Electronic Supplementary Information

Non-innocence and mixed valency in tri- and tetranuclear ruthenium complexes of a heteroquinone bridging ligand

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Table S1 Selected experimental and DFT calculated bond angles (deg) for **1** and **2**

1 (Molecule A)			**1** (Molecule B)		**2**•2CH_3CN		
bond angle	X-ray	DFT (*S*=0)	bond angle	X-ray	bond angle	X-ray	DFT (*S*=0)
N1-Ru1-O1	81.5(5)	79.382	N5-Ru4-O15	80.3(5)	N1-Ru1-O1	81.74(11)	79.474
N1-Ru1-O3	82.8(5)	90.008	N5-Ru4-O17	170.6(5)	N1-Ru1-O2	174.44(11)	174.173
N1-Ru1-O4	100.5(5)	101.387	N5-Ru4-O18	96.7(5)	N1-Ru1-O3	87.96(11)	85.695
N1-Ru1-O5	170.9(5)	172.164	N5-Ru4-O19	103.9(6)	N1-Ru1-O4	100.56(11)	101.385
N1-Ru1-O6	94.7(5)	91.597	N5-Ru4-O20	84.2(5)	N1-Ru1-O5	90.42(11)	94.873
O1-Ru1-O3	85.7(5)	85.602	O15-Ru4-O17	94.4(5)	O1-Ru1-O2	92.78(10)	95.168
O1-Ru1-O4	177.0(4)	176.795	O15-Ru4-O18	92.1(5)	O1-Ru1-O3	86.90(10)	89.128
O1-Ru1-O5	91.8(5)	93.064	O15-Ru4-O19	175.7(5)	O1-Ru1-O4	174.39(10)	177.251
O1-Ru1-O6	93.4(5)	95.316	O15-Ru4-O20	86.8(6)	O1-Ru1-O5	93.64(10)	92.048
O3-Ru1-O4	92.4(5)	91.279	O17-Ru4-O18	91.2(5)	O2-Ru1-O3	92.69(11)	91.975
O3-Ru1-O5	90.6(5)	87.314	O17-Ru4-O19	81.4(5)	O2-Ru1-O4	84.99(11)	83.863
O3-Ru1-O6	177.4(5)	178.274	O17-Ru4-O20	87.8(5)	O2-Ru1-O5	88.99(11)	87.561
O4-Ru1-O5	86.0(5)	86.043	O18-Ru4-O19	87.2(5)	O3-Ru1-O4	88.06(11)	88.336
O4-Ru1-O6	88.6(5)	87.783	O18-Ru4-O20	178.5(6)	O3-Ru1-O5	178.21(11)	178.770
O5-Ru1-O6	91.8(5)	91.175	O19-Ru4-O20	93.7(6)	O4-Ru1-O5	91.47(11)	90.482
N2-Ru2-O2	82.7(6)	79.343	N6-Ru5-O16	81.3(5)	N2-Ru2-O1$^{/}$	81.76(11)	79.401
N2-Ru2-O7	93.5(5)	95.199	N6-Ru5-O25	95.1(5)	N2-Ru2-O6	175.22(11)	173.969
N2-Ru2-O8	99.3(6)	100.250	N6-Ru5-O26	99.8(6)	N2-Ru2-O7	87.33(11)	85.570
N2-Ru2-O9	173.5(6)	85.022	N6-Ru5-O27	172.7(6)	N2-Ru2-O8	98.22(11)	101.344
N2-Ru2-O10	85.4(5)	174.369	N6-Ru5-O28	85.0(6)	N2-Ru2-O9	92.14(11)	95.060
O2-Ru2-O7	92.7(5)	93.113	O16-Ru5-O25	93.0(5)	O1$^{/}$-Ru2-O6	93.49(10)	95.091
O2-Ru2-8	174.2(5)	176.097	O16-Ru5-O26	173.9(5)	O1$^{/}$-Ru2-O7	86.17(10)	89.414
O2-Ru2-O9	90.9(5)	87.995	O16-Ru5-O27	91.4(5)	O1$^{/}$-Ru2-O8	174.09(9)	177.274
O2-Ru2-O10	88.7(6)	95.823	O16-Ru5-O28	88.3(5)	O1$^{/}$-Ru2-O9	93.60(10)	92.027
O7-Ru2-O8	92.6(6)	90.789	O25-Ru5-O26	92.8(5)	O6-Ru2-O7	92.93(10)	91.960
O7-Ru2-O9	88.2(6)	178.891	O25-Ru5-O27	85.7(5)	O6-Ru2-O8	86.57(10)	84.045

O7-Ru2-O10	178.1(6)	87.905	O25-Ru5-O28	178.6(6)	O6-Ru2-O9	87.58(10)	87.542
O8-Ru2-O9	86.9(6)	88.103	O26-Ru5-O27	87.4(6)	O7-Ru2-O8	87.93(10)	88.034
O8-Ru2-O10	86.1(6)	84.374	O26-Ru5-O28	85.8(5)	O7-Ru2-O9	179.45(11)	178.512
O9-Ru2-O10	93.1(6)	91.964	O27-Ru5-O28	94.3(6)	O8-Ru2-O9	92.31(10)	90.519
N3-Ru3-O2	81.8(6)	79.280	N7-Ru6-O16	81.4(5)	-	-	-
N3-Ru3-O11	85.8(5)	86.643	N7-Ru6-O21	85.1(6)	-	-	-
N3-Ru3-O12	175.0(6)	173.953	N7-Ru6-O22	174.8(6)	-	-	-
N3-Ru3-O13	98.4(6)	93.670	N7-Ru6-O23	101.8(5)	-	-	-
N3-Ru3-O14	95.1(5)	102.212	N7-Ru6-O24	94.1(5)	-	-	-
O2-Ru3-O11	86.2(5)	90.362	O16-Ru6-O21	87.3(5)	-	-	-
O2-Ru3O12	93.2(5)	94.862	O16-Ru6-O22	93.5(5)	-	-	-
O2-Ru3-O13	171.4(5)	91.025	O16-Ru6-O23	173.0(5)	-	-	-
O2-Ru3-O14	96.0(5)	177.957	O16-Ru6-O24	94.1(5)	-	-	-
O11-Ru3-O12	94.3(6)	91.934	O21-Ru6-O22	94.4(6)	-	-	-
O11-Ru3-O13	85.2(5)	178.612	O21-Ru6-O23	86.7(5)	-	-	-
O11-Ru3-O14	177.7(5)	88.341	O21-Ru6-O24	178.3(6)	-	-	-
O12-Ru3-O13	86.6(5)	87.892	O22-Ru6-O23	83.3(5)	-	-	-
O12-Ru3-O14	84.9(6)	83.608	O22-Ru6-O24	86.4(5)	-	-	-
O13-Ru3-O14	92.5(5)	90.271	O23-Ru6-O24	91.9(5)	-	-	-

Table S2 Selected DFT calculated bond lengths (Å) for $\mathbf{1}^n$ (Molecule A)

Bond length		DFT					
	$\mathbf{1}^{2+}$ (S=1)	$\mathbf{1}^{+}$ (S=1/2)	**1** (S=0)	**1** (S=1)	$\mathbf{1}^{-}$ (S=1/2)	$\mathbf{1}^{2-}$ (S=1)	$\mathbf{1}^{3-}$ (S=1/2)
Ru1-O1	2.076	2.030	2.054	1.999	2.060	2.058	2.072
Ru1-N1	2.153	2.147	2.057	2.136	2.077	2.109	2.120
Ru1-O3	2.027	2.041	2.060	2.066	2.071	2.101	2.131
Ru1-O4	2.021	2.047	2.064	2.076	2.087	2.085	2.087
Ru1-O5	2.010	2.036	2.069	2.063	2.082	2.117	2.090
Ru1-O6	2.018	2.023	2.067	2.040	2.077	2.084	2.120
Ru2-O2	2.166	2.091	2.113	2.156	2.119	2.136	2.158
Ru2-N2	2.163	2.157	2.095	2.076	2.108	2.124	2.125
Ru2-O7	2.027	2.047	2.079	2.059	2.083	2.087	2.086
Ru2-O8	2.013	2.029	2.053	2.072	2.084	2.096	2.104
Ru2-O9	2.017	2.025	2.055	2.067	2.070	2.078	2.086
Ru2-O10	2.017	2.046	2.058	2.077	2.078	2.096	2.118
Ru3-O2	2.055	2.080	2.095	2.065	2.112	2.130	2.146
Ru3-N3	2.138	2.162	2.114	2.148	2.114	2.125	2.131
Ru3-O11	2.02	2.026	2.053	2.029	2.070	2.080	2.088
Ru3-O12	2.043	2.053	2.061	2.058	2.080	2.097	2.120
Ru3-O13	2.061	2.053	2.078	2.049	2.083	2.086	2.084
Ru3-O14	2.013	2.029	2.065	2.048	2.091	2.103	2.111
C1-O1	1.257	1.282	1.266	1.290	1.272	1.296	1.295
C1-C2	1.457	1.435	1.442	1.431	1.441	1.425	1.437
C2-N1	1.340	1.347	1.349	1.346	1.349	1.358	1.376
C2-C9	1.426	1.435	1.417	1.432	1.426	1.432	1.409
N1-C3	1.367	1.357	1.383	1.372	1.376	1.377	1.377
C3-C4	1.416	1.423	1.412	1.415	1.416	1.413	1.412
C3-C8	1.451	1.456	1.440	1.443	1.443	1.439	1.448
C4-C5	1.376	1.371	1.382	1.379	1.379	1.385	1.393

C5-C6	1.416	1.42179	1.409	1.411	1.414	1.40574	1.39959
C6-C7	1.378	1.37216	1.382	1.381	1.378	1.38617	1.39355
C7-C8	1.415	1.42314	1.411	1.414	1.418	1.41011	1.41092
C8-N2	1.367	1.35243	1.381	1.380	1.368	1.38328	1.37880
N2-C9	1.349	1.36313	1.346	1.369	1.361	1.34987	1.37531
C9-C10	1.424	1.39818	1.424	1.401	1.410	1.42056	1.42591
C10-O2	1.314	1.35184	1.304	1.340	1.328	1.32236	1.31976
C10-C11	1.423	1.40565	1.424	1.410	1.412	1.41687	1.42621
C11-N3	1.350	1.36108	1.352	1.357	1.365	1.35704	1.37980
C11-C18	1.433	1.44667	1.439	1.449	1.446	1.45245	1.42505
N3-C12	1.365	1.35415	1.374	1.363	1.365	1.37657	1.37942
C12-C13	1.414	1.42226	1.415	1.419	1.420	1.41396	1.40981
C12-C17	1.450	1.45256	1.440	1.444	1.442	1.43754	1.44880
C13-C14	1.380	1.37382	1.379	1.378	1.37737	1.38473	1.39824
C14-C15	1.419	1.42497	1.416	1.419	1.41881	1.41132	1.40062
C15-C16	1.375	1.36922	1.377	1.374	1.37484	1.38173	1.39306
C16-C17	1.420	1.42716	1.418	1.422	1.42160	1.41835	1.41910
C17-N4	1.349	1.34011	1.358	1.352	1.35376	1.36003	1.35843
N4-C18	1.321	1.32968	1.318	1.325	1.32286	1.32937	1.35812
C18-C1	1.464	1.44650	1.471	1.448	1.46238	1.45095	1.45193

Table S3 Selected DFT calculated bond angles (deg) for $\mathbf{1}^n$ (Molecule A)

Bond angle		DFT					
	$\mathbf{1}^{2+}$ (S=1)	$\mathbf{1}^{+}$ (S=1/2)	**1** (S=0)	**1** (S=1)	$\mathbf{1}^{-}$ (S=1/2)	$\mathbf{1}^{2-}$ (S=1)	$\mathbf{1}^{3-}$ (S=1/2)
N1-Ru1-O1	77.882	79.334	79.382	79.330	79.196	79.447	79.144
N1-Ru1-O3	91.779	92.324	90.008	93.030	90.040	90.437	90.600
N1-Ru1-O4	102.618	102.572	101.387	103.686	102.339	103.159	104.017
N1-Ru1-O5	170.282	170.970	172.164	171.002	171.995	171.984	171.841
N1-Ru1-O6	88.697	87.336	91.597	87.455	91.372	90.601	90.570
O1-Ru1-O3	87.187	88.513	85.602	90.339	86.540	88.389	88.729
O1-Ru1-O4	176.506	176.590	176.795	176.878	177.258	177.272	176.773
O1-Ru1-O5	92.454	91.685	93.064	91.676	93.072	92.723	92.838
O1-Ru1-O6	93.106	92.850	95.316	92.214	93.899	91.824	91.398
O3-Ru1-O4	89.340	88.582	91.279	88.700	91.174	90.774	90.576
O3-Ru1-O5	88.723	88.349	87.314	87.241	87.404	87.608	87.686
O3-Ru1-O6	179.485	178.508	178.274	177.447	178.577	178.961	178.826
O4-Ru1-O5	87.091	86.445	86.043	85.311	85.305	84.647	83.984
O4-Ru1-O6	90.365	90.073	87.783	88.750	88.350	88.967	89.233
O5-Ru1-O6	90.841	92.214	91.175	92.672	91.220	91.366	91.142
N2-Ru2-O2	78.699	80.000	79.343	79.949	79.637	78.784	79.070
N2-Ru2-O7	92.695	93.737	95.199	94.839	95.162	95.143	94.809
N2-Ru2-O8	101.302	100.586	100.250	101.694	101.653	102.608	103.080
N2-Ru2-O9	86.467	84.932	85.022	86.384	85.368	85.488	85.967
N2-Ru2-O10	172.597	174.073	174.369	174.426	174.150	173.811	173.819
O2-Ru2-O7	90.057	90.430	93.113	85.917	90.644	90.360	88.763
O2-Ru2-O8	179.941	179.250	176.097	177.316	177.937	177.956	177.846
O2-Ru2-O9	89.302	90.906	87.995	92.778	90.049	89.906	90.955
O2-Ru2-O10	94.434	94.768	95.823	95.755	95.356	95.836	95.478
O7-Ru2-O8	89.884	89.065	90.789	91.814	90.840	91.001	90.928

O7-Ru2-O9	179.032	177.924	178.891	178.026	179.195	179.352	179.108
O7-Ru2-O10	90.049	89.058	87.905	88.357	87.875	87.895	87.933
O8-Ru2-O9	90.757	89.614	88.103	89.453	87.875	88.717	89.323
O8-Ru2-O10	85.568	84.670	84.374	82.734	83.267	82.692	82.380
O9-Ru2-O10	90.724	92.414	91.964	90.302	91.651	91.490	91.252
N3-Ru3-O2	79.080	79.769	79.280	79.811	79.690	78.953	79.384
N3-Ru3-O11	84.340	84.814	86.643	83.529	86.200	86.545	86.491
N3-Ru3-O12	174.197	174.381	173.953	173.066	174.133	173.956	174.003
N3-Ru3-O13	95.385	93.764	93.670	95.541	94.064	93.733	93.934
N3-Ru3-O14	100.064	100.722	102.212	101.089	102.370	103.123	103.085
O2-Ru3-O11	89.462	91.291	90.362	92.421	91.337	91.070	91.293
O2-Ru3-O12	95.838	95.278	94.862	94.816	94.914	95.382	95.124
O2-Ru3-O13	94.175	90.396	91.025	88.363	89.019	88.850	88.140
O2-Ru3-O14	177.044	179.240	177.957	177.435	177.931	177.916	177.400
O11-Ru3-O12	92.868	92.693	91.934	92.381	91.659	91.494	91.260
O11-Ru3-O13	176.236	177.568	178.612	178.657	179.590	179.691	179.217
O11-Ru3-O14	87.635	89.332	88.341	90.070	88.999	89.242	89.684
O12-Ru3-O13	87.733	88.896	87.892	88.640	88.108	88.216	88.254
O12-Ru3-O14	84.870	84.257	83.608	84.466	83.035	82.551	82.444
O13-Ru3-O14	88.719	88.994	90.271	89.158	90.637	90.826	90.861

Table S4 Selected DFT calculated bond lengths (Å) for $\mathbf{2}^n$

Bond length		DFT					
	$\mathbf{2}^{2+}$ (S=1)	$\mathbf{2}^{+}$ (S=1/2)	**2** (S=0)	**2** (S=1)	$\mathbf{2}^{-}$ (S=1/2)	$\mathbf{2}^{2-}$ (S=1)	$\mathbf{2}^{3-}$ (S=1/2)
Ru1-O1	2.118	2.097	2.106	2.076	2.117	2.129	2.139
Ru1-O2	2.033	2.046	2.059	2.051	2.075	2.093	2.109
Ru1-O3	2.020	2.024	2.054	2.026	2.067	2.076	2.084
Ru1-O4	2.017	2.026	2.060	2.047	2.083	2.097	2.122
Ru1-O5	2.036	2.044	2.078	2.043	2.082	2.086	2.086
Ru1-N1	2.172	2.159	2.110	2.148	2.115	2.128	2.134
Ru2-O1′	2.122	2.082	2.106	2.146	2.115	2.128	2.139
Ru2-O6	2.031	2.055	2.054	2.063	2.075	2.092	2.109
Ru2-O7	2.021	2.031	2.059	2.072	2.067	2.077	2.085
Ru2-O8	2.020	2.033	2.060	2.076	2.083	2.097	2.122
Ru2-O9	2.033	2.059	2.078	2.069	2.082	2.086	2.086
Ru2-N2	2.162	2.155	2.110	2.087	2.116	2.129	2.134
C1-O1	1.331	1.345	1.305	1.336	1.319	1.323	1.339
C1-C2	1.411	1.406	1.423	1.410	1.415	1.417	1.407
C2-N1	1.355	1.351	1.346	1.353	1.355	1.351	1.363
C2-C9	1.439	1.440	1.426	1.437	1.434	1.438	1.452
N1-C3	1.354	1.364	1.378	1.369	1.368	1.380	1.368
C3-C4	1.423	1.418	1.413	1.417	1.419	1.412	1.419
C3-C8	1.459	1.450	1.443	1.445	1.446	1.439	1.448
C4-C5	1.371	1.375	1.380	1.378	1.375	1.384	1.381
C5-C6	1.422	1.415	1.410	1.411	1.415	1.406	1.412
C6-C7	1.371	1.375	1.380	1.379	1.375	1.384	1.380
C7-C8	1.422	1.418	1.413	1.415	1.419	1.412	1.419
C8-N2	1.355	1.364	1.378	1.379	1.368	1.380	1.368
N2-C9	1.358	1.352	1.346	1.360	1.355	1.351	1.363

Table S5 Selected DFT calculated bond angles (deg) for $\mathbf{2}^n$

Bond angle		DFT					
	$\mathbf{2}^{2+}$ (*S*=1)	$\mathbf{2}^{+}$ (*S*=1/2)	**2** (*S*=0)	**2** (*S*=1)	$\mathbf{2}^{-}$ (*S*=1/2)	$\mathbf{2}^{2-}$ (*S*=1)	$\mathbf{2}^{3-}$ (*S*=1/2)
N1-Ru1-O1	78.943	79.799	79.474	80.125	79.524	79.034	79.357
N1-Ru1-O2	173.192	173.833	174.173	173.100	174.049	174.011	174.017
N1-Ru1-O3	84.998	85.009	85.695	85.440	85.593	85.784	86.988
N1-Ru1-O4	101.274	100.760	101.385	101.495	102.241	102.802	103.350
N1-Ru1-O5	93.928	93.633	94.873	93.482	95.076	94.799	93.738
O1-Ru1-O2	95.027	94.705	95.168	93.527	95.189	95.584	94.954
O1-Ru1-O3	90.665	90.115	89.128	91.487	90.156	90.127	90.865
O1-Ru1-O4	179.014	179.429	177.251	177.627	177.838	177.915	177.278
O1-Ru1-O5	89.681	90.746	92.048	88.782	90.348	89.945	88.759
O2-Ru1-O3	91.968	92.252	91.975	92.071	91.732	91.644	91.277
O2-Ru1-O4	84.809	84.731	83.863	84.935	82.987	82.536	82.350
O2-Ru1-O5	89.160	89.207	87.561	89.052	87.638	87.772	87.949
O3-Ru1-O4	90.312	89.819	88.336	90.375	88.742	89.029	89.579
O3-Ru1-O5	178.787	178.241	178.770	178.826	179.226	179.416	179.107
O4-Ru1-O5	89.345	89.336	90.482	89.386	90.735	90.880	90.758
N2-Ru2-O1′	79.130	79.621	79.401	79.831	79.480	79.016	79.344
N2-Ru2-O6	173.064	174.279	173.969	174.653	173.744	173.614	174.022
N2-Ru2-O7	85.177	85.004	85.570	87.105	85.500	85.684	86.697
N2-Ru2-O8	101.236	100.930	101.344	102.330	102.299	102.922	103.375
N2-Ru2-O9	94.126	94.465	95.060	94.319	95.166	94.833	94.071
O1′-Ru2-O6	94.855	95.191	95.091	95.341	94.964	90.682	95.083
O1′-Ru2-O7	90.944	90.942	89.414	91.710	90.596	95.253	91.354
O1′-Ru2-O8	178.641	179.219	177.274	177.799	177.895	177.920	177.197
O1′-Ru2-O9	89.053	91.214	92.027	88.239	90.207	89.673	88.167
O6-Ru2-O7	91.519	92.721	91.960	90.767	91.727	91.615	91.308

O6-Ru2-O8	84.858	84.234	84.045	82.516	83.201	82.774	82.225
O6-Ru2-O9	89.188	88.016	87.542	87.788	87.679	87.897	87.866
O7-Ru2-O8	90.392	88.558	88.034	88.827	88.431	88.721	89.495
O7-Ru2-O9	179.291	177.650	178.512	178.543	179.040	179.421	179.004
O8-Ru2-O9	89.614	89.296	90.519	91.170	90.749	90.909	90.943

Table S6 Selected crystallographic parameters of **1** and **2**

	2 x **1**	**2**•2CH_3CN
Empirical formula	C_{102} H_{100} N_8 $O_{32.50}$ Ru_6	$C_{62}H_{70}N_6O_{18}Ru_4$
Formula weight	2564.31	1591.52
Crystal system	Triclinic	Monoclinic
Space group	*P*1	$P2_1/c$
a / (Å)	11.7442(2)	13.5507(7)
b / (Å)	14.8795(3)	15.9746(6)
c / (Å)	17.1035(3)	15.9722(7)
α / (°)	106.199(2)	90
β / (°)	103.748(2)	110.089(6)
γ / (°)	100.635(2)	90
V / (Å^3)	2685.20(9)	3247.1(3)
Z	1	2
μ (mm^{-1})	7.355	0.987
ρ_{calcd} (g cm^{-3})	1.585	1.628
T / K	100.0(3)	150(2)
F (000)	1292	1608
θ range (deg)	2.828 to 75.038	2.555 to 31.215
data/restraints/parameters	18456/4/1332	5678/0/415
R_1, wR_2 [$I > 2\sigma(I)$]	0.0670, 0.1754	0.0379, 0.0905
R_1, wR_2(all data)	0.0703, 0.1790	0.0473, 0.0970
GOF on F^2	1.034	1.045
Largest difference in peak / hole (e Å^{-3})	2.038, –1.149	0.63, –0.68

Table S7 Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) calculated optimised structures of $\mathbf{1}^{n}$ (Molecule A)

compd	$E_{(S=0)}$ (Hartrees)	$E_{(S=1/2)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$E_{(S=3/2)}$ (Hartrees)	$\Delta E_{(\mathrm{HE-LE})}{}^{a}$
$\mathbf{1}^{2+}$	–3412.8304		–3412.8629		0.0325 Hartrees 85.329 kJ mol^{-1} 7133 cm^{-1}
$\mathbf{1}^{+}$		–3413.1510			
1	–3413.3319		–3413.3287		0.0032 Hartrees 8.402 kJ mol^{-1} 702 cm^{-1}
$\mathbf{1}^{-}$		–3413.4229			
$\mathbf{1}^{2-}$	–3413.4023		–3413.4110		0.0087 Hartrees 22.842 kJ mol^{-1} 1909 cm^{-1}
$\mathbf{1}^{3-}$		–3413.2916		–3413.2754	0.0162 Hartrees 42.533 kJ mol^{-1} 3555 cm^{-1}

[a]HE = spin state higher in energy, LE = spin state lower in energy

Table S8 Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) calculated optimised structures of $\mathbf{2}^{n}$

compd	$E_{(S=0)}$ (Hartrees)	$E_{(S=1/2)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$E_{(S=3/2)}$ (Hartrees)	$\Delta E_{(\mathrm{HE-LE})}{}^{a}$
$\mathbf{2}^{2+}$	–4197.3251		–4197.3757		0.0506 Hartrees 132.850 kJ mol^{-1} 11105 cm^{-1}
$\mathbf{2}^{+}$		–4197.6335			
2	–4197.8065		–4197.8058		0.0007 Hartrees 1.838 kJ mol^{-1} 154 cm^{-1}
$\mathbf{2}^{-}$		–4197.9003			
$\mathbf{2}^{2-}$	–4197.8913		–4197.8980		0.0067 Hartrees 17.591 kJ mol^{-1} 1470 cm^{-1}
$\mathbf{2}^{3-}$		–4197.7926		–4197.7779	0.0147 Hartrees 38.595 kJ mol^{-1} 3226 cm^{-1}

[a]HE = spin state higher in energy, LE = spin state lower in energy

Table S9 Composition and energy of selected molecular orbitals of **1** (*S*=0) (Molecule A)

MO	Energy	Composition				
	(eV)	Ru1	Ru2	Ru3	L	acac
HOMO–5	–5.197	0.07	0.51	0.11	0.09	0.22
HOMO–4	–5.132	0.36	0.01	0.24	0.17	0.22
HOMO–3	–4.955	0.36	0.05	0.08	0.09	0.41
HOMO–2	–4.913	0.20	0.30	0.30	0.09	0.28
HOMO–1	–4.752	0.02	0.36	0.25	0.05	0.32
HOMO	–4.661	0.08	0.29	0.22	0.18	0.22
LUMO	–3.145	0.15	0.14	0.15	0.44	0.13
LUMO+1	–2.907	0.17	0.09	0.10	0.56	0.09
LUMO+2	–1.913	0.02	0.02	0.03	0.89	0.03
LUMO+3	–1.031	0.00	0.05	0.01	0.03	0.90
LUMO+4	–0.853	0.02	0.00	0.01	0.81	0.16
LUMO+5	–0.761	0.00	0.01	0.03	0.04	0.92

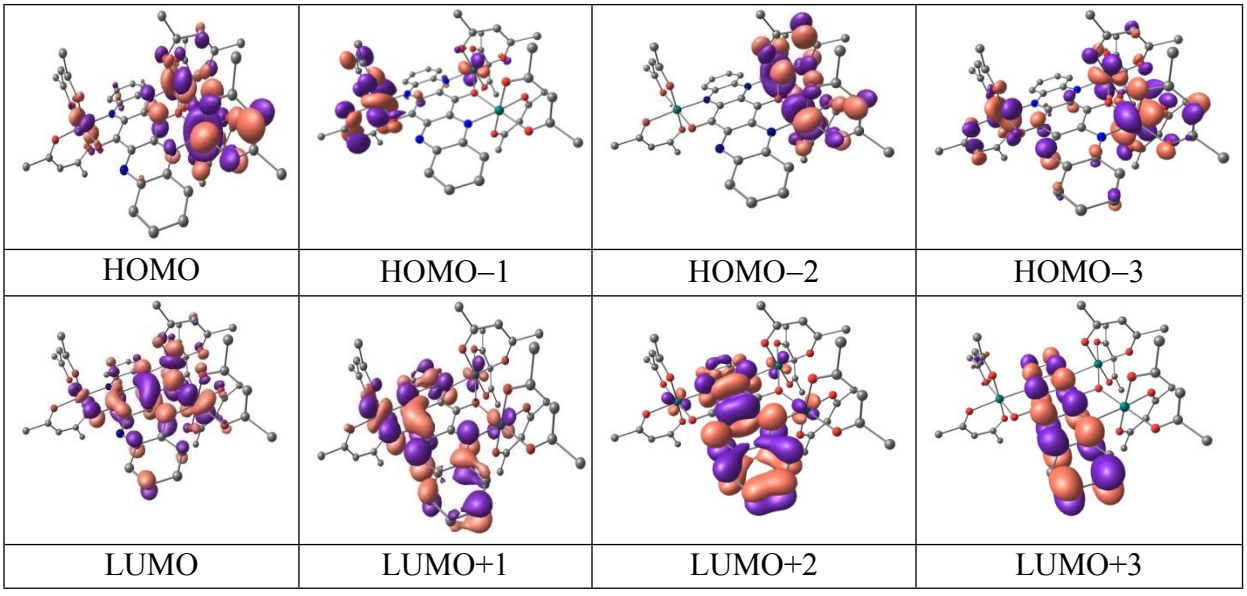


Table S10 Composition and energy of selected molecular orbitals of **1** (*S*=1) (Molecule A)

MO	Energy (eV)	Composition				
		Ru1	Ru2	Ru3	L	acac
			α-spin			
HOMO–5	–5.520	0.04	0.41	0.10	0.10	0.36
HOMO–4	–5.350	0.00	0.50	0.07	0.10	0.32
HOMO–3	–5.160	0.29	0.07	0.02	0.16	0.46
HOMO–2	–5.050	0.36	0.27	0.01	0.09	0.26
SOMO2	–4.834	0.33	0.31	0.01	0.11	0.24
SOMO1	–4.254	0.47	0.00	0.00	0.06	0.47
LUMO	–2.786	0.02	0.27	0.42	0.09	0.21
LUMO+1	–1.660	0.42	0.03	0.06	0.35	0.14
LUMO+2	–1.249	0.07	0.20	0.23	0.35	0.15
LUMO+3	–1.052	0.03	0.03	0.02	0.86	0.06
LUMO+4	–0.857	0.00	0.05	0.02	0.04	0.88
LUMO+5	–0.628	0.00	0.05	0.02	0.03	0.89
			β-spin			
HOMO–5	–5.349	0.14	0.01	0.01	0.80	0.04
HOMO–4	–5.160	0.02	0.01	0.2	0.91	0.03
HOMO–3	–4.937	0.00	0.03	0.01	0.03	0.92
HOMO–2	–4.845	0.00	0.02	0.02	0.03	0.94
HOMO–1	–4.719	0.00	0.00	0.06	0.04	0.90
HOMO	–4.394	0.03	0.01	0.01	0.65	0.31
LUMO	–3.234	0.00	0.16	0.19	0.12	0.53
LUMO+1	–2.408	0.04	0.01	0.01	0.19	0.75
LUMO+2	–2.360	0.00	0.07	0.20	0.18	0.54
LUMO+3	–1.724	0.03	0.05	0.13	0.62	0.17
LUMO+4	–1.142	0.01	0.03	0.36	0.31	0.28
LUMO+5	–0.983	0.01	0.04	0.07	0.82	0.05

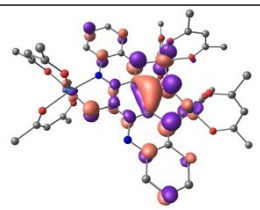
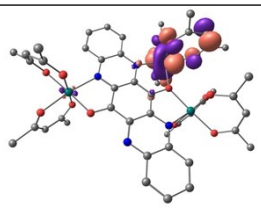
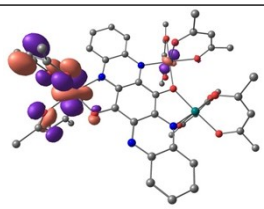
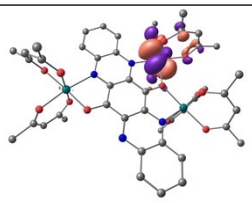
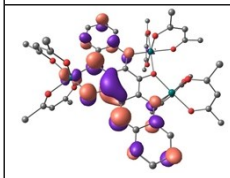
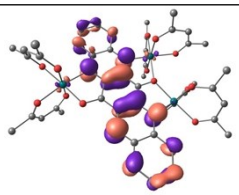
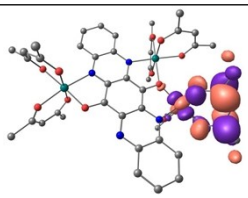
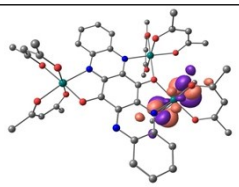
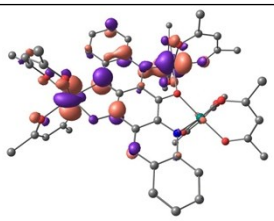
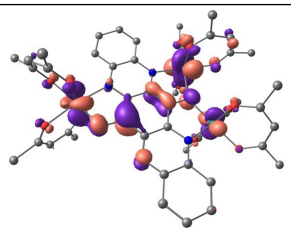
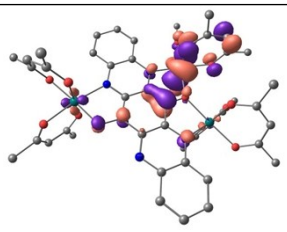
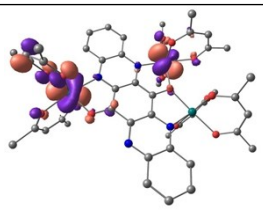
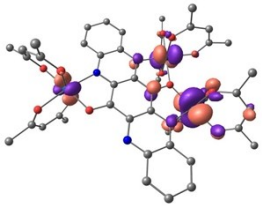
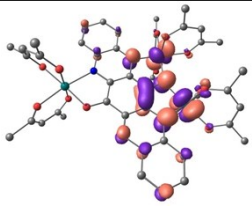
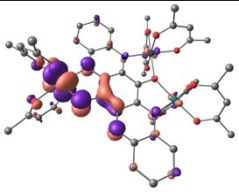
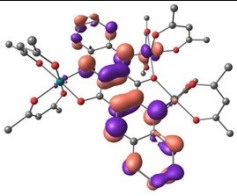
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Composition and energy of selected molecular orbitals of $\mathbf{1}^{+}$ (S=1/2) (Molecule A)

MO	Energy (eV)	Composition				
		Ru1	Ru2	Ru3	L	acac
			α-spin			
HOMO–5	–8.264	0.00	0.01	0.55	0.04	0.40
HOMO–4	–8.076	0.49	0.02	0.06	0.11	0.31
HOMO–3	–7.983	0.15	0.00	0.40	0.11	0.35
HOMO–2	–7.728	0.30	0.01	0.00	0.08	0.61
HOMO–1	–7.396	0.29	0.02	0.05	0.20	0.44
SOMO	–7.322	0.14	0.02	0.17	0.44	0.23
LUMO	–5.704	0.01	0.02	0.58	0.23	0.17
LUMO+1	–5.412	0.13	0.01	0.00	0.83	0.03
LUMO+2	–4.698	0.02	0.01	0.03	0.92	0.02
LUMO+3	–3.893	0.00	0.42	0.07	0.11	0.41
LUMO+4	–3.593	0.00	0.12	0.06	0.06	0.76
LUMO+5	–3.447	0.00	0.04	0.04	0.06	0.89
			β-spin			
HOMO–5	–8.283	0.00	0.01	0.26	0.05	0.68
HOMO–4	–8.076	0.29	0.02	0.00	0.07	0.62
HOMO–3	–7.963	0.00	0.01	0.390	0.04	0.56
HOMO–2	–7.688	0.60	0.01	0.00	0.08	0.31
HOMO–1	–7.495	0.34	0.02	0.00	0.30	0.33
HOMO	–7.044	0.38	0.03	0.01	0.28	0.30
LUMO	–6.118	0.08	0.52	0.01	0.21	0.19
LUMO+1	–5.761	0.03	0.25	0.04	0.60	0.09
LUMO+2	–5.231	0.43	0.01	0.00	0.46	0.10
LUMO+3	–4.617	0.02	0.02	0.02	0.91	0.02
LUMO+4	–3.750	0.00	0.25	0.11	0.08	0.56
LUMO+5	–3.557	0.00	0.09	0.20	0.08	0.62

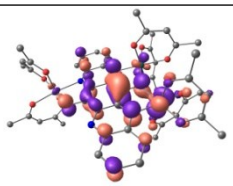
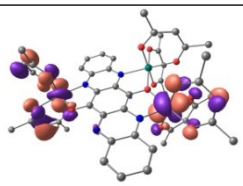
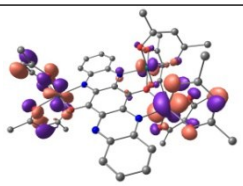
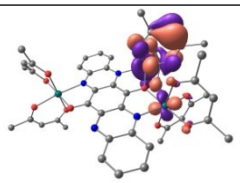
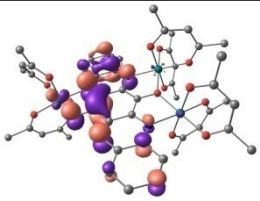
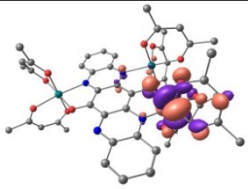
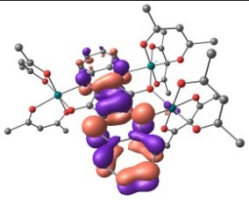
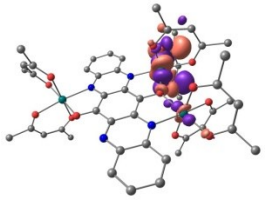
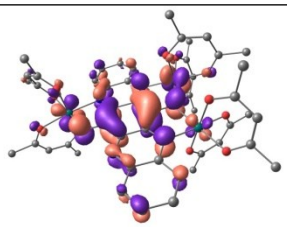
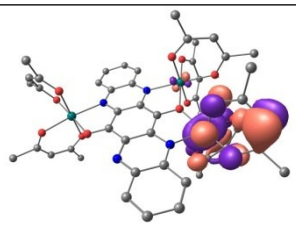
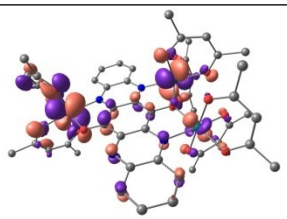
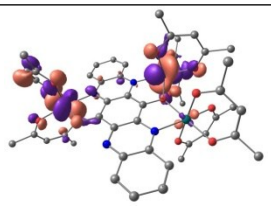
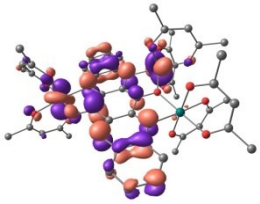
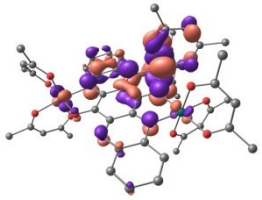
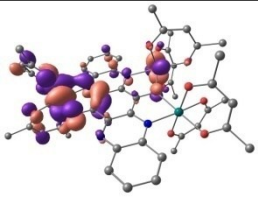
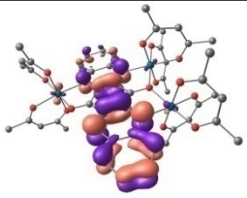
α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Composition and energy of selected molecular orbitals of $\mathbf{1}^{2+}$ (*S*=1) (Molecule A)

MO	Energy (eV)	Composition				
		Ru1	Ru2	Ru3	L	acac
			α-spin			
HOMO–5	–10.696	0.02	0.02	0.59	0.07	0.31
HOMO–4	–10.679	0.18	0.01	0.05	0.06	0.71
HOMO–3	–10.534	0.00	0.23	0.02	0.02	0.73
HOMO–2	–10.341	0.04	0.02	0.44	0.14	0.37
SOMO2	–10.257	0.22	0.00	0.07	0.03	0.67
SOMO1	–9.824	0.03	0.01	0.30	0.33	0.33
LUMO	–8.550	0.02	0.03	0.36	0.44	0.15
LUMO+1	–8.132	0.06	0.02	0.04	0.85	0.03
LUMO+2	–7.043	0.01	0.01	0.03	0.95	0.01
LUMO+3	–6.072	0.00	0.34	0.06	0.12	0.48
LUMO+4	–5.841	0.00	0.00	0.00	0.98	0.02
LUMO+5	–5.764	0.00	0.20	0.09	0.12	0.58
			β-spin			
HOMO–5	–10.711	0.07	0.04	0.47	0.10	0.31
HOMO–4	–10.625	0.07	0.23	0.05	0.08	0.57
HOMO–3	–10.593	0.28	0.10	0.05	0.08	0.49
HOMO–2	–10.518	0.17	0.01	0.19	0.07	0.56
HOMO–1	–10.382	0.28	0.01	0.05	0.10	0.56
HOMO	–9.651	0.04	0.03	0.31	0.31	0.32
LUMO	–8.751	0.04	0.09	0.28	0.37	0.22
LUMO+1	–8.145	0.12	0.03	0.02	0.77	0.05
LUMO+2	–8.026	0.07	0.56	0.02	0.08	0.28
LUMO+3	–7.766	0.53	0.07	0.01	0.14	0.25
LUMO+4	–7.013	0.03	0.02	0.02	0.92	0.02
LUMO+5	–5.935	0.00	0.20	0.06	0.08	0.66

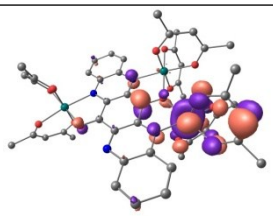
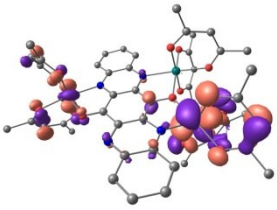
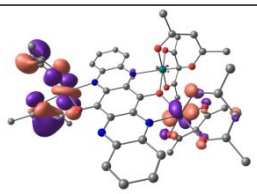
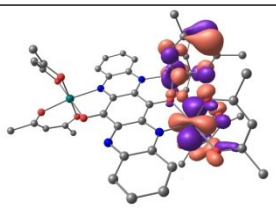
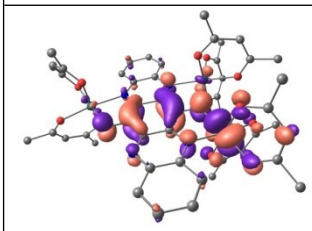
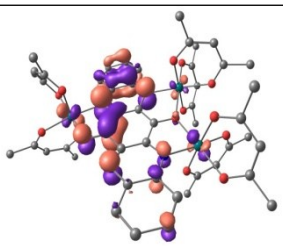
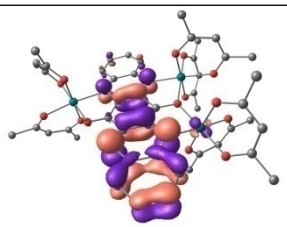
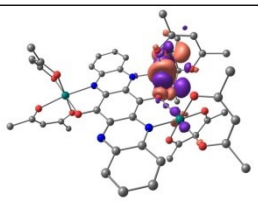
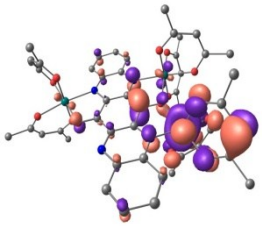
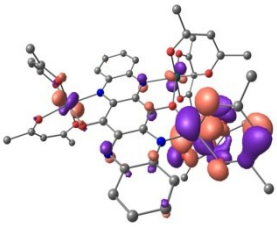
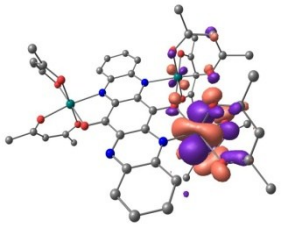
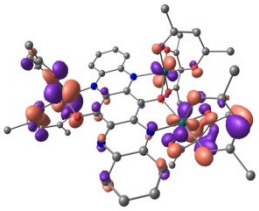
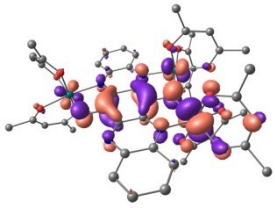
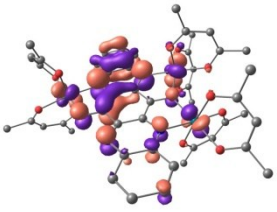
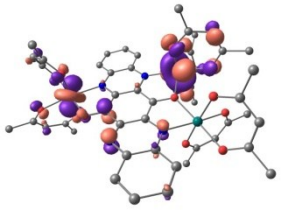
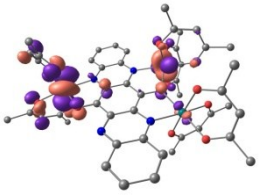
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Composition and energy of selected molecular orbitals of $\mathbf{1}^{-}$ (S=1/2) (Molecule A)

MO	Energy (eV)	Composition				
		Ru1	Ru2	Ru3	L	acac
			α-spin			
HOMO−5	−2.529	0.15	0.16	0.37	0.08	0.25
HOMO−4	−2.464	0.01	0.29	0.47	0.06	0.16
HOMO−3	−2.373	0.54	0.12	0.01	0.07	0.25
HOMO−2	−2.142	0.04	0.36	0.30	0.04	0.26
HOMO−1	−2.019	0.04	0.27	0.36	0.08	0.25
SOMO	−1.472	0.03	0.15	0.15	0.59	0.09
LUMO	−0.473	0.18	0.02	0.02	0.72	0.05
LUMO+1	0.433	0.03	0.02	0.03	0.90	0.02
LUMO+2	1.439	0.03	0.00	0.00	0.06	0.91
LUMO+3	1.589	0.04	0.00	0.00	0.03	0.92
LUMO+4	1.647	0.00	0.03	0.01	0.03	0.93
LUMO+5	1.663	0.00	0.01	0.03	0.07	0.88
			β-spin			
HOMO−5	−2.463	0.17	0.29	0.26	0.09	0.20
HOMO−4	−2.359	0.00	0.35	0.42	0.07	0.16
HOMO−3	−2.310	0.28	0.08	0.25	0.18	0.20
HOMO−2	−2.108	0.06	0.36	0.30	0.08	0.21
HOMO−1	−1.876	0.01	0.56	0.09	0.11	0.22
HOMO	−1.832	0.02	0.11	0.57	0.09	0.22
LUMO	−0.369	0.16	0.02	0.01	0.76	0.05
LUMO+1	−0.019	0.00	0.19	0.18	0.52	0.10
LUMO+2	0.511	0.02	0.03	0.03	0.89	0.03
LUMO+3	1.437	0.03	0.00	0.00	0.05	0.91
LUMO+4	1.593	0.04	0.00	0.00	0.03	0.92
LUMO+5	1.670	0.00	0.02	0.03	0.03	0.92

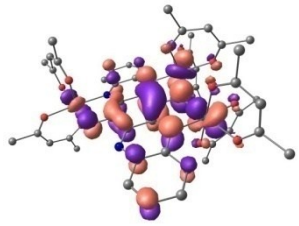
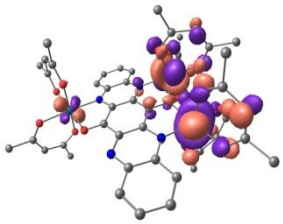
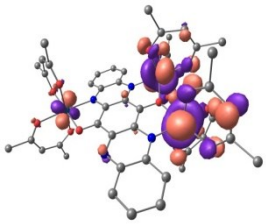
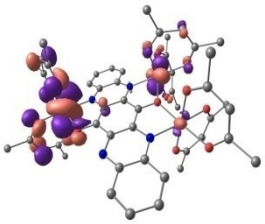
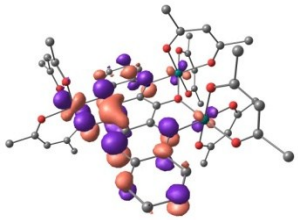
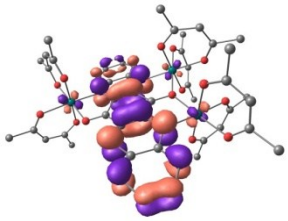
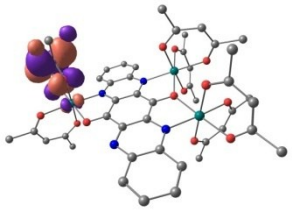
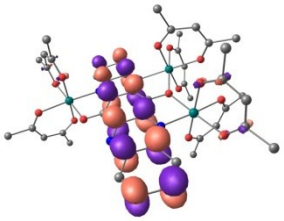
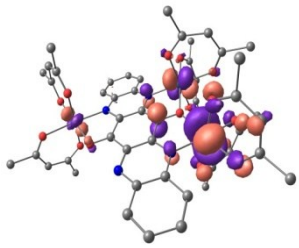
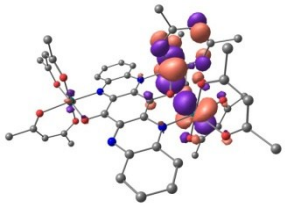
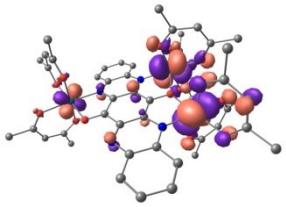
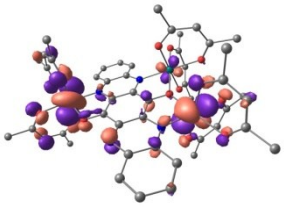
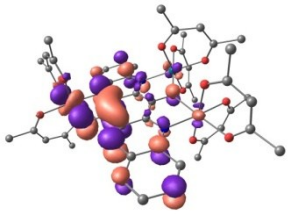
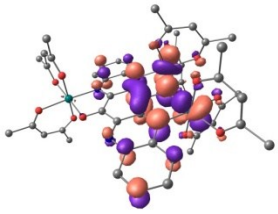
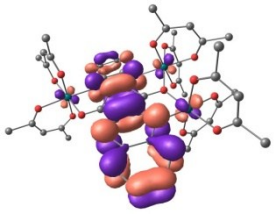
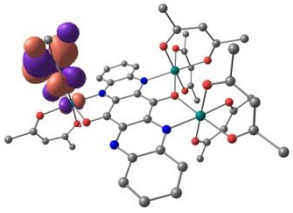
α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Composition and energy of selected molecular orbitals of $\mathbf{1}^{2-}$ (*S*=1) (Molecule A)

MO	Energy (eV)	Composition				
		Ru1	Ru2	Ru3	L	$acac^-$
			α-spin			
HOMO–5	0.124	0.67	0.06	0.02	0.08	0.16
HOMO–4	0.253	0.08	0.23	0.42	0.05	0.22
HOMO–3	0.389	0.07	0.37	0.27	0.08	0.21
HOMO–2	0.451	0.67	0.07	0.01	0.06	0.19
SOMO2	0.937	0.06	0.14	0.14	0.59	0.08
SOMO1	1.366	0.14	0.03	0.03	0.76	0.04
LUMO	2.919	0.02	0.02	0.02	0.03	0.91
LUMO+1	3.813	0.00	0.00	0.04	0.04	0.92
LUMO+2	3.846	0.00	0.04	0.00	0.03	0.93
LUMO+3	3.926	0.03	0.00	0.00	0.04	0.93
LUMO+4	4.035	0.06	0.00	0.00	0.04	0.90
LUMO+5	4.095	0.00	0.03	0.04	0.04	0.91
			β-spin			
HOMO–5	0.201	0.18	0.11	0.41	0.12	0.18
HOMO–4	0.248	0.65	0.05	0.03	0.12	0.15
HOMO–3	0.376	0.13	0.12	0.49	0.06	0.21
HOMO–2	0.435	0.21	0.36	0.13	0.09	0.19
HOMO–1	0.573	0.47	0.22	0.06	0.08	0.17
HOMO	0.623	0.32	0.23	0.15	0.13	0.17
LUMO	2.429	0.01	0.15	0.14	0.63	0.08
LUMO+1	2.830	0.14	0.01	0.01	0.79	0.05
LUMO+2	3.377	0.03	0.02	0.02	0.86	0.08
LUMO+3	3.835	0.00	0.00	0.05	0.05	0.89
LUMO+4	3.877	0.00	0.06	0.00	0.04	0.90
LUMO+5	3.936	0.04	0.00	0.00	0.05	0.91

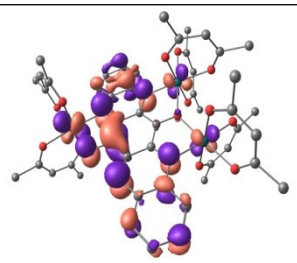
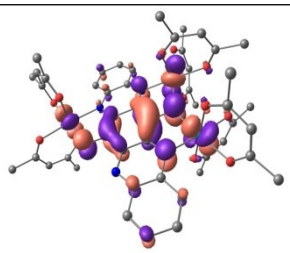
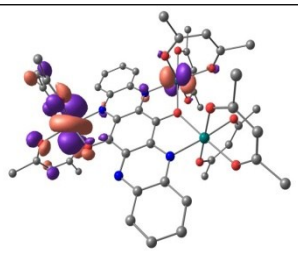
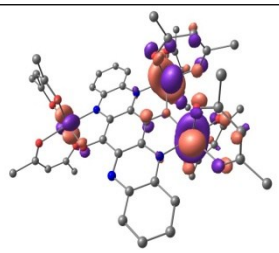
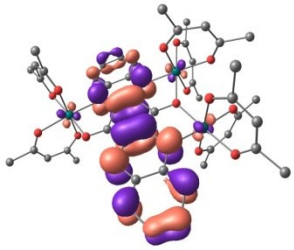
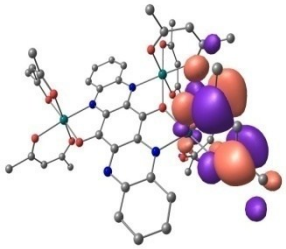
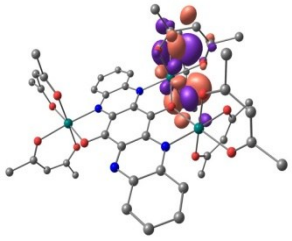
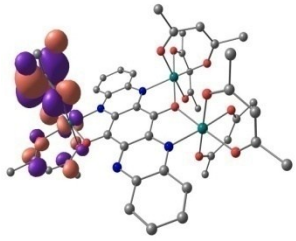
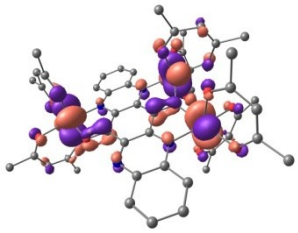
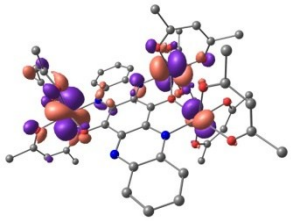
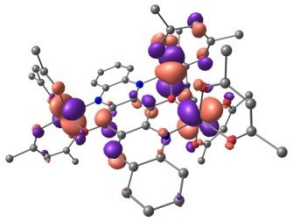
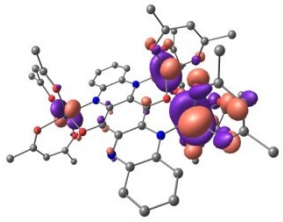
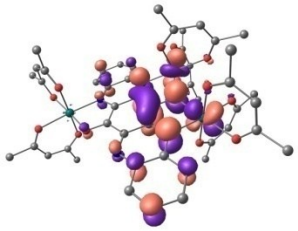
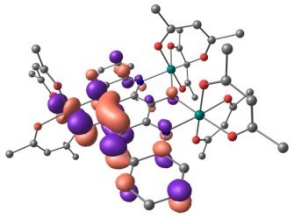
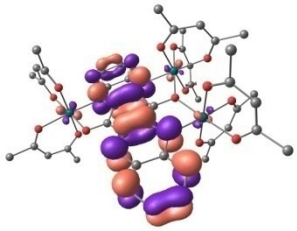
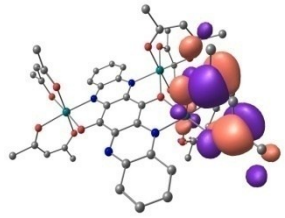
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 Composition and energy of selected molecular orbitals of $\mathbf{1}^{3-}$ (*S*=1/2) (Molecule A)

MO	Energy (eV)	Composition				
		Ru1	Ru2	Ru3	L	acac
			α-spin			
HOMO–5	2.856	0.00	0.55	0.25	0.05	0.15
HOMO–4	2.908	0.06	0.43	0.29	0.05	0.17
HOMO–3	3.085	0.01	0.31	0.46	0.04	0.18
HOMO–2	3.212	0.04	0.39	0.25	0.16	0.16
HOMO–1	3.748	0.11	0.07	0.05	0.72	0.05
SOMO	4.213	0.01	0.14	0.12	0.67	0.07
LUMO	5.689	0.01	0.01	0.02	0.88	0.08
LUMO+1	5.941	0.03	0.00	0.00	0.03	0.94
LUMO+2	6.046	0.07	0.00	0.00	0.04	0.89
LUMO+3	6.292	0.00	0.00	0.05	0.05	0.90
LUMO+4	6.344	0.00	0.06	0.00	0.03	0.91
LUMO+5	6.574	0.00	0.04	0.06	0.04	0.87
			β-spin			
HOMO–5	2.825	0.40	0.01	0.31	0.11	0.15
HOMO–4	2.860	0.00	0.58	0.22	0.05	0.15
HOMO–3	2.933	0.11	0.48	0.19	0.06	0.17
HOMO–2	3.110	0.02	0.29	0.47	0.04	0.18
HOMO–1	3.286	0.02	0.26	0.45	0.10	0.17
HOMO	4.258	0.01	0.12	0.12	0.69	0.07
LUMO	5.259	0.09	0.01	0.01	0.82	0.07
LUMO+1	5.893	0.01	0.01	0.01	0.58	0.39
LUMO+2	5.978	0.05	0.00	0.00	0.21	0.73
LUMO+3	6.062	0.07	0.00	0.00	0.05	0.88
LUMO+4	6.290	0.00	0.00	0.05	0.05	0.89
LUMO+5	6.356	0.00	0.06	0.00	0.05	0.89

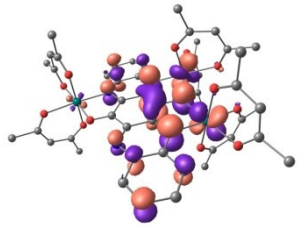
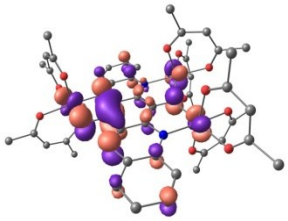
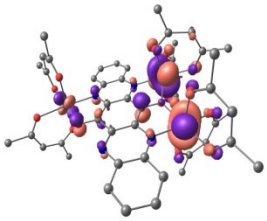
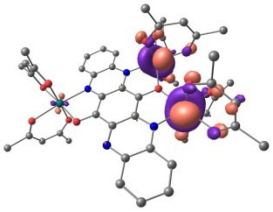
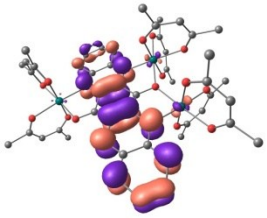
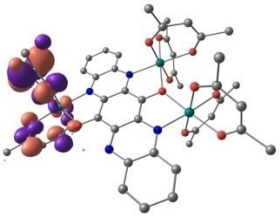
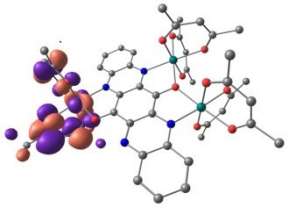
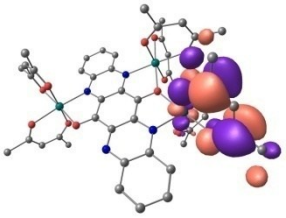
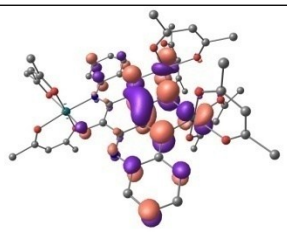
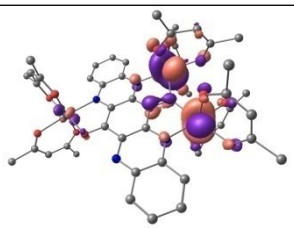
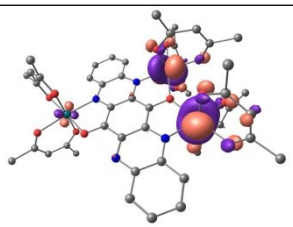
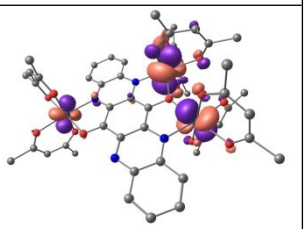
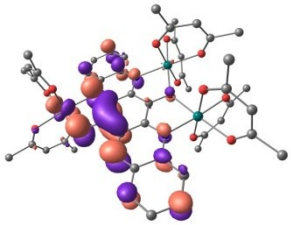
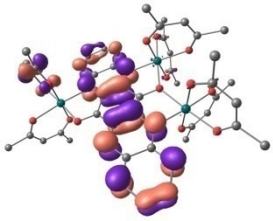
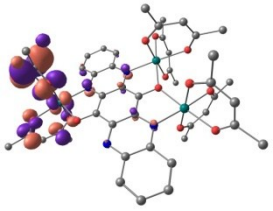
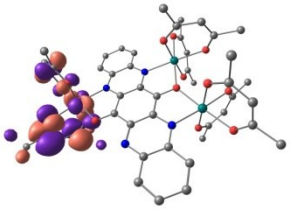
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 Composition and energy of selected molecular orbitals of **2** (*S*=0)

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
HOMO–5	–5.120	0.36	0.34	0.05	0.24
HOMO–4	–4.878	0.39	0.36	0.06	0.19
HOMO–3	–4.662	0.18	0.41	0.13	0.28
HOMO–2	–4.556	0.23	0.40	0.02	0.35
HOMO–1	–4.544	0.43	0.19	0.02	0.35
HOMO	–4.330	0.36	0.18	0.17	0.28
LUMO	–3.213	0.25	0.24	0.36	0.14
LUMO+1	–2.980	0.17	0.18	0.57	0.09
LUMO+2	–2.097	0.04	0.04	0.90	0.02
LUMO+3	–0.813	0.05	0.00	0.07	0.87
LUMO+4	–0.810	0.06	0.00	0.03	0.91
LUMO+5	–0.790	0.01	0.00	0.91	0.08

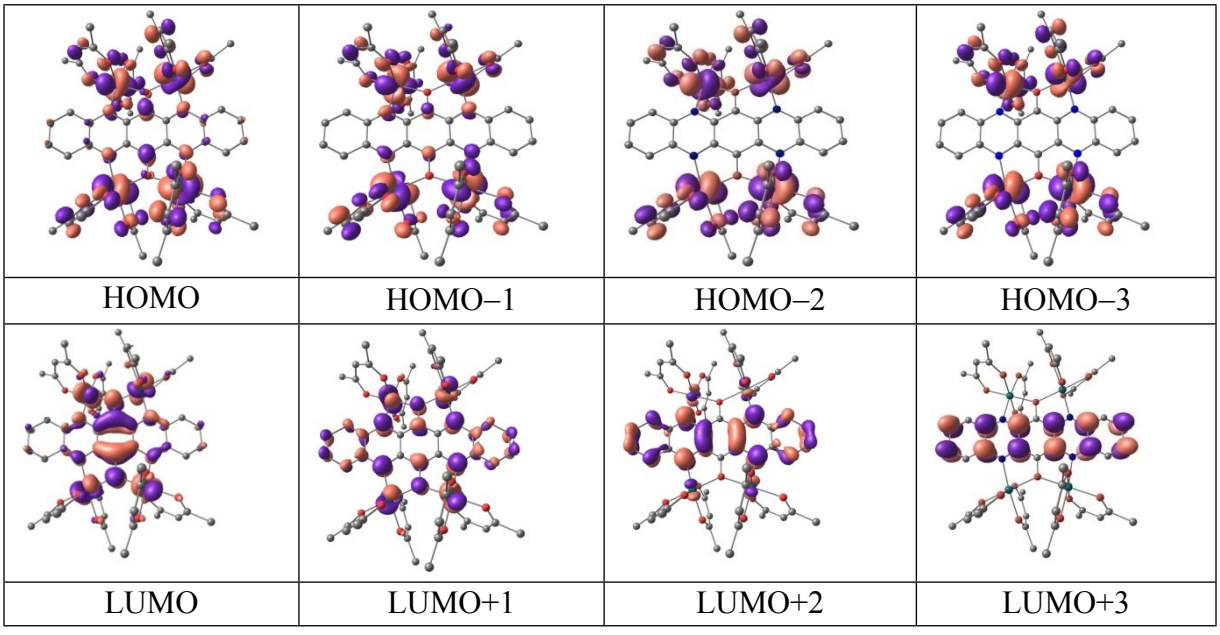


Table S17 Composition and energy of selected molecular orbitals of **2** (*S*=1)

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO−5	−5.109	0.05	0.71	0.06	0.18
HOMO−4	−5.096	0.20	0.49	0.05	0.27
HOMO−3	−5.075	0.03	0.60	0.15	0.22
HOMO−2	−4.506	0.03	0.48	0.22	0.28
SOMO2	−4.358	0.03	0.41	0.31	0.24
SOMO1	−3.872	0.30	0.04	0.54	0.12
LUMO	−2.680	0.04	0.41	0.43	0.12
LUMO+1	−1.852	0.02	0.05	0.91	0.03
LUMO+2	−1.260	0.09	0.00	0.04	0.86
LUMO+3	−0.927	0.04	0.01	0.03	0.93
LUMO+4	−0.921	0.07	0.00	0.04	0.89
LUMO+5	−0.734	0.00	0.06	0.03	0.90
			β-spin		
HOMO−5	−5.161	0.56	0.09	0.08	0.27
HOMO−4	−4.903	0.03	0.74	0.06	0.17
HOMO−3	−4.643	0.02	0.56	0.09	0.33
HOMO−2	−4.595	0.05	0.54	0.18	0.23
HOMO−1	−4.385	0.19	0.24	0.37	0.20
HOMO	−3.877	0.15	0.39	0.25	0.21
LUMO	−3.125	0.63	0.05	0.12	0.21
LUMO+1	−2.662	0.48	0.05	0.33	0.14
LUMO+2	−2.422	0.14	0.32	0.42	0.12
LUMO+3	−1.708	0.03	0.05	0.88	0.04
LUMO+4	−1.217	0.07	0.00	0.04	0.89
LUMO+5	−0.893	0.06	0.00	0.04	0.90

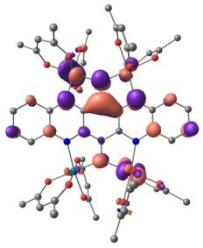
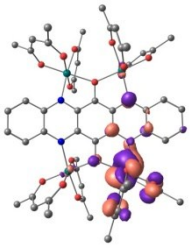
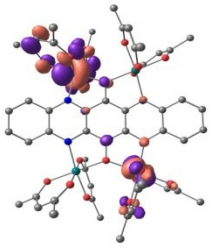
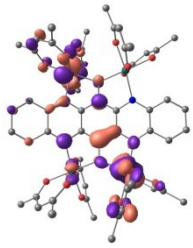
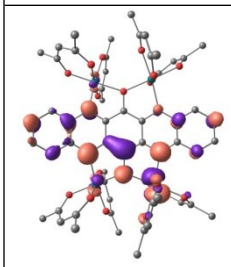
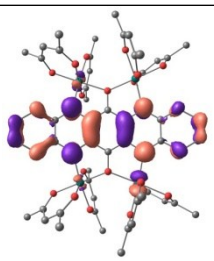
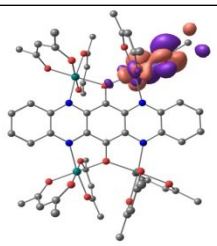
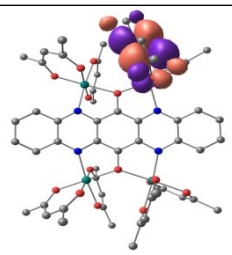
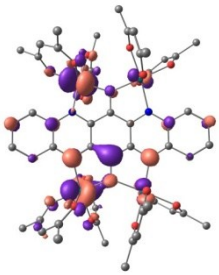
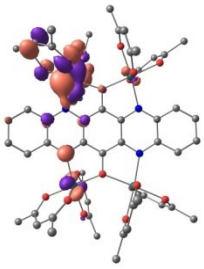
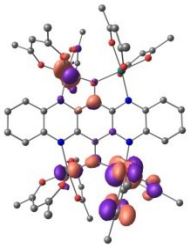
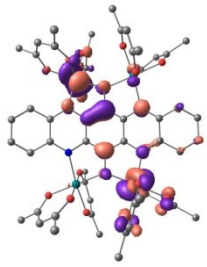
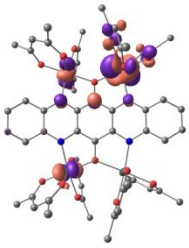
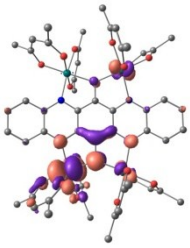
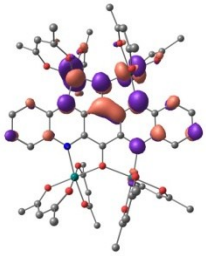
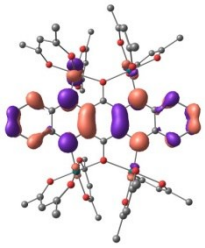
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO–5	–7.495	0.07	0.52	0.15	0.25
HOMO–4	–7.466	0.05	0.65	0.10	0.21
HOMO–3	–7.342	0.03	0.38	0.34	0.24
HOMO–2	–7.194	0.08	0.43	0.22	0.26
HOMO–1	–7.016	0.02	0.50	0.20	0.28
SOMO	–6.664	0.03	0.38	0.41	0.18
LUMO	–5.072	0.05	0.41	0.39	0.15
LUMO+1	–4.854	0.02	0.43	0.40	0.15
LUMO+2	–4.419	0.03	0.16	0.74	0.07
LUMO+3	–3.139	0.12	0.01	0.07	0.80
LUMO+4	–3.132	0.11	0.01	0.05	0.84
LUMO+5	–2.893	0.00	0.02	0.73	0.25
			β-spin		
HOMO–5	–7.649	0.09	0.13	0.12	0.67
HOMO–4	–7.640	0.04	0.57	0.08	0.31
HOMO–3	–7.517	0.21	0.28	0.10	0.41
HOMO–2	–7.191	0.02	0.54	0.06	0.38
HOMO–1	–7.159	0.07	0.52	0.06	0.35
HOMO	–6.625	0.18	0.15	0.54	0.13
LUMO	–5.471	0.35	0.06	0.44	0.15
LUMO+1	–5.108	0.33	0.06	0.46	0.14
LUMO+2	–5.047	0.58	0.03	0.18	0.21
LUMO+3	–4.290	0.05	0.06	0.86	0.03
LUMO+4	–3.090	0.09	0.00	0.06	0.84
LUMO+5	–3.088	0.09	0.01	0.04	0.87

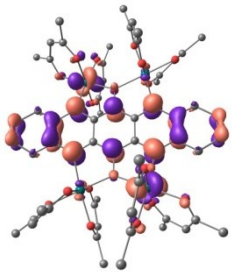
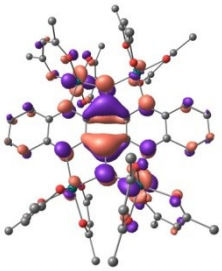
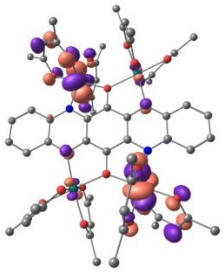
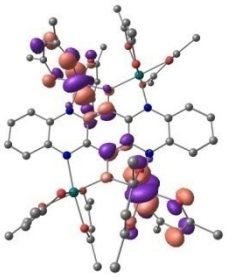
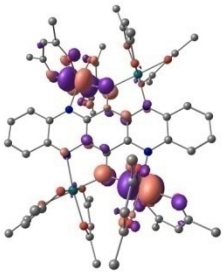
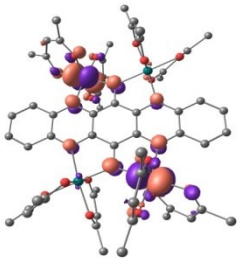
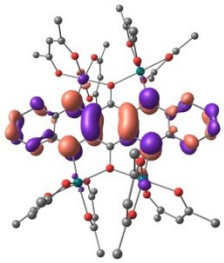
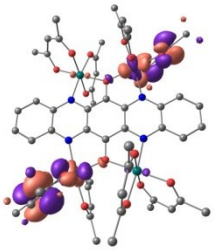
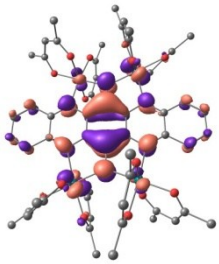
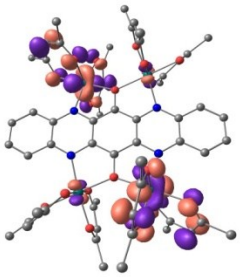
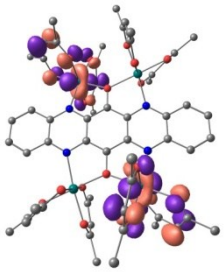
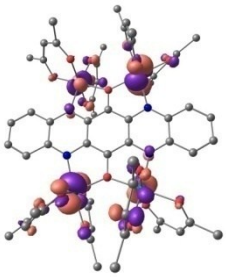
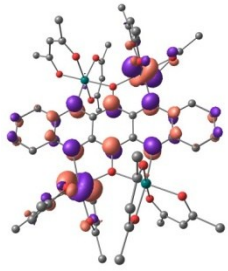
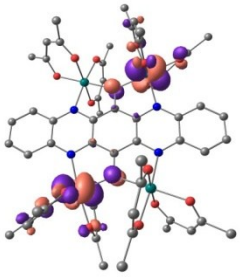
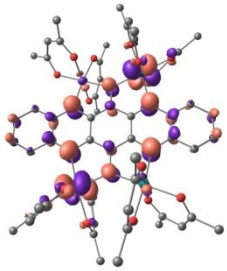
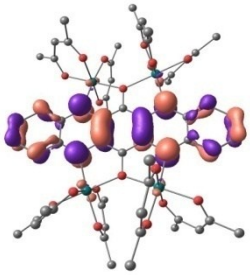
α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO–5	–10.205	0.36	0.06	0.04	0.54
HOMO–4	–10.111	0.44	0.04	0.10	0.42
HOMO–3	–10.037	0.17	0.14	0.02	0.66
HOMO–2	–10.034	0.02	0.22	0.04	0.72
SOMO2	–9.902	0.14	0.15	0.03	0.68
SOMO1	–9.291	0.16	0.09	0.65	0.10
LUMO	–7.843	0.07	0.06	0.84	0.03
LUMO+1	–7.367	0.66	0.01	0.08	0.25
LUMO+2	–6.794	0.04	0.03	0.92	0.01
LUMO+3	–5.618	0.24	0.23	0.14	0.39
LUMO+4	–5.538	0.13	0.29	0.09	0.49
LUMO+5	–5.414	0.00	0.00	0.97	0.03
			β-spin		
HOMO–5	–10.190	0.26	0.23	0.12	0.39
HOMO–4	–10.146	0.14	0.20	0.05	0.62
HOMO–3	–10.097	0.09	0.28	0.07	0.57
HOMO–2	–10.02	0.14	0.38	0.06	0.42
HOMO–1	–9.908	0.26	0.07	0.03	0.63
HOMO	–9.316	0.13	0.16	0.59	0.13
LUMO	–7.885	0.05	0.19	0.69	0.07
LUMO+1	–7.602	0.35	0.35	0.03	0.28
LUMO+2	–7.419	0.03	0.58	0.17	0.21
LUMO+3	–7.212	0.32	0.34	0.12	0.22
LUMO+4	–6.779	0.04	0.05	0.90	0.02
LUMO+5	–5.515	0.27	0.13	0.12	0.49

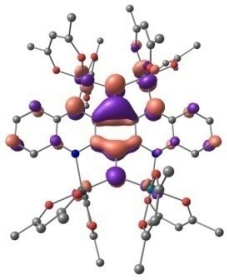
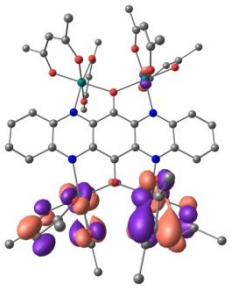
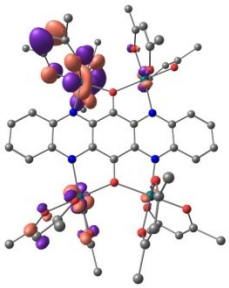
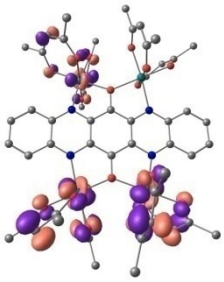
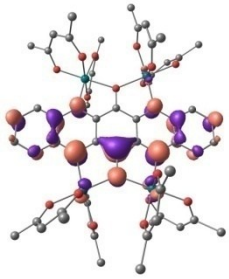
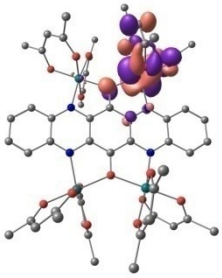
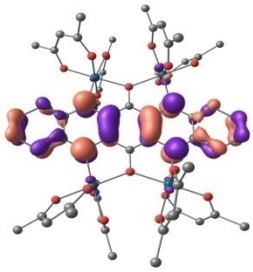
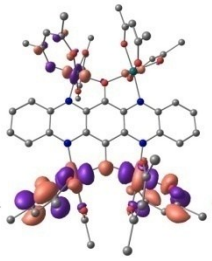
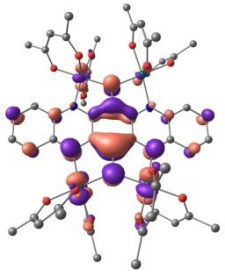
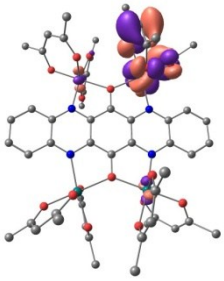
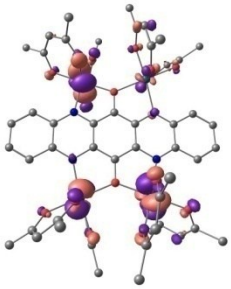
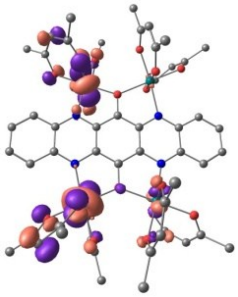
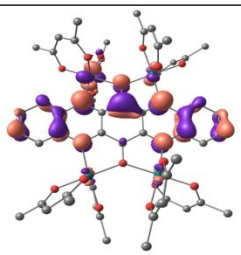
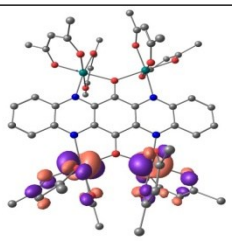
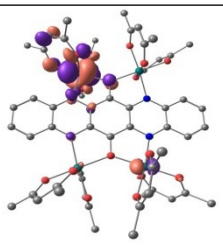
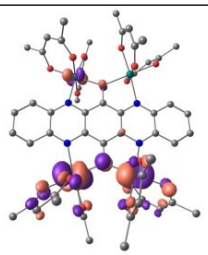
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 Composition and energy of selected molecular orbitals of $\mathbf{2}^{-}$ (S=1/2)

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO–5	–2.626	0.36	0.34	0.05	0.25
HOMO–4	–2.304	0.19	0.45	0.03	0.33
HOMO–3	–2.211	0.19	0.50	0.04	0.27
HOMO–2	–2.135	0.46	0.19	0.08	0.26
HOMO–1	–2.097	0.49	0.15	0.05	0.31
SOMO	–1.635	0.19	0.19	0.51	0.11
LUMO	–0.550	0.10	0.10	0.75	0.05
LUMO+1	0.531	004	0.03	0.90	0.03
LUMO+2	1.406	005	0.00	0.03	0.92
LUMO+3	1.410	0.05	0.00	0.03	0.92
LUMO+4	1.444	0.00	0.04	0.03	0.92
LUMO+5	1.444	0.00	0.05	0.03	0.92
			β-spin		
HOMO–5	–2.491	0.37	0.34	0.06	0.23
HOMO–4	–2.256	0.39	0.37	0.05	0.19
HOMO–3	–2.113	0.28	0.31	0.18	0.23
HOMO–2	–1.769	0.16	0.52	0.08	0.24
HOMO–1	–1.760	0.40	0.33	0.01	0.27
HOMO	–1.697	0.46	0.07	0.26	0.20
LUMO	–0.241	0.24	0.24	0.39	0.13
LUMO+1	–0.225	0.26	0.26	0.35	0.14
LUMO+2	0.364	0.04	0.04	0.89	0.03
LUMO+3	1.416	0.05	0.00	0.03	0.91
LUMO+4	1.420	0.05	0.00	0.04	0.91
LUMO+5	1.456	0.00	0.05	0.04	0.91

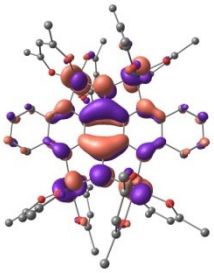
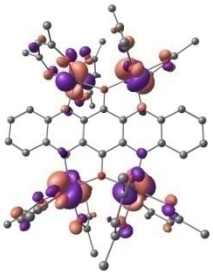
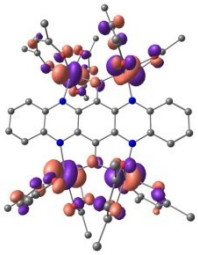
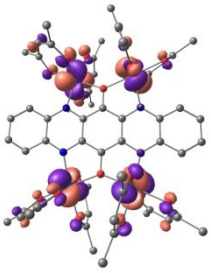
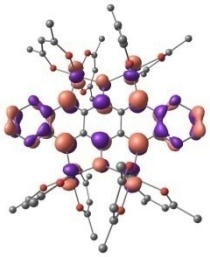
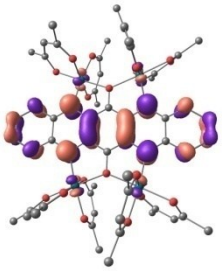
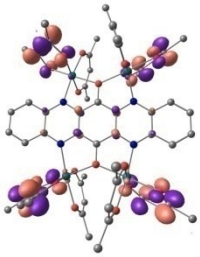
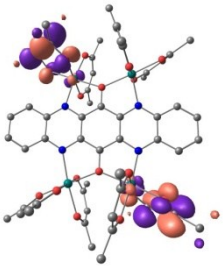
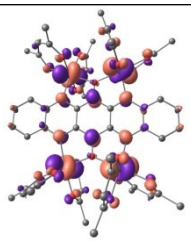
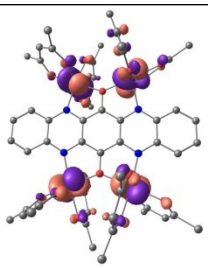
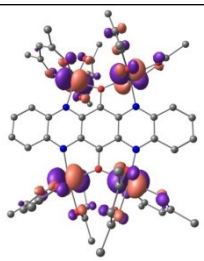
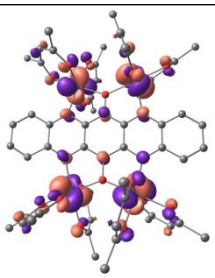
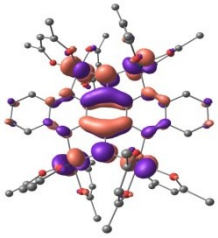
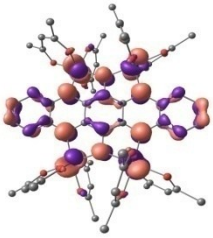
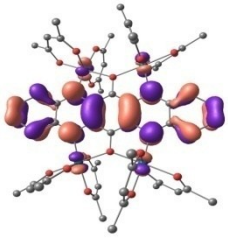
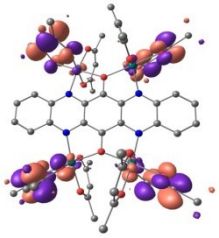
α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S21 Composition and energy of selected molecular orbitals of $\mathbf{2}^{2-}$ (*S*=1)

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO–5	–0.014	0.35	0.36	0.03	0.25
HOMO–4	0.109	0.37	0.38	0.04	0.21
HOMO–3	0.147	0.35	0.35	0.11	0.19
HOMO–2	0.195	0.36	0.35	0.05	0.24
SOMO2	0.626	0.21	0.21	0.48	0.10
SOMO1	0.986	0.14	0.13	0.67	0.06
LUMO	2.591	0.04	0.04	0.88	0.04
LUMO+1	3.651	0.02	0.02	0.04	0.92
LUMO+2	3.661	0.03	0.01	0.04	0.91
LUMO+3	3.664	0.02	0.03	0.03	0.92
LUMO+4	3.667	0.02	0.03	0.02	0.93
LUMO+5	3.931	0.05	0.04	0.03	0.87
			β-spin		
HOMO–5	–0.088	0.23	0.47	0.10	0.20
HOMO–4	0.180	0.38	0.38	0.03	0.22
HOMO–3	0.215	0.39	0.38	0.01	0.22
HOMO–2	0.268	0.36	0.36	0.09	0.19
HOMO–1	0.309	0.39	0.38	0.06	0.17
HOMO	0.466	0.32	0.34	0.16	0.18
LUMO	2.127	0.17	0.17	0.58	0.08
LUMO+1	2.288	0.15	0.15	0.62	0.09
LUMO+2	3.022	0.04	0.04	0.84	0.09
LUMO+3	3.669	0.02	0.02	0.04	0.92
LUMO+4	3.683	0.03	0.03	0.05	0.89
LUMO+5	3.697	0.03	0.03	0.03	0.91

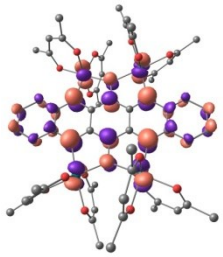
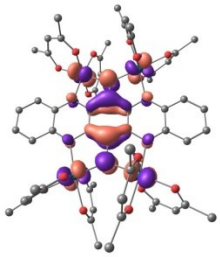
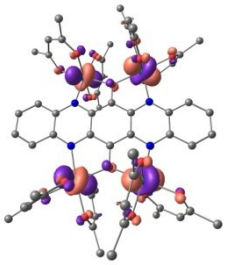
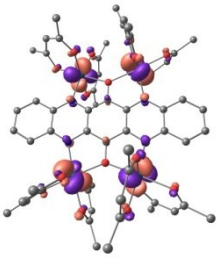
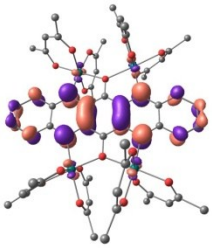
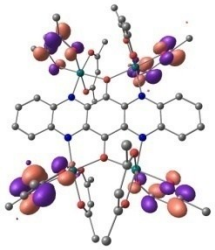
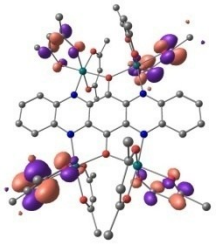
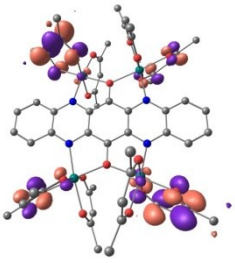
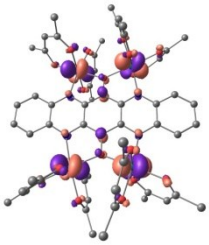
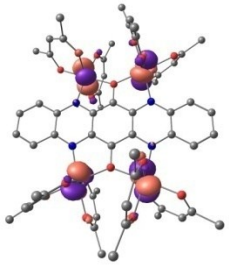
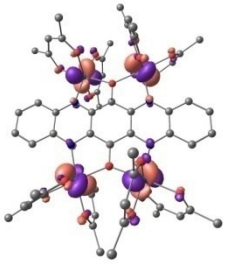
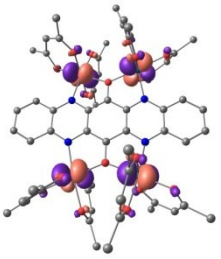
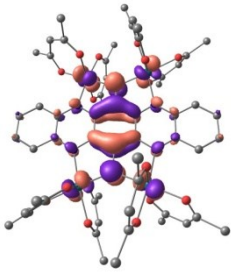
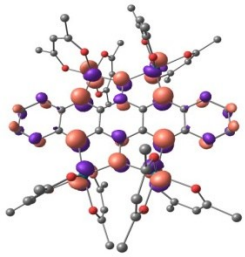
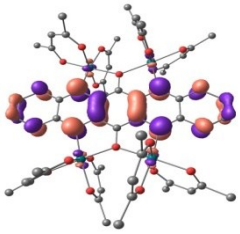
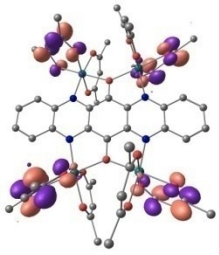
α-spin			
			
SOMO1	SOMO2	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22 Composition and energy of selected molecular orbitals of $\mathbf{2}^{3-}$ (S=1/2)

MO	Energy (eV)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO−5	2.491	0.39	0.38	0.02	0.21
HOMO−4	2.586	0.40	0.39	0.04	0.18
HOMO−3	2.643	0.35	0.37	0.10	0.17
HOMO−2	2.737	0.36	0.38	0.08	0.18
HOMO−1	3.537	0.15	0.15	0.64	0.06
SOMO	3.568	0.14	0.14	0.65	0.07
LUMO	5.128	0.03	0.03	0.86	0.86
LUMO+1	5.851	0.03	0.02	0.03	0.03
LUMO+2	5.861	0.03	0.02	0.04	0.04
LUMO+3	5.869	0.02	0.03	0.02	0.02
LUMO+4	5.877	0.02	0.03	0.04	0.04
LUMO+5	6.141	0.07	0.06	0.03	0.03
			β-spin		
HOMO−5	2.500	0.40	0.39	0.02	0.19
HOMO−4	2.525	0.40	0.39	0.01	0.20
HOMO−3	2.668	0.39	0.39	0.06	0.16
HOMO−2	2.715	0.37	0.38	0.08	0.17
HOMO−1	2.791	0.36	0.37	0.10	0.17
HOMO	3.840	0.14	0.14	0.66	0.07
LUMO	4.591	0.11	0.11	0.69	0.08
LUMO+1	5.503	0.02	0.02	0.74	0.21
LUMO+2	5.862	0.03	0.02	0.03	0.92
LUMO+3	5.874	0.03	0.03	0.04	0.90
LUMO+4	5.891	0.03	0.04	0.03	0.91
LUMO+5	5.920	0.03	0.04	0.12	0.81

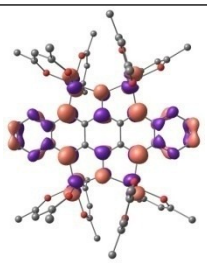
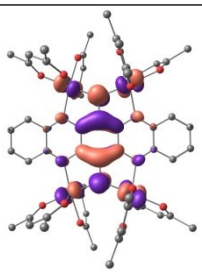
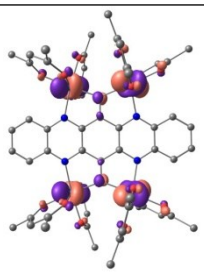
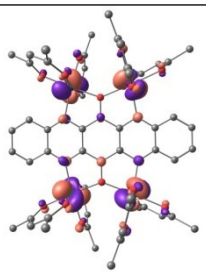
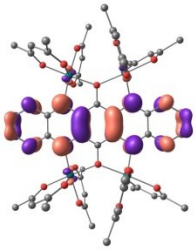
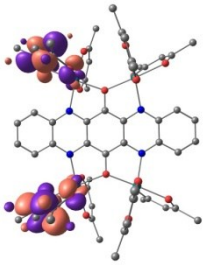
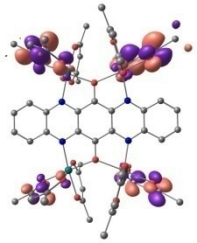
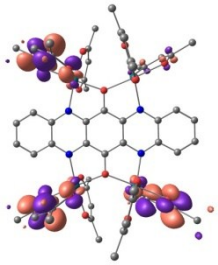
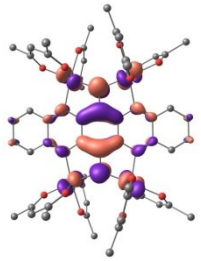
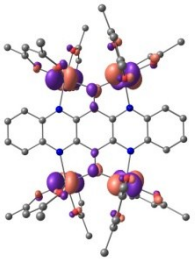
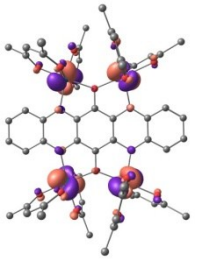
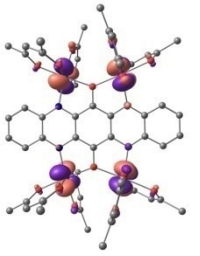
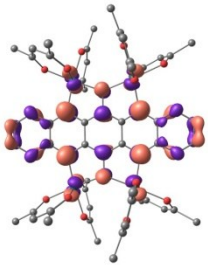
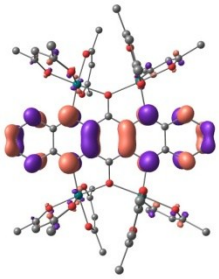
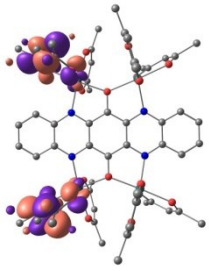
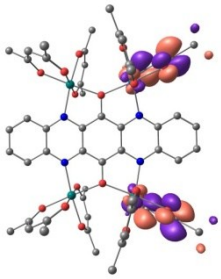
α-spin			
			
SOMO1	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 Experimental and TD-DFT ((U)B3LYP/CPCM/CH_3CN) calculated electronic transitions for **1**^{n}

λ_{max} [a, b] (expt.) (ε /dm^3 mol^{-1}cm^{-1}) [c]	λ [b] (DFT) (f) [d]	Transitions	Character
1 (*S*=0)			
	2064 (0.01)	HOMO→LUMO(0.62)	Ru2(dπ)/acac(π)/Ru3(dπ)→L(π*)/Ru1(dπ)/Ru3(dπ)
	1040 (0.01)	HOMO→LUMO+1(0.57)	Ru2(dπ)/acac(π)/Ru3(dπ)→L(π*)/Ru1(dπ)
1023 (7320)	939 (0.03) 902 (0.12)	HOMO−1→LUMO+1(0.46) HOMO−3→LUMO(0.53)	Ru2(dπ)/acac(π)/Ru3(dπ)→L(π*)/Ru1(dπ) acac(π)/Ru1(dπ)→L(π*)/Ru1(dπ)/Ru3(dπ)
	775 (0.11)	HOMO−4→LUMO(0.47)	Ru1(dπ)/Ru3(dπ)/acac(π)→L(π*)/Ru1(dπ)/Ru3(dπ)
599 (37800)	668 (0.14)	HOMO−4→LUMO+1(0.64)	Ru1(dπ)/Ru3(dπ)/acac(π)→L(π*)/Ru1(dπ)
	542 (0.12)	HOMO−11→LUMO(0.48) HOMO−2→LUMO+2(0.37)	acac(π)→L(π*)/Ru1(dπ)/Ru3(dπ) Ru2(dπ)/acac(π)/Ru1(dπ)→L(π*)
325 (65300)	348 (0.34)	HOMO−20→LUMO+1(0.51)	L(π)→L(π*)/Ru1(dπ)
1 (*S*=1)			
	2933 (0.01)	HOMO(β)→LUMO+2(β) (0.50) HOMO−4(β)→LUMO+2(β) (0.33)	L(π)/Ru2(dπ)/Ru1(dπ)→L(π*)/Ru3(dπ)/Ru2(dπ) acac(π)/Ru2(dπ)/Ru1(dπ)→L(π*)/Ru3(dπ)/Ru2(dπ)
	1463 (0.05)	HOMO−2(β)→LUMO(β) (0.46) HOMO−1(β)→LUMO+1(β) (0.29)	Ru2(dπ)/L(π)/acac(π)→Ru3(dπ)/Ru2(dπ)/acac(π*) Ru1(dπ) acac(π)/→Ru1(dπ)/L(π*)
	1232 (0.02)	HOMO(β)→LUMO(β) (0.47) HOMO−2(β)→LUMO(β) (0.45) HOMO(β)→LUMO+1(β) (0.42)	L(π)/Ru2(dπ)/Ru1(dπ)→Ru3(dπ)/Ru2(dπ)/acac(π*) Ru2(dπ)/L(π)/acac(π)→Ru3(dπ)/Ru2(dπ)/acac(π*) L(π)/Ru2(dπ)/Ru1(dπ)→Ru1(dπ)/L(π*)/acac(π*)
	1184 (0.06)	HOMO−1(β)→LUMO(β) (0.50) HOMO−6(β)→LUMO(β) (0.42)	Ru1(dπ)/acac(π)→Ru3(dπ)/Ru2(dπ)/acac(π*) Ru3(dπ)/acac(π)→Ru3(dπ)/Ru2(dπ)/acac(π*)
1023 (7320)	1077 (0.01)	HOMO−1(β)→LUMO+2(β) (0.58) HOMO−4(β)→LUMO+2(β) (0.32)	Ru1(dπ)/acac(π)→L(π*)/Ru3(dπ)/Ru2(dπ) acac(π)/Ru2(dπ)/Ru1(dπ)→L(π*)/Ru3(dπ)/Ru2(dπ)
	986 (0.03)	HOMO(β)→LUMO+1(β) (0.66)	L(π)/Ru2(dπ)/Ru1(dπ)→ Ru1(dπ)/L(π*)/acac(π*)
	859 (0.02)	SOMO2(α)→LUMO(α) (0.86)	Ru1(dπ)/acac(π)→L(π*)
	774 (0.06)	SOMO1(α)→LUMO+2(α) (0.71)	L(π)→L(π*)

599 (37800)	580 (0.10)	HOMO−4(α)→LUMO(α) (0.70) HOMO−7(α)→LUMO+2(α) (0.41)	acac(π)/Ru1(dπ)→L(π*) acac(π)/Ru3(dπ)→L(π*)
325 (65300)	371 (0.04)	HOMO−15(β)→LUMO+1(β) (0.41) HOMO−13(β)→LUMO+2(β) (0.34) HOMO−14(β)→LUMO+2(β) (0.34)	acac(π)→Ru1(dπ)/L(π*)/acac(π*) L(π)/acac(π)→L(π*)/Ru3(dπ)/Ru2(dπ) L(π)/acac(π)→Ru1(dπ)/L(π*)/acac(π*)
		1^{+} (*S*=1/2)	
	2304 (0.01)	HOMO(β)→LUMO+3(β)(0.53)	Ru1(dπ)/acac(π)/L(π)→L(π*)/Ru1(dπ)
	1303 (0.06)	SOMO(α)→LUMO(α)(0.74)	L(π)/acac(π)→Ru3(dπ)/L(π*)
	1122 (0.05)	HOMO(β)→LUMO+1(β)(0.54)	Ru1(dπ)/acac(π)/L(π)→L(π*)/Ru2(dπ)
	1051 (0.03)	SOMO1(α)→LUMO+1(α)(0.53)	L(π)/acac(π)→L(π*)
700sh	646 (0.03)	SOMO1(α)→LUMO+2(α)(0.62)	L(π)/acac(π)→L(π*)
	620 (0.03)	HOMO−2(α)→LUMO+1(α)(0.78)	acac(π)/Ru1(dπ)→L(π*)
572 (31250)	567 (0.09)	HOMO−5(α)→LUMO(α)(0.52)	Ru3(dπ)/acac(π)→Ru3(dπ)/ L(π*)
	421 (0.04)	HOMO−1(α)→LUMO+2(α)(0.39) HOMO−12(α)→LUMO(α)(0.30)	acac(π)/Ru1(dπ)→L(π*) acac(π)→Ru3(dπ)/L(π*)
	381 (0.04)	HOMO−5(β)→LUMO+3(β)(0.42) HOMO−17(β)→LUMO(β)(0.25)	acac(π)/Ru3(dπ)→L(π*) L(π)/acac(π)→Ru2(dπ)/L(π*)
329 (62600)	369 (0.02)	HOMO−15(α)→LUMO+1(α)(0.50) HOMO−18(β)→LUMO+2(β)(0.20)	Ru2(dπ)/acac(π)/L(π)→L(π*) acac(π)/L(π)→L(π*)/Ru1(dπ)
		1^{2+} (*S*=1)	
	2902 (0.003)	HOMO(β)→LUMO+2(β)(0.51)	acac(π)/Ru3(dπ)/L(π)→Ru2(dπ)/acac(π*)
	2491 (0.003)	HOMO(β)→LUMO+2(β)(0.55)	acac(π)/Ru3(dπ)/L(π)→Ru1(dπ)/acac(π*)
	1794 (0.005)	HOMO(β)→LUMO+1(β)(0.36) HOMO−(β)→LUMO+1(β)(0.24)	acac(π)/Ru3(dπ)/L(π)→L(π*) acac(π)/Ru1(dπ)→L(π*)
	1494 (0.03)	HOMO(β)→LUMO(β)(0.90)	acac(π)/Ru3(dπ)/L(π)→L(π*)/Ru3(dπ)/acac(π*)
	961 (0.01)	HOMO(β)→LUMO+1(β)(0.78)	acac(π)/Ru3(dπ)/L(π)→L(π*)
	866 (0.02)	HOMO(β)→LUMO+3(β)(0.59)	acac(π)/Ru3(dπ)/L(π)→Ru1(dπ)/acac(π*)
654 (21870)	695 (0.11)	HOMO−3(α)→LUMO(α)(0.30) HOMO(β)→LUMO+4(β)(0.34)	acac(π)→L(π*)/Ru3(dπ) acac(π)/Ru3(dπ)/L(π)→L(π*)
	618 (0.07)	HOMO−6(β)→LUMO(β)(0.39)	acac(π)/Ru1(dπ)→L(π*)/Ru3(dπ)/acac(π*)

584sh	587 (0.04)	HOMO−9(α)→LUMO(α)(0.39) HOMO−11(β)→LUMO+1(β)(0.26)	Ru1(dπ)/ acac(π)→L(π*)/Ru3(dπ) acac(π)/Ru3(dπ)/L(π)→L(π*)
	509 (0.02)	HOMO−5(α)→LUMO+1(α)(0.47)	Ru3(dπ)/acac(π)→L(π*)
358 (48500)	374 (0.01)	HOMO−13(β)→LUMO+3(β)(0.32) HOMO−14(β)→LUMO+2(β)(0.21)	acac(π)/Ru3(dπ)/L(π)→Ru3(dπ)/acac(π*) acac(π)/L(π)→Ru2(dπ)/acac(π*)
1^{-} (*S*=1/2)			
	3198 (0.01)	SOMO(α)→LUMO(α)(0.90)	L(π)→L(π*)
	2007 (0.01)	HOMO (β)→LUMO+1(β)(0.69)	Ru3(dπ)/acac(π)→L(π*)/Ru2(dπ)/ Ru3(dπ)
1800 (2500)	1638 (0.02)	HOMO−2(β)→LUMO+1(β)(0.64) HOMO−1(β)→LUMO+1(β)(0.58)	Ru2(dπ)/Ru3(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru3(dπ) Ru2(dπ)/acac(π)→L(π*)/Ru2(dπ)/ Ru3(dπ)
	1433 (0.03)	HOMO−2(β)→LUMO+1(β)(0.51)	Ru2(dπ)/Ru3(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru3(dπ)
	1142 (0.012)	HOMO(β)→LUMO(β)(0.63)	Ru3(dπ)/acac(π)→L(π*)
	915 (0.11)	HOMO−5(β)→LUMO+1(β)(0.48) HOMO−9(α)→LUMO(α)(0.37)	Ru2(dπ)/Ru3(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru3(dπ) Ru1(dπ)/acac(π)→L(π*)
691 (29050)	666 (0.12)	HOMO−9(α)→LUMO(α)(0.73)	Ru1(dπ)/acac(π)→L(π*)
561 (15320)	574 (0.11)	HOMO−2(α)→LUMO+1(α)(0.67)	Ru2(dπ)/Ru3(dπ)/acac(π)→L(π*)
	463 (0.05)	HOMO−14(β)→LUMO(β)(0.36) HOMO−8(β)→LUMO+2(β)(0.30)	acac(π)→L(π*) Ru1(dπ)/acac(π)→L(π*)
	403 (0.04)	HOMO−21(α)→LUMO(α)(0.31) HOMO−1(β)→LUMO+7(β)(0.26)	L(π)/acac(π)→L(π*) Ru2(dπ)/acac(π)→L(π*)
370sh	389 (0.03)	HOMO−15(β)→LUMO(β)(0.52)	L(π)→L(π*)
1^{2-} (*S*=1)			
	1590 (0.01)	HOMO(β)→LUMO(β)(0.85)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
	1269 (0.02)	SOMO1(α)→LUMO(α)(0.70)	L(π)→L(π*)
	1089 (0.04)	SOMO2(α)→LUMO(α)(0.70)	L(π)→L(π*)
976sh	979 (0.10)	SOMO2(α)→LUMO(α)(0.66)	L(π)→L(π*)
811 (20400)	905 (0.24)	HOMO(β)→LUMO+1(β)(0.36) HOMO(β)→LUMO(β)(0.36)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*) Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
	836 (0.02)	HOMO−5(β)→LUMO(β)(0.53) HOMO−4(β)→LUMO+2(β)(0.46)	Ru3(dπ)/acac(π)/Ru1(dπ)→L(π*) Ru1(dπ)→L(π*)

710 (20250)	647 (0.04)	HOMO−3(α)→LUMO(α)(0.74)	Ru2(dπ)/Ru3(dπ)/acac(π)→L(π*)
	589 (0.10)	HOMO(β)→LUMO+2(β)(0.87)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
	520 (0.04)	SOMO1(α)→LUMO+7(α)(0.40) HOMO−3(β)→LUMO+2(β)(0.34)	L(π)→L(π*) Ru3(dπ)/acac(π)→L(π*)
450sh	421 (0.12)	SOMO2(α)→LUMO+7(α)(0.56)	L(π)→L(π*)
	382 (0.05)	HOMO−5(α)→LUMO+3(α)(0.53)	Ru1(dπ)→acac(π*)
338 (46400)	361 (0.013)	HOMO−12(α)→LUMO(α)(0.32) SOMO1(α)→LUMO+12(α)(0.21) HOMO−18(β)→LUMO(β)(0.19)	acac(π)→L(π*) L(π)→L(π*)/acac(π*)/Ru1(dπ) L(π)→L(π*)

[a]From OTTLE spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6. [b]In nm. [c]Molar extinction coefficients in $dm^3\ mol^{-1}\ cm^{-1}$. [d]Calculated oscillator strengths.

Table S24 Experimental and TD-DFT ((U)B3LYP/CPCM/CH_3CN) calculated electronic transitions for **2**^{n}

λ_{max} [a, b] (expt.) (ε/dm^3 mol^{-1}cm^{-1}) [c]	λ [b] (DFT) (f) [d]	Transitions	Character
		2 (S=0)	
	1032 (0.01)	HOMO–3→LUMO+1(0.60)	Ru2(dπ)/acac(π)→L(π*)/Ru1(dπ)/Ru2(dπ)
1290(sh)	1020 (0.10)	HOMO–1→LUMO+1(0.58)	Ru1(dπ)/acac(π)/Ru2(dπ)→L(π*)/Ru2(dπ)/Ru1(dπ)
	983 (0.11) 816 (0.11)	HOMO–4→LUMO(0.55) HOMO–10→LUMO(0.63)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)/Ru1(dπ)/Ru2(dπ) Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)/Ru1(dπ)/Ru2(dπ)
673 (39850)	688 (0.13) 671 (0.11) 617 (0.15)	HOMO–9→LUMO+1(0.64) HOMO→LUMO+2(0.45) HOMO–12→LUMO(0.57)	Ru2(dπ)/acac(π)/Ru1(dπ)→L(π*)/Ru2(dπ)/Ru1(dπ) Ru1(dπ)/acac(π)/Ru2(dπ)→L(π*) acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
345 (65440)	348 (0.52)	HOMO–26→LUMO+1(0.54) HOMO–1→LUMO+3(0.36)	L(π)→L(π*)/Ru2(dπ)/ Ru1(dπ) Ru1(dπ)/acac(π)/Ru2(dπ)→acac(π*)
		2 (S=1)	
	3525 (0.006)	HOMO(β)→LUMO(β) (0.60)	Ru2(dπ)/L(π)/acac(π)→Ru1(dπ)/acac(π*)
	3277 (0.007)	HOMO(β)→LUMO+1(β) (0.50) HOMO–1(β)→LUMO+1(β) (0.41)	Ru2(dπ)/L(π)/acac(π)→Ru1(dπ)/L(π*) L(π)/Ru2(dπ)/ acac(π)→Ru1(dπ)/acac(π*)
	1659 (0.03)	HOMO(β)→LUMO(β) (0.58)	Ru2(dπ)/L(π)/acac(π)→Ru1(dπ)/acac(π*)
1290(sh)	1220 (0.03)	HOMO–3(β)→LUMO(β) (0.47) HOMO(β)→LUMO(β) (0.41)	Ru2(dπ)/ acac(π)→Ru1(dπ)/acac(π*) Ru2(dπ)/L(π)/acac(π)→Ru1(dπ)/acac(π*)
	1075 (0.03)	HOMO(β)→LUMO+2(β) (0.43) HOMO–1(β)→LUMO+2(β) (0.41)	Ru2(dπ)/L(π)/acac(π)→L(π*)/Ru2(dπ)/ Ru1(dπ) L(π)/Ru2(dπ)/acac(π)→L(π*)/Ru2(dπ)/ Ru1(dπ)
	949 (0.03)	HOMO–2(α)→LUMO(α) (0.64) HOMO–3(α)→LUMO+2(α) (0.43)	Ru2(dπ)/acac(π)/L(π)→L(π*)Ru2(dπ)/acac(π*) Ru2(dπ)/acac(π)→L(π*)Ru2(dπ)/acac(π*)
	816 (0.05)	SOMO1(α)→LUMO+1(α) (0.75)	L(π)/Ru2(dπ)/acac(π)→L(π*)
	716 (0.06)	HOMO–6(β)→LUMO(β) (0.54) HOMO(β)→LUMO+3(β) (0.48)	Ru2(dπ)/acac(π)→Ru1(dπ)/acac(π*) Ru2(dπ)/L(π)/acac(π)→L(π*)
673 (39850)	604 (0.02)	HOMO–5(β)→LUMO+2(β) (0.45) HOMO–8(β)→LUMO(β) (0.36)	Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/ Ru1(dπ) Ru2(dπ)/ Ru1(dπ) acac(π)→Ru1(dπ)/acac(π*)

345 (65440)	454 (0.04)	HOMO−6(β)→LUMO+3(β) (0.63)	Ru2(dπ)/acac(π)→L(π*)
2^{+} (*S*=1/2)			
	3348 (0.02)	HOMO−1(β)→LUMO(β)(0.52)	Ru2(dπ)/acac(π)→L(π*)/Ru1(dπ)
	2016 (0.01)	SOMO(α)→LUMO(α)(0.53) HOMO−2(β)→LUMO+2(β)(0.51)	L(π)/Ru2(dπ)→ Ru2(dπ)/L(π*) Ru2(dπ)/acac(π)→Ru1(dπ)/ acac(π*)
1700 (br, 3230)	1703 (0.002)	HOMO−1(β)→LUMO+2(β)(0.48)	Ru2(dπ)/acac(π)→Ru1(dπ)/ acac(π*)
	1409 (0.02)	HOMO−2(α)→LUMO(α)(0.54)	Ru2(dπ)/acac(π)→Ru2(dπ)/L(π*)
	1161 (0.07)	HOMO−2(α)→LUMO(α)(0.64)	Ru2(dπ)/acac(π)→Ru2(dπ)/L(π*)
	1066 (0.05)	SOMO(α)→LUMO+1(α)(0.66)	L(π)/Ru2(dπ)→ Ru2(dπ)/L(π*)
800(sh)	744 (0.09)	HOMO−3(α)→LUMO(α)(0.49) HOMO−2(α)→LUMO+1(α)(0.44)	Ru2(dπ)/L(π)→Ru2(dπ)/L(π*) Ru2(dπ)/acac(π)→Ru2(dπ)/L(π*)
	712 (0.02)	HOMO−2(β)→LUMO+1(β)(0.76)	Ru2(dπ)/acac(π)→L(π*)/Ru1(dπ)
617 (32610)	692 (0.08)	HOMO−5(β)→LUMO+2(β)(0.42) HOMO−5(α)→LUMO(α)(0.40)	acac(π)→Ru1(dπ)/acac(π*) Ru2(dπ)/acac(π)→Ru2(dπ)/L(π*)
	513 (0.05)	HOMO−2(β)→LUMO+3(β)(0.46) HOMO−12(α)→LUMO+1(α)(0.32)	Ru2(dπ)/acac(π)→L(π*) Ru1(dπ)/acac(π)→Ru2(dπ)/L(π*)
331 (59630)	416 (0.01)	HOMO−7(β)→LUMO+3(β)(0.61)	acac(π)→L(π*)
2^{2+} (*S*=1)			
1186 (8870)	1301 (0.11) 950 (0.02)	HOMO(β)→LUMO(β)(0.69) SOMO1(α)→LUMO+1(α)(0.70)	L(π)/Ru1(dπ)/Ru2(dπ)→L(π*)/Ru2(dπ) L(π)/Ru1(dπ)→ Ru1(dπ)/acac(π*)
608 (22810)	709 (0.04)	HOMO−2(β)→LUMO(β)(0.61) HOMO−3(β)→LUMO(β)(0.52)	acac(π)/Ru1(dπ)/Ru2(dπ)→L(π*) acac(π)/Ru2(dπ)→L(π*)
	650 (0.02)	HOMO−6(β)→LUMO (β)(0.48) HOMO−4(α)→LUMO(α)(0.45)	acac(π)/Ru2(dπ)/Ru1(dπ)→L(π*) Ru1(dπ)/acac(π)→L(π*)
	616 (0.03)	HOMO−5(α)→LUMO(α)(0.52)	acac(π)/Ru2(dπ)/Ru1(dπ)→L(π*)
	602 (0.06)	HOMO−7(β)→LUMO(β)(0.52)	Ru1(dπ)/acac(π)/Ru2(dπ)→L(π*)
454 (19340)	435 (0.04)	HOMO−2(β)→LUMO+4(β)(0.60)	acac(π)/Ru2(dπ)/Ru1(dπ)→L(π*)
	431 (0.02)	HOMO−3(α)→LUMO+2(α)(0.35) HOMO−4(α)→LUMO+2(α)(0. 57)	acac(π)/Ru1(dπ)/Ru2(dπ)→L(π*) Ru1(dπ)/acac(π)→L(π*)

350 (69490)	410 (0.02)	HOMO−4(β)→LUMO+4(β)(0.50)	acac(π)/Ru2(dπ)→L(π*)
2^{-} (*S*=1/2)			
	3298 (0.03)	SOMO→LUMO(α)(0. 98)	L(π)/Ru1(dπ)/Ru2(dπ)→L(π*)/Ru2(dπ)/ Ru1(dπ)
1900 (br, 3960)	1823 (0.04)	HOMO−2(β)→LUMO+1(β)(0.62) HOMO−1(β)→LUMO(β)(0.57)	Ru2(dπ)/acac(π)/Ru1(dπ)→L(π*) Ru1(dπ)/Ru2(dπ) acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
940(sh)	1043 (0.13)	HOMO−3(β)→LUMO+1(β)(0.49) HOMO−11(β)→LUMO(β)(0.40)	Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ) Ru2(dπ)/ Ru1(dπ)/L(π)→L(π*)/Ru2(dπ)/ Ru1(dπ)
743 (46500)	752 (0.07) 708 (0.08) 704 (0.06)	HOMO(β)→LUMO+2(β)(0.90) HOMO−1(β)→LUMO+2(β)(0.51) HOMO−5(β)→LUMO+1(β)(0.61)	Ru1(dπ)/acac(π)/L(π)→L(π*) Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ) Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
420(sh)	585 (0.19)	HOMO−3(α)→LUMO+1(α)(0.68)	Ru2(dπ)/acac(π)/Ru1(dπ)→L(π*)
	520 (0.09)	HOMO−16(α)→LUMO(α)(0.49)	acac(π)→L(π*)
		HOMO−5(α)→LUMO+1(α)(0.68)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
370(sh)	440 (0.10)	HOMO−11(α)→LUMO+1(α)(0.62) SOMO(α)→LUMO+2(α)(0.57)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*) L(π)/Ru1(dπ)/Ru2(dπ)→acac(π*)
321 (61420)	401 (0.04)	SOMO(α)→LUMO+10(α)(0.64)	L(π)/Ru1(dπ)/Ru2(dπ)→acac(π*)
2^{2-} (*S*=1)			
	1772 (0.02)	HOMO(β)→LUMO(β)(0.80)	Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
1196 (10870)	1066 (0.22)	SOMO1(α)→LUMO(α)(0.62) HOMO−1(β)→LUMO(β)(0.57)	L(π)→L(π*) Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
	951 (0.15)	HOMO−2(β)→LUMO+1(β)(0.68) HOMO(β)→LUMO(β)(0.57)	Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ) Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
760 (49580)	827 (0.06)	HOMO−6(β)→LUMO+1(β)(0.57)	Ru1(dπ)/L(π)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
	678 (0.08)	HOMO−4(α)→LUMO(α)(0.66)	Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)
	635 (0.09)	HOMO(β)→LUMO+2(β)(0.65)	Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)
435 (36180)	552 (0.24)	HOMO−8(α)→LUMO(α)(0.71)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
	425 (0.03)	HOMO−18(β)→LUMO (β)(0.51)	L(π)/acac(π)→L(π*)/Ru2(dπ)/Ru1(dπ)
	420 (0.09)	SOMO2(α)→LUMO+5(α)(0.51)	L(π)/Ru2(dπ)/Ru1(dπ)→acac(π*)

327 (56650)	413 (0.01)	HOMO−1(β)→LUMO+8(β) (0.52)	Ru1(dπ)/Ru2(dπ)/acac(π)→acac(π*)
2^{3-} (*S*=1/2)			
	4433 (0.04)	HOMO(β)→LUMO(β)(0.99)	L(π)/Ru2(dπ)/Ru1(dπ)→L(π*)
1754 (10860)	1490 (0.003)	HOMO−1(α)→LUMO(α)(0.78)	L(π)/Ru2(dπ)/Ru1(dπ)→L(π*)
1386 (7240)	1345 (0.12)	SOMO(α)→LUMO(α)(0.97)	L(π)/Ru2(dπ)/Ru1(dπ)→acac(π*)
	1240 (0.04)	HOMO−2(β)→LUMO(β)(0.96)	Ru2(dπ)/Ru1(dπ)/acac(π)→L(π*)
998 (13960)	1038 (0.10)	HOMO−4(β)→LUMO(β)(0.95)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
771 (34810)	784 (0.04)	HOMO−11(β)→LUMO(β)(0.91)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
583(sh)	589 (0.02)	HOMO−10(α)→LUMO(α)(0.83)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
	579 (0.21)	HOMO−3(β)→LUMO+1(β)(0.61)	Ru1(dπ)/Ru2(dπ)/acac(π)→L(π*)
500(sh)	484 (0.02)	HOMO−1(α)→LUMO+9(α)(0.57)	L(π)/Ru2(dπ)/Ru1(dπ)→L(π*)
445 (44220)	434 (0.11)	HOMO−12(β)→LUMO+1(β)(0.40)	Ru1(dπ)/Ru2(dπ)/L(π)→L(π*)
	433 (0.11)	HOMO−12 (β)→LUMO+1(β)(0.38) HOMO−3(β)→LUMO+2(β)(0.32)	Ru1(dπ)/Ru2(dπ)/L(π)→L(π*) Ru2(dπ)/Ru1(dπ)/acac(π)→acac(π*)

[a]From OTTLE spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6. [b]In nm. [c]Molar extinction coefficients in $dm^3\ mol^{-1}\ cm^{-1}$. [d]Calculated oscillator strengths.

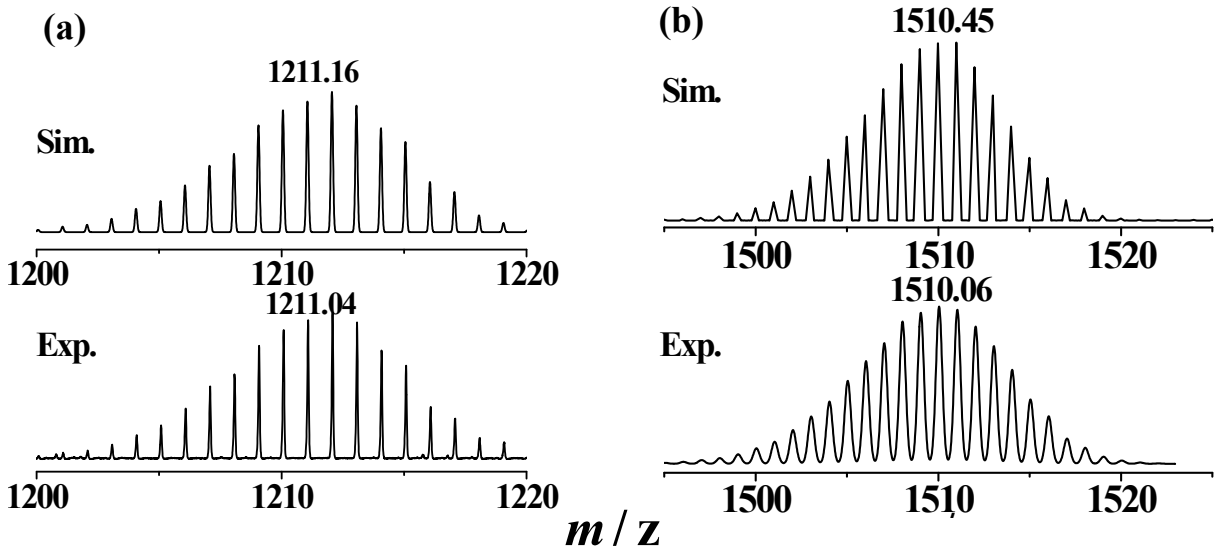


Fig. S1 Experimental and simulated ESI-MS(+) spectra of (a) $\mathbf{1}^+$ and (b) $\mathbf{2}^+$ in CH_3CN.

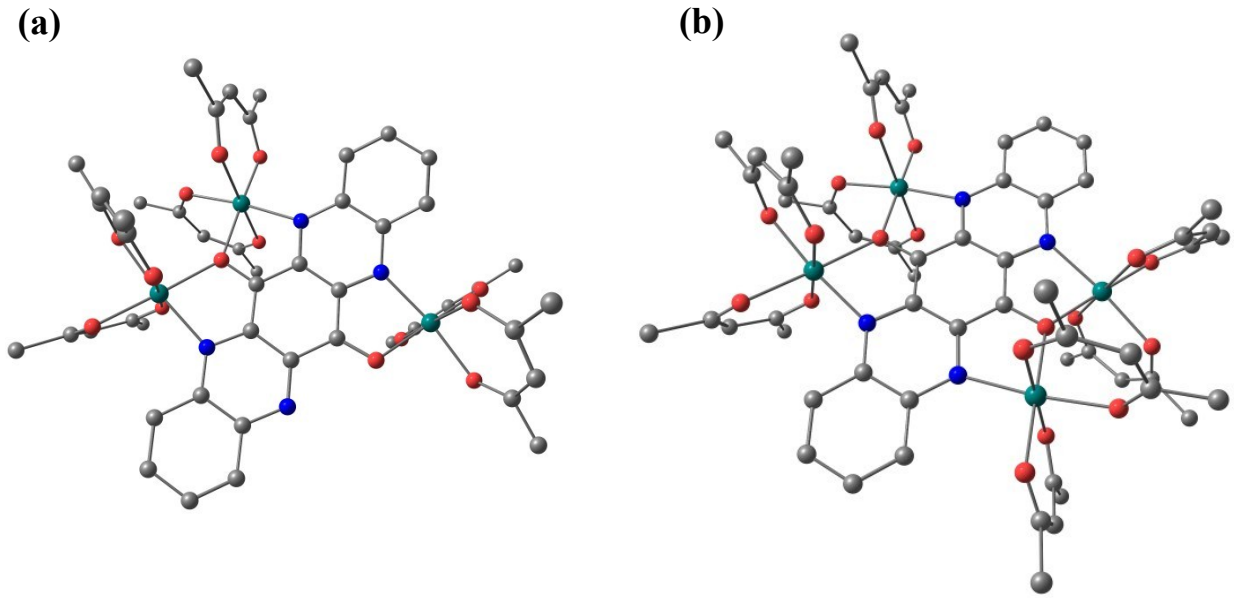


Fig. S2 DFT (B3LYP/LanL2DZ/6-31G*) optimised structures of (a) **1** (*S*=0) and (b) **2** (*S*=0).

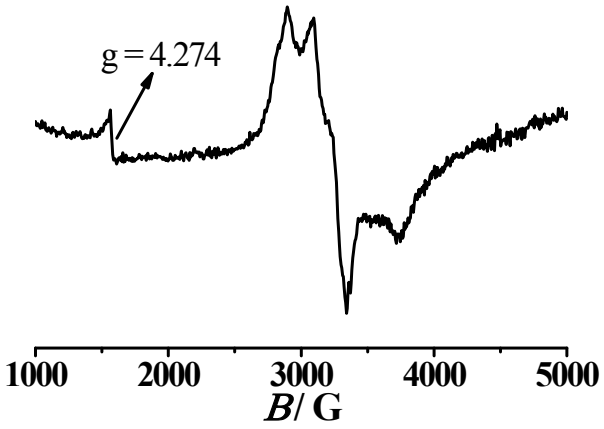


Fig. S3 EPR spectrum of partially oxidised **1** in CH_3CN/Bu_4NPF_6 at 4 K with half-field signal.

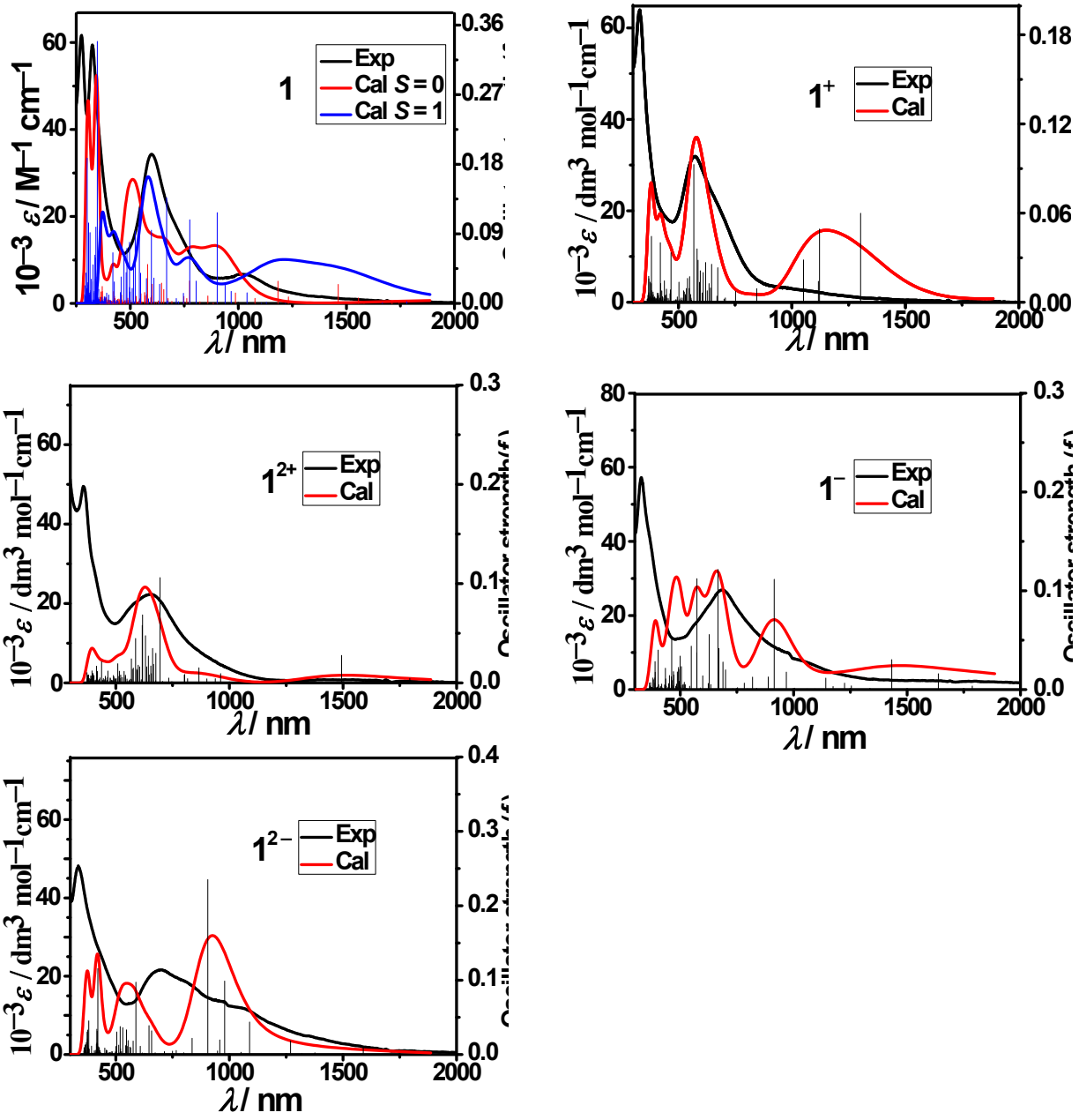


Fig. S4 Experimental (UV-vis-NIR/CH_3CN) and TD-DFT ((U)B3LYP/CPCM/CH_3CN) calculated spectra of $\mathbf{1}^n$. Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of 2000 cm^{-1}.

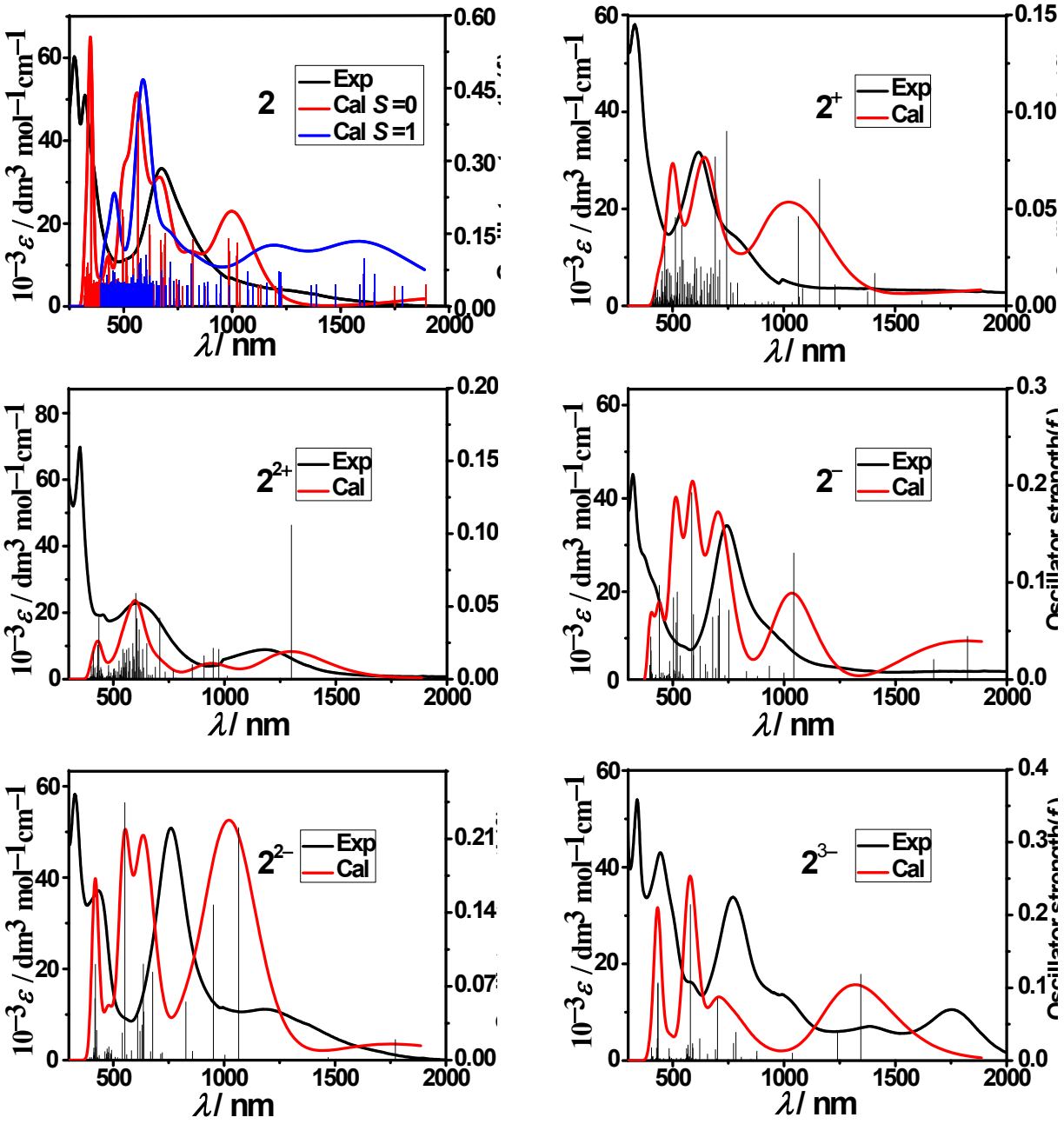


Fig. S5 Experimental (UV-vis-NIR/CH_3CN) and TD-DFT ((U)B3LYP/CPCM/CH_3CN) calculated spectra of $\mathbf{2}^n$. Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of 2000 cm^{-1}.