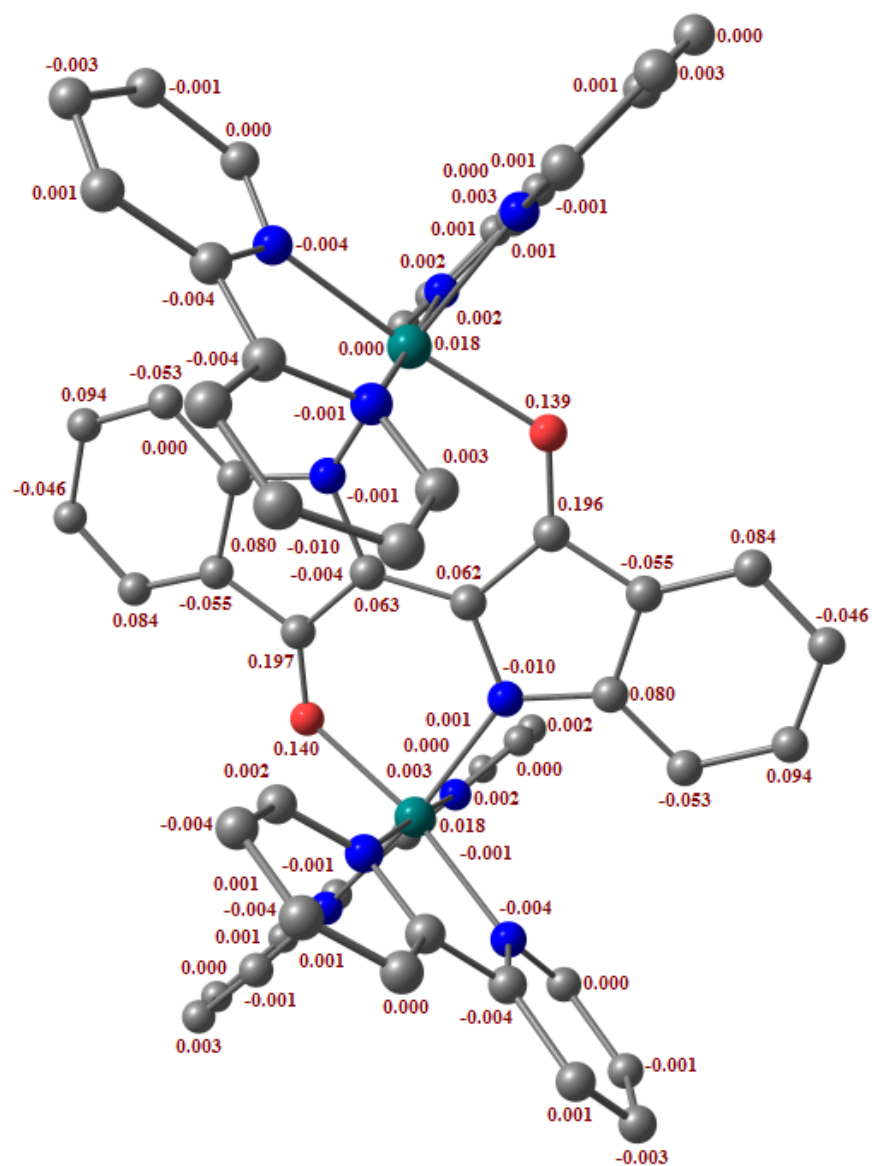


Fig. S16 DFT calculated Mulliken spin density value on each atoms of $rac\text{-}2^+$ ($S = 1/2$).

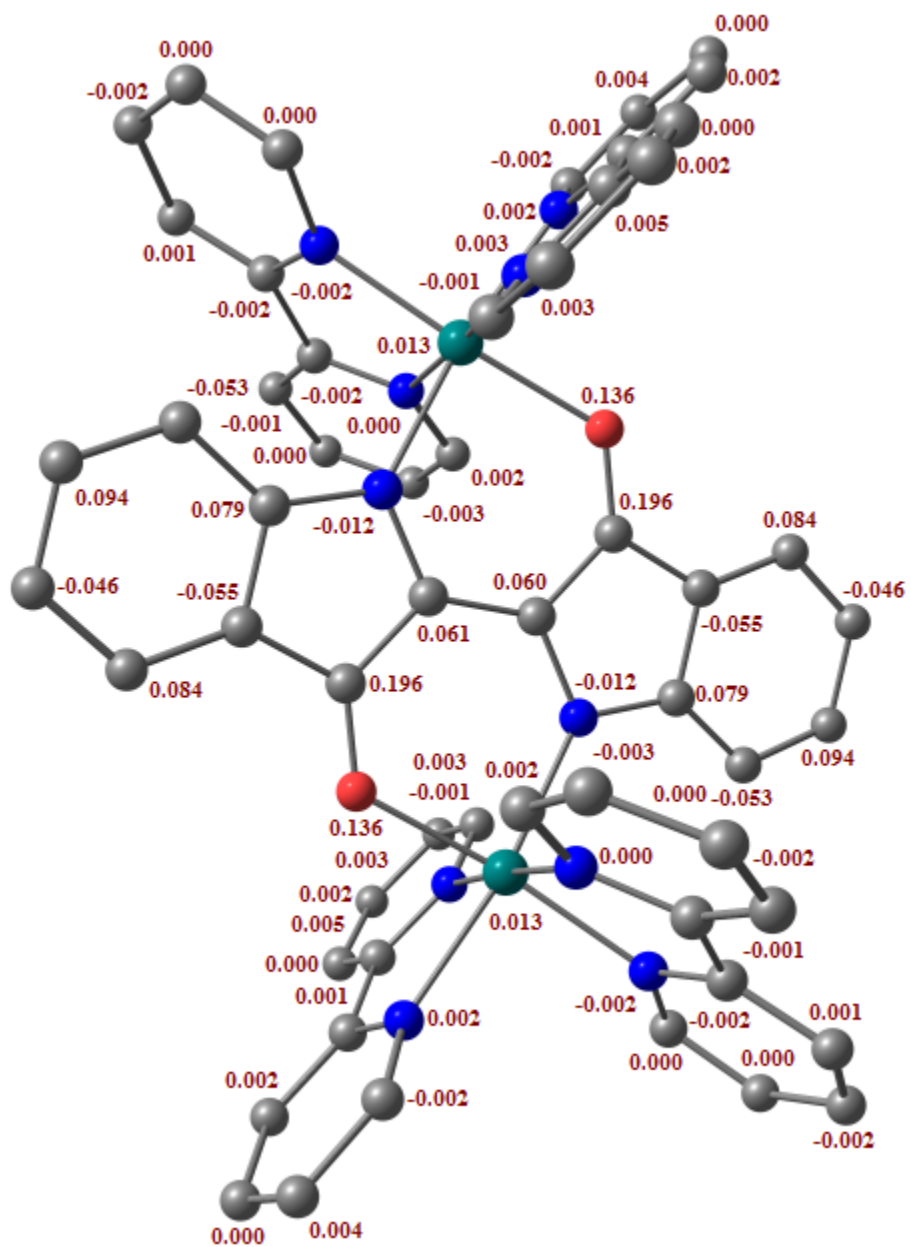


Fig. S17 DFT calculated Mulliken spin density value on each atoms of *meso*-2⁺ ($S = 1/2$).

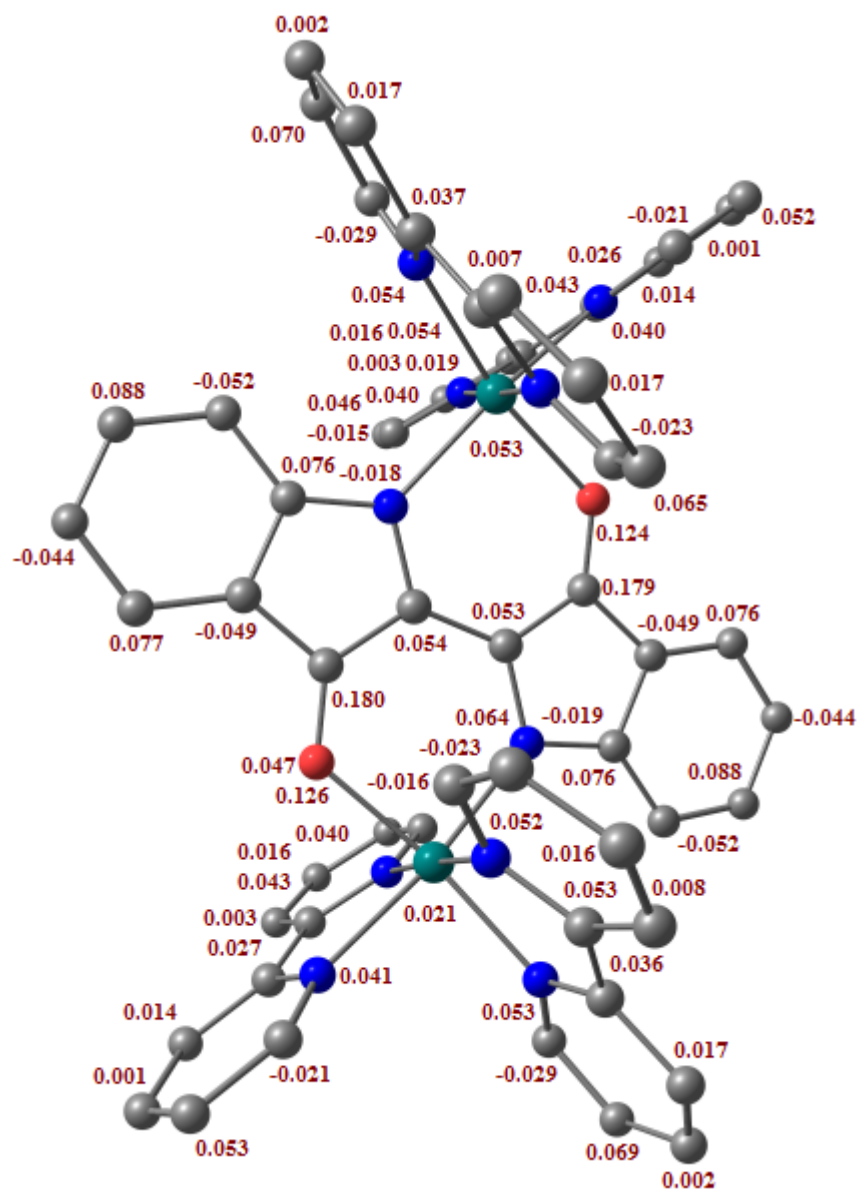


Fig. S18 DFT calculated Mulliken spin density value on each atoms of *rac-2* ($S = 1$).

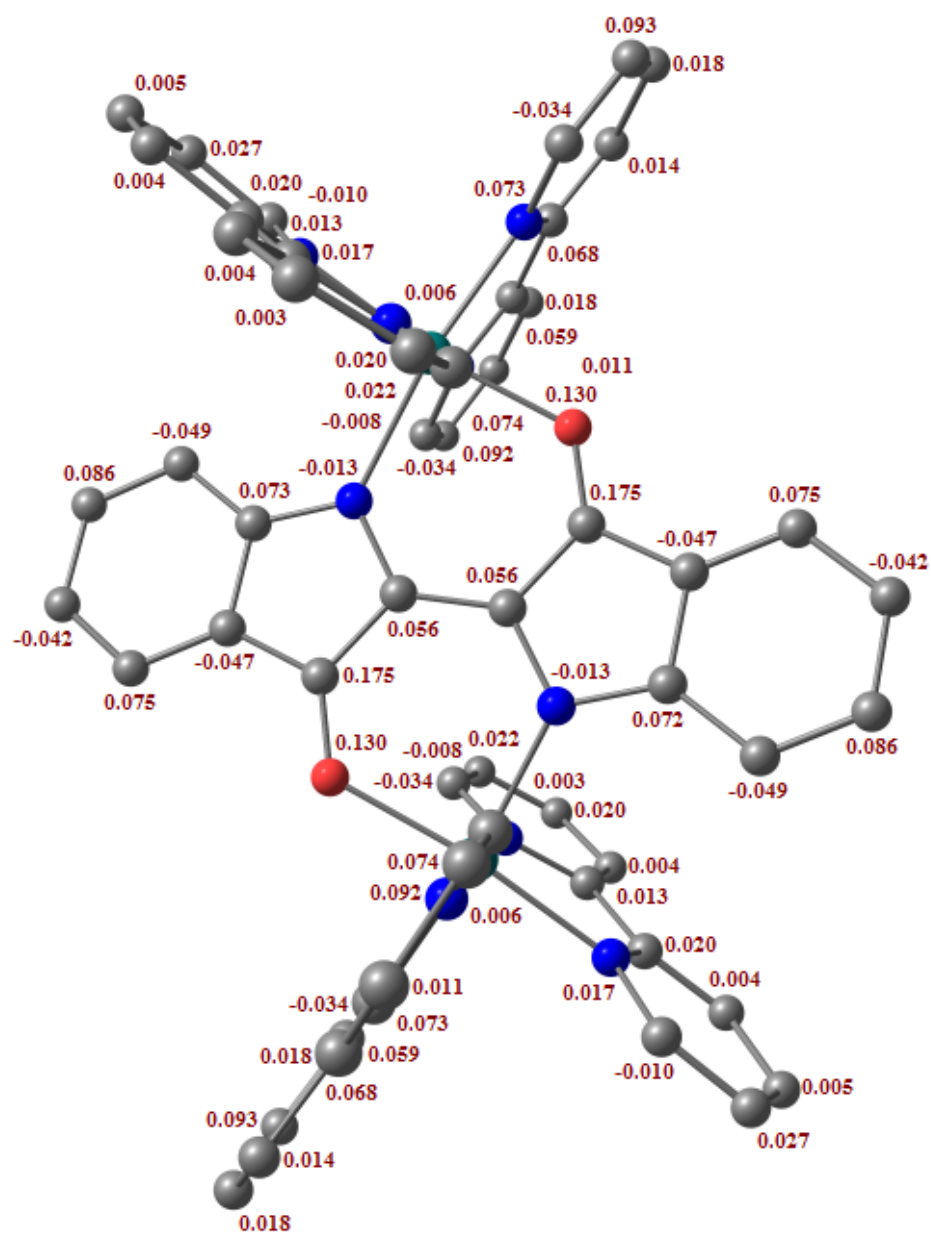


Fig. S19 DFT calculated Mulliken spin density value on each atoms of *meso*-2 ($S = 1$).

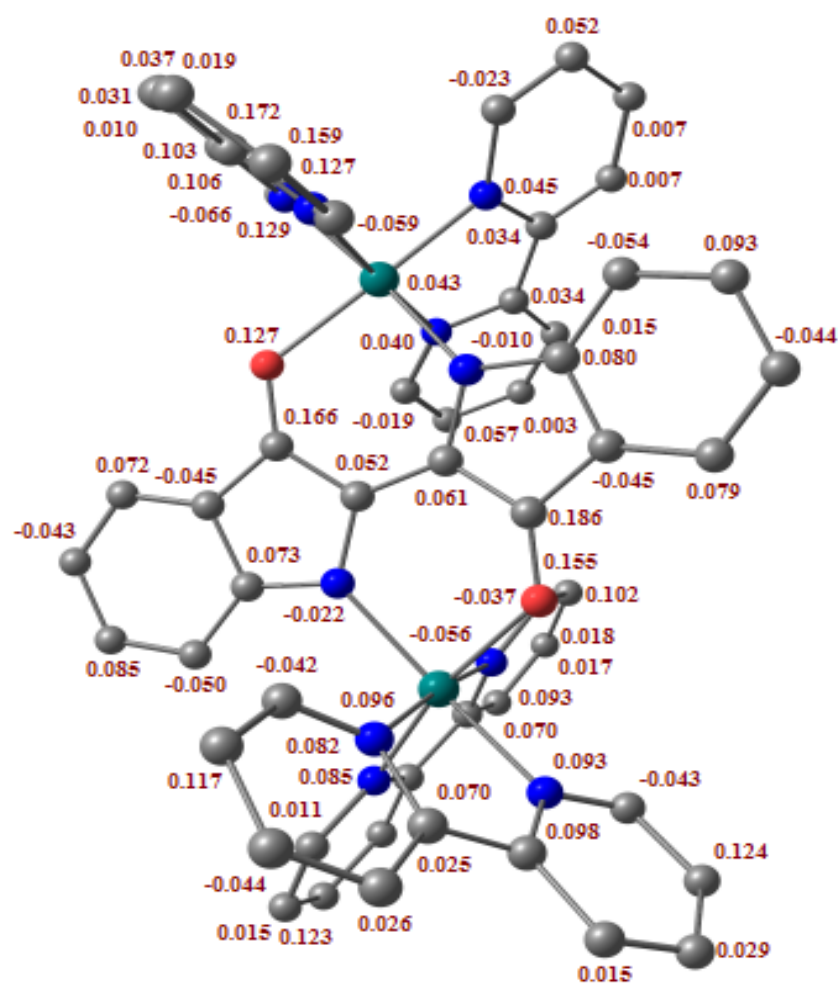


Fig. S20 DFT calculated Mulliken spin density value on each atoms of *rac*-2⁻ ($S = 3/2$).

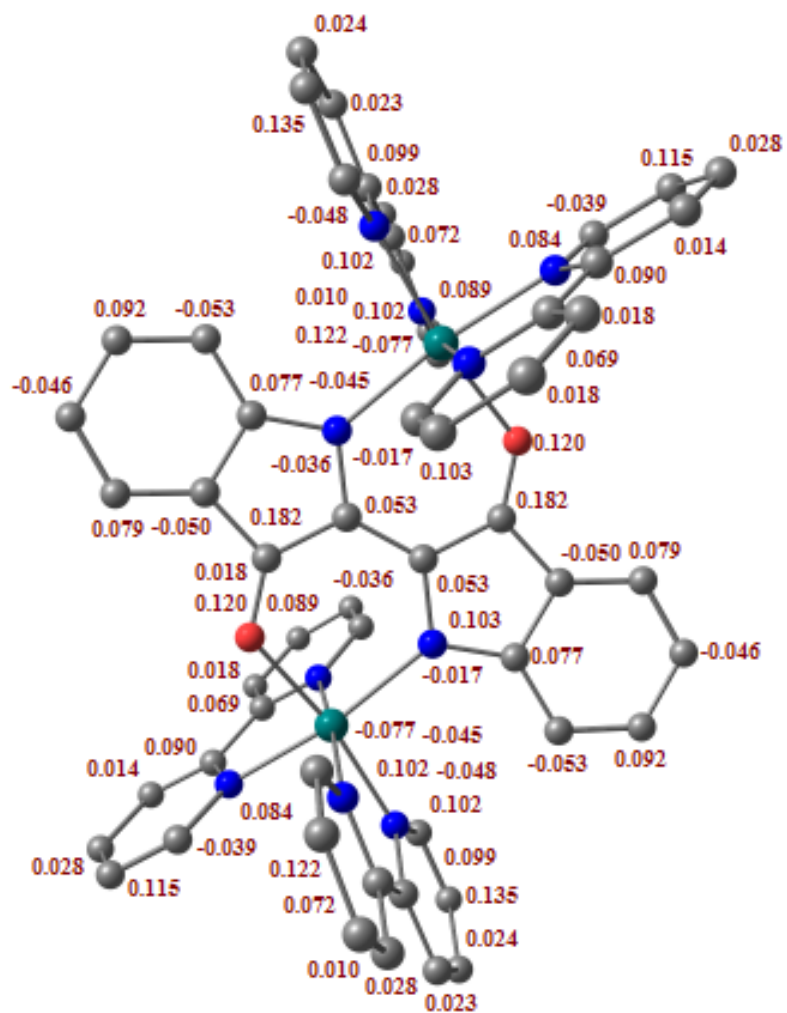


Fig. S21 DFT calculated Mulliken spin density value on each atoms of *meso*-2⁻ ($S = 3/2$).

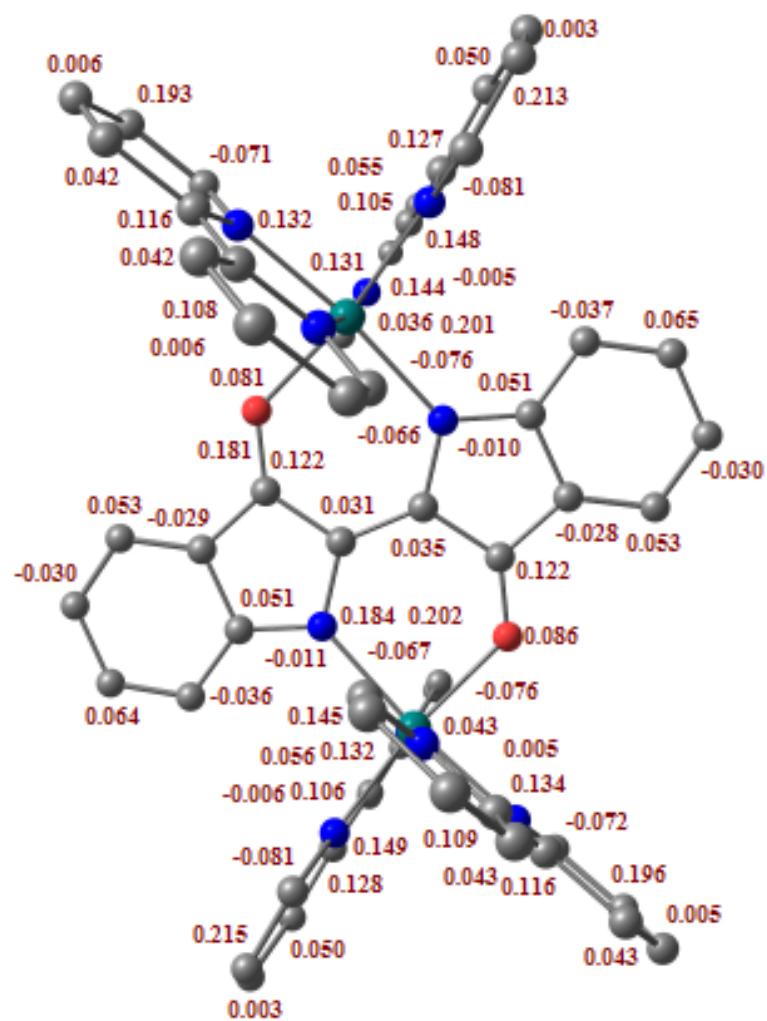


Fig. S22 DFT calculated Mulliken spin density value on each atoms of *rac*-2²⁻ (*S* = 2).

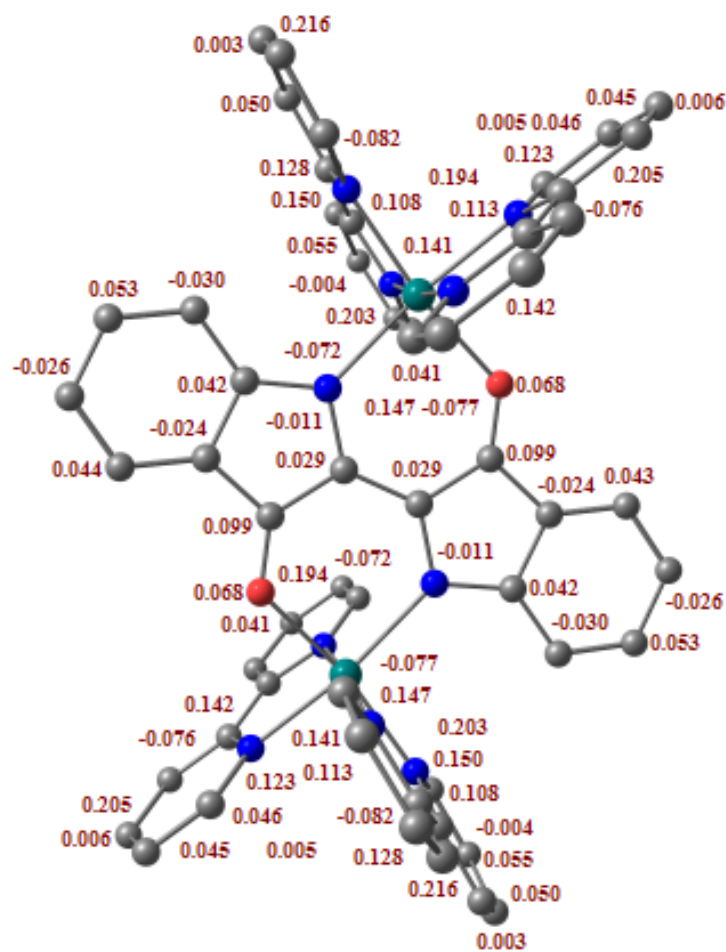


Fig. S23 DFT calculated Mulliken spin density value on each atoms of *meso*-2²⁻ (*S* = 2).

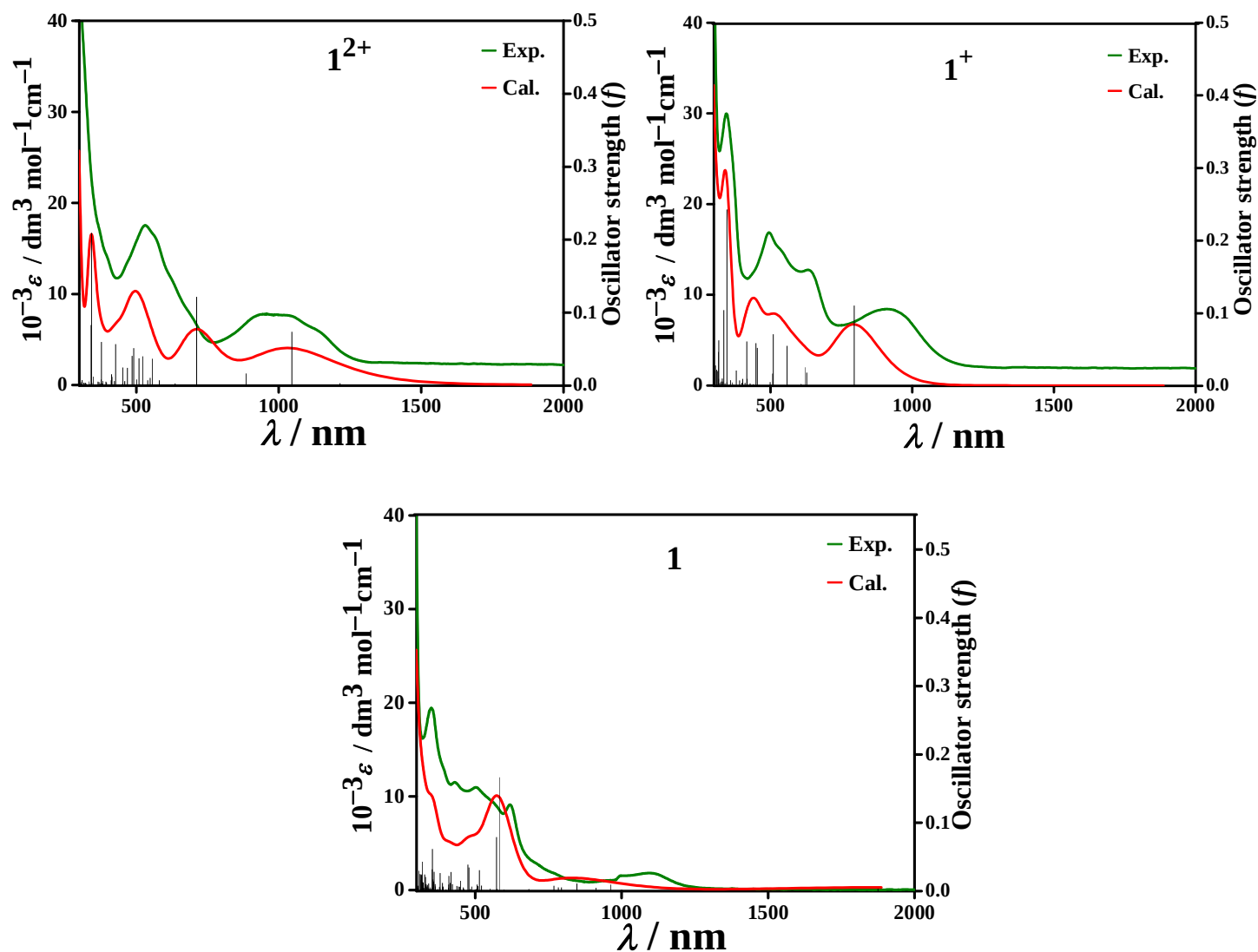


Fig. S24 Experimental (CH_3CN) and TD-DFT ((U)B3LYP/CPCM/ CH_3CN) calculated spectra of 1^n (Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of 3000 cm^{-1}).

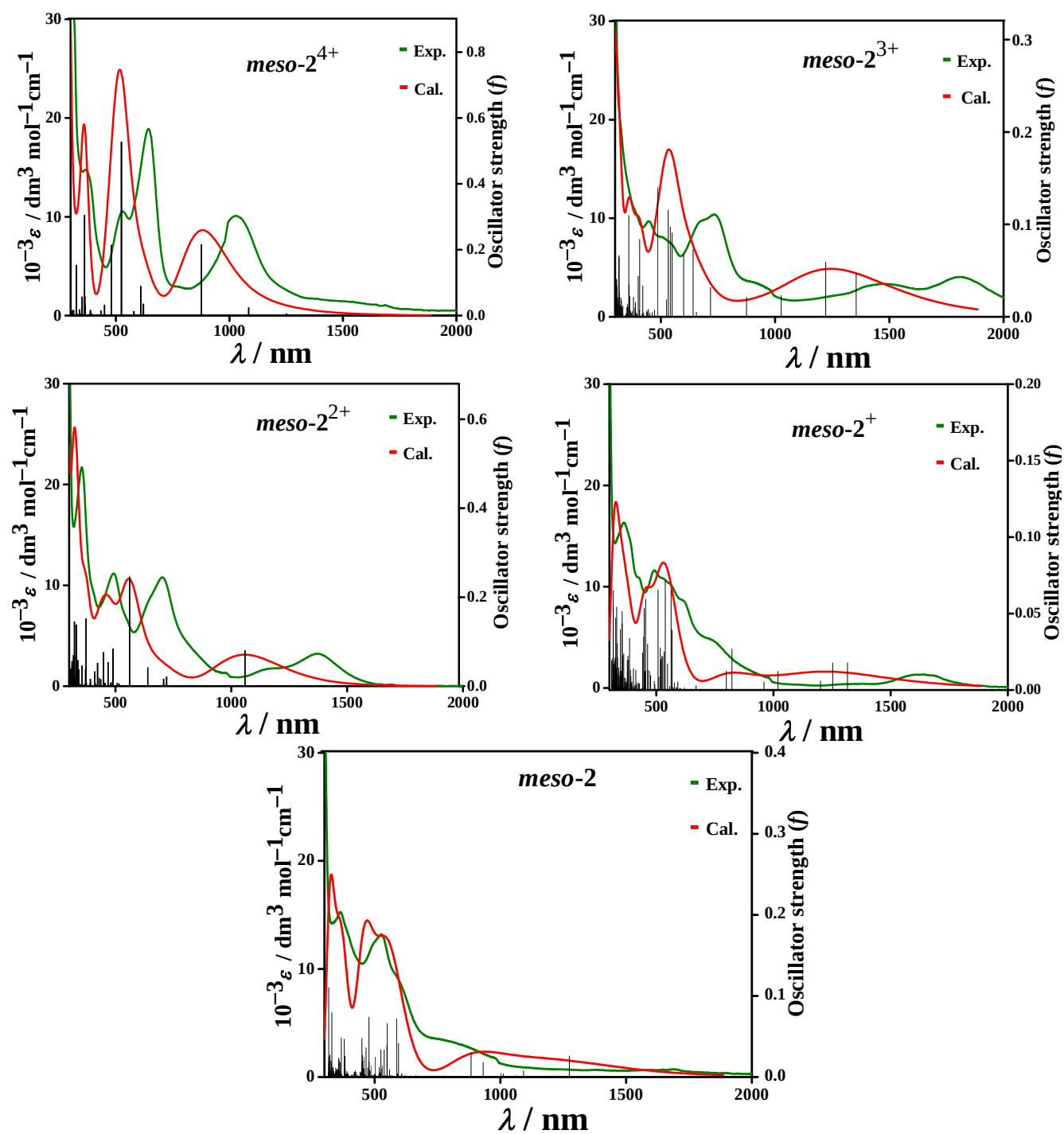


Fig. S25 Experimental (CH₃CN) and TD-DFT ((U)B3LYP/CPCM/CH₃CN) calculated spectra of *meso-2ⁿ* (Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of 3000 cm⁻¹)

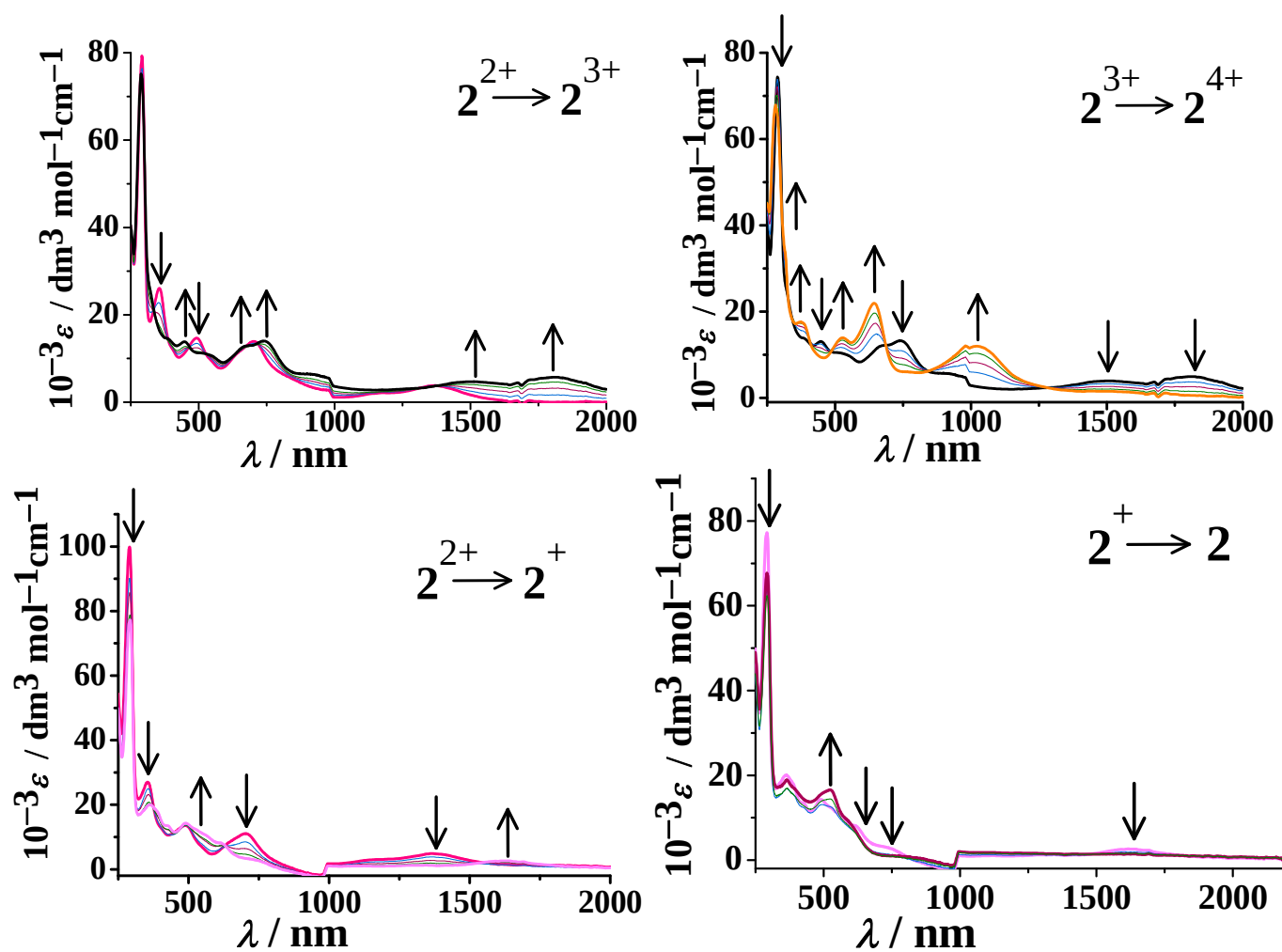


Fig. S26 UV-vis-NIR spectroelectrochemistry of *rac*- 2^n ($n = +4, +3, +2, +, 0$) in CH_3CN / 0.1 M Bu_4NPF_6 .