Supporting Information

A family of Ru(II) complexes built on a novel sexipyridine building block: Synthesis, photophysical properties and the rare structural characterization of a triruthenium species.

Baptiste Laramée-Milette[†], Félix Lussier[†], Ilaria Ciofini[‡*] and Garry S. Hanan[†*]

[†] Département de Chimie, Université de Montréal, Montréal, Québec, Canada, H3T 2B1.

[‡] PSL Research University, Institut de Recherche de Chimie Paris IRCP, CNRS – Chimie ParisTech, 11 rue Pierre et Marie Curie, F-75005 Paris, France.

Table of Contents

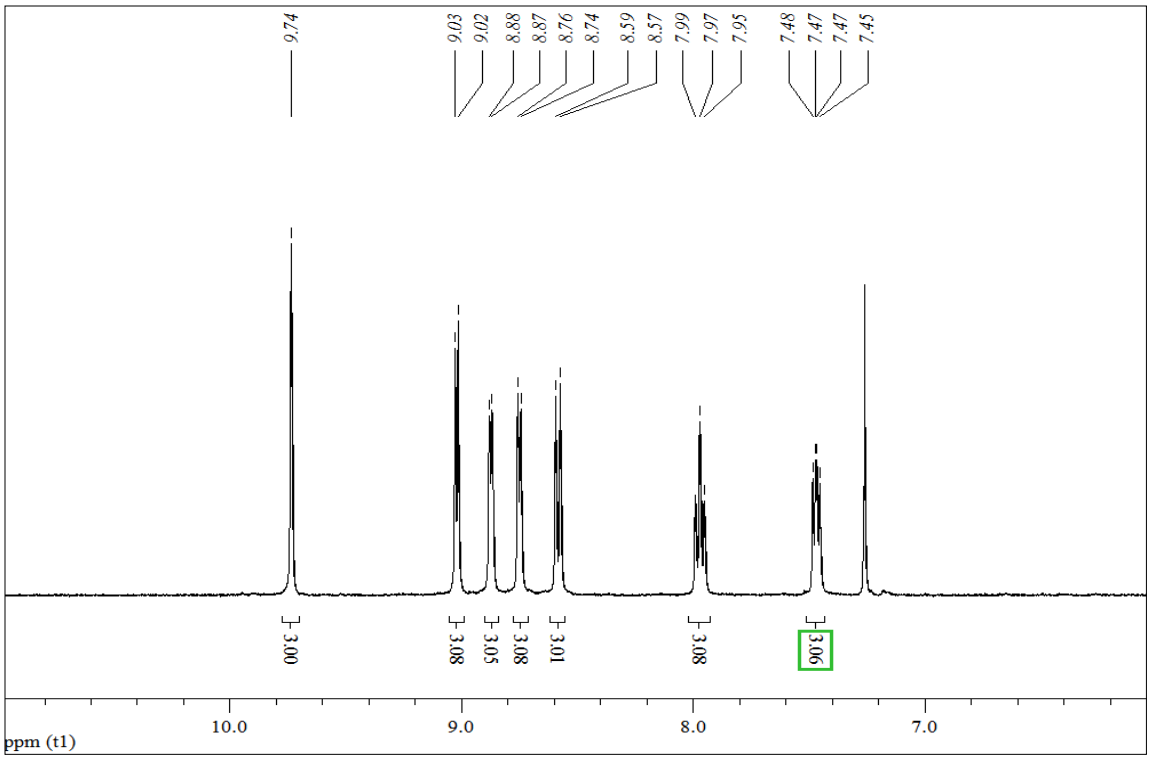

Figure S1. ^{1}H-NMR spectrum (400 MHz) of **L** in $CDCl_3$.

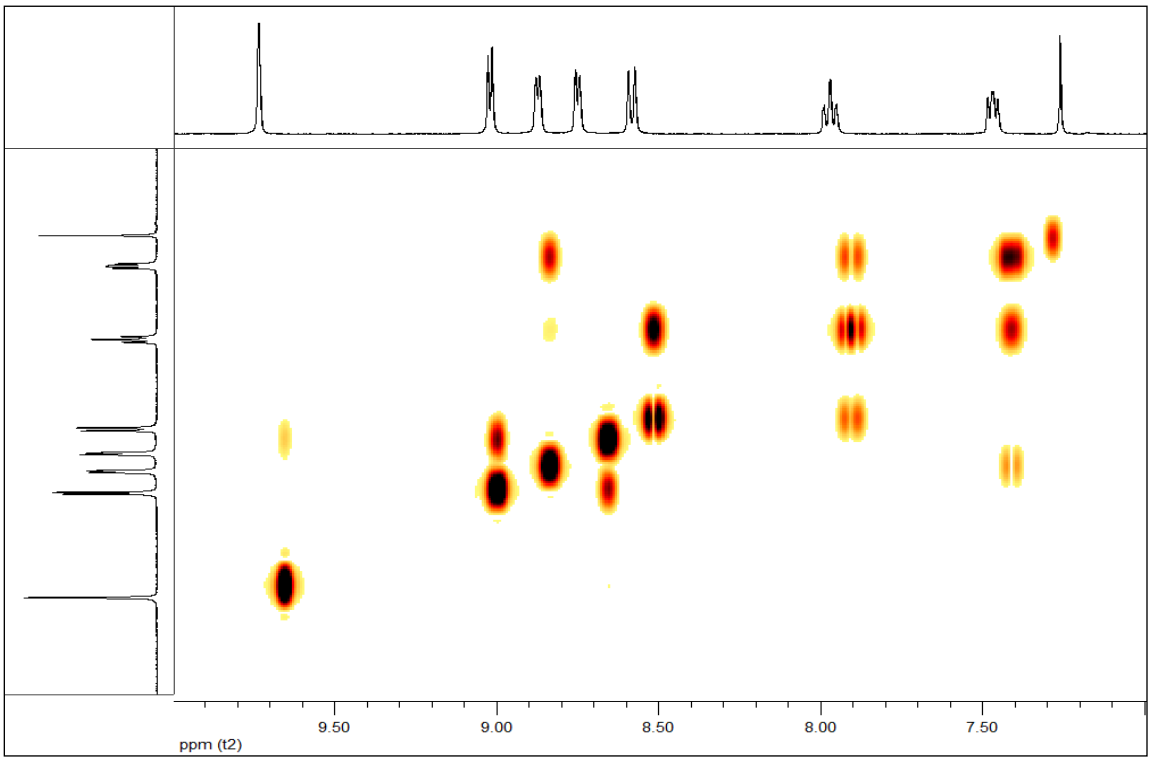

Figure S2. Expanded ^{1}H-^{1}H COSY spectrum (400 MHz) of **L** in $CDCl_3$.

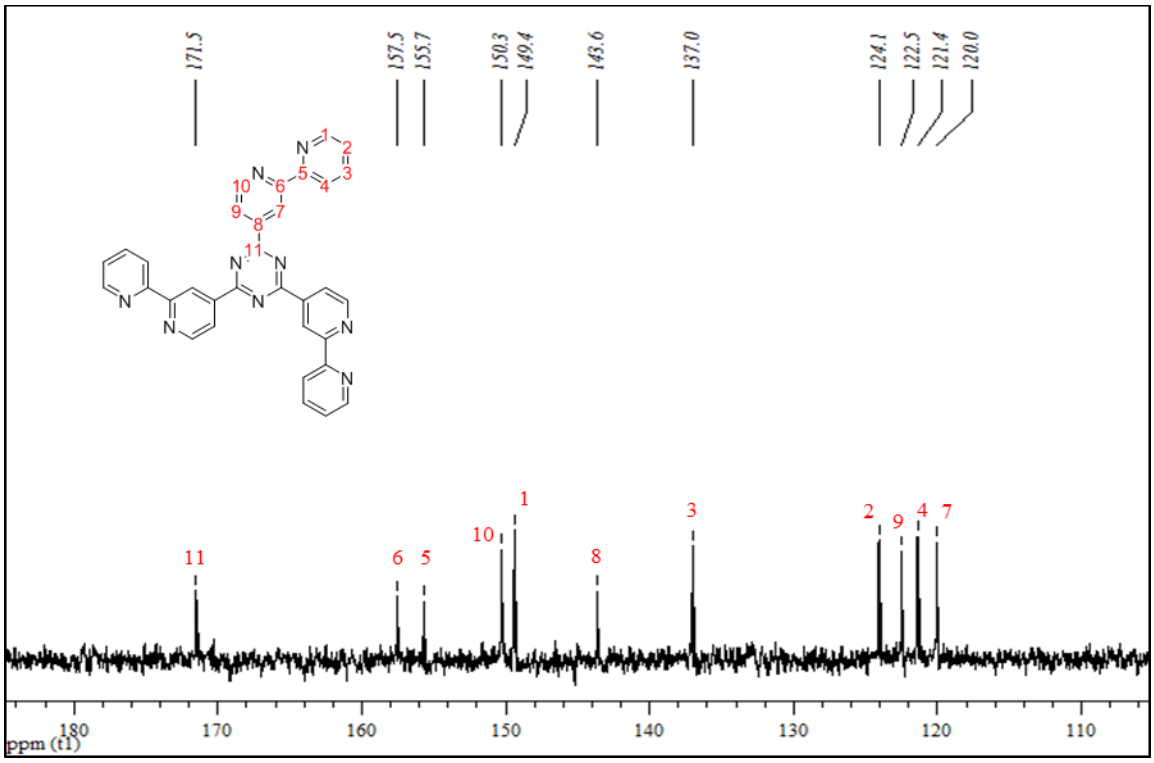

Figure S3. ^{13}C-NMR spectrum (100 MHz) of **L** in $CDCl_3$.

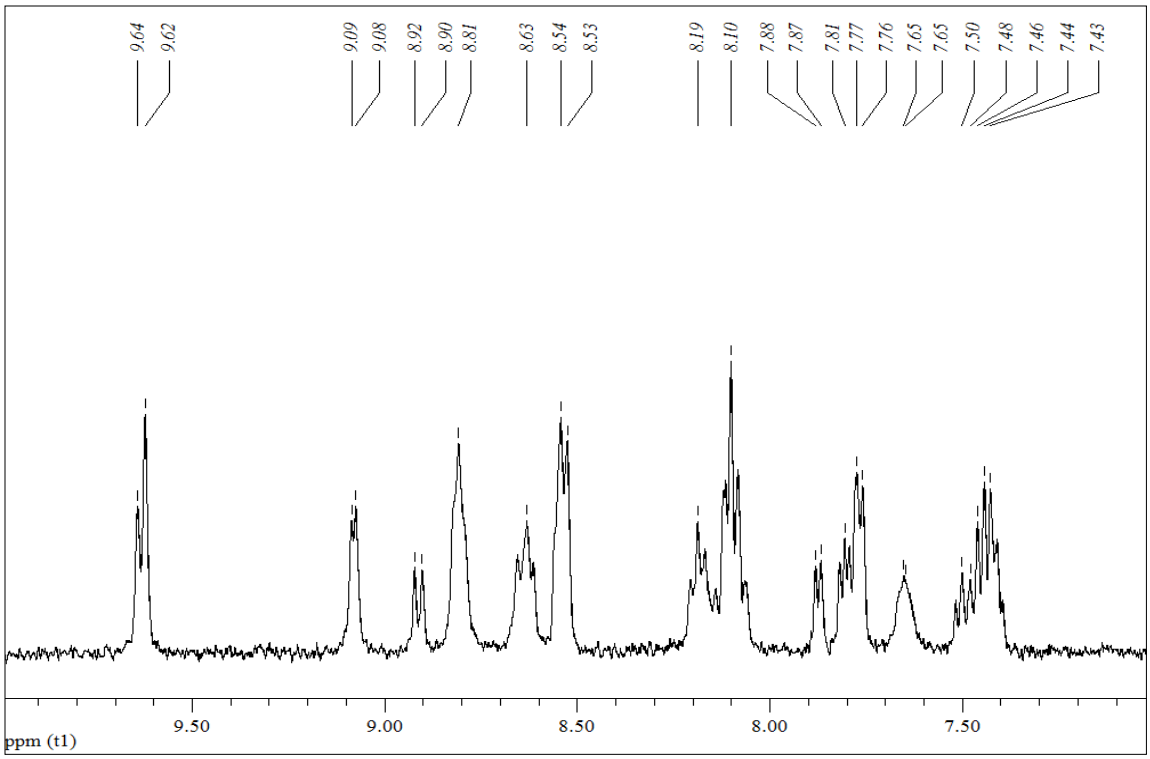

Figure S4. ^{1}H-NMR spectrum (400 MHz) of **[RuL][(PF$_6$)$_2$]** in CD_3CN, at 1mg/mL.

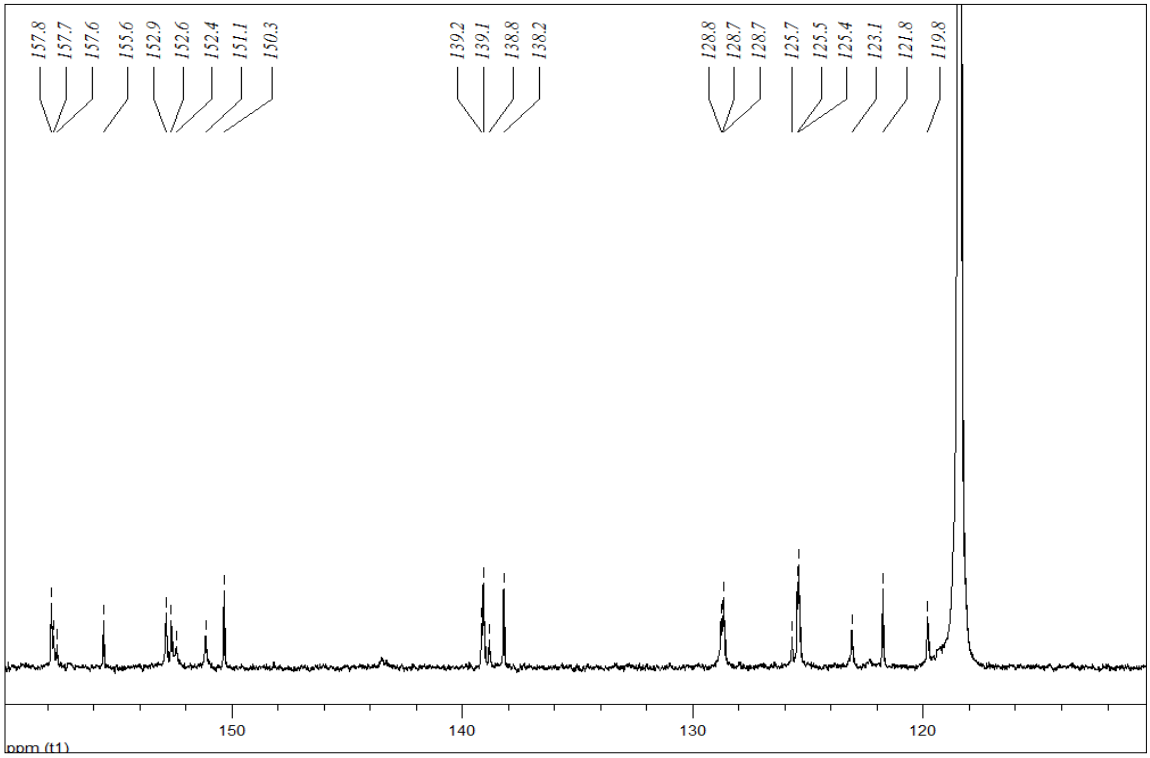

Figure S5. ^{13}C-NMR spectrum (100 MHz) of **[RuL][(PF$_6$)$_2$]** in CD_3CN.

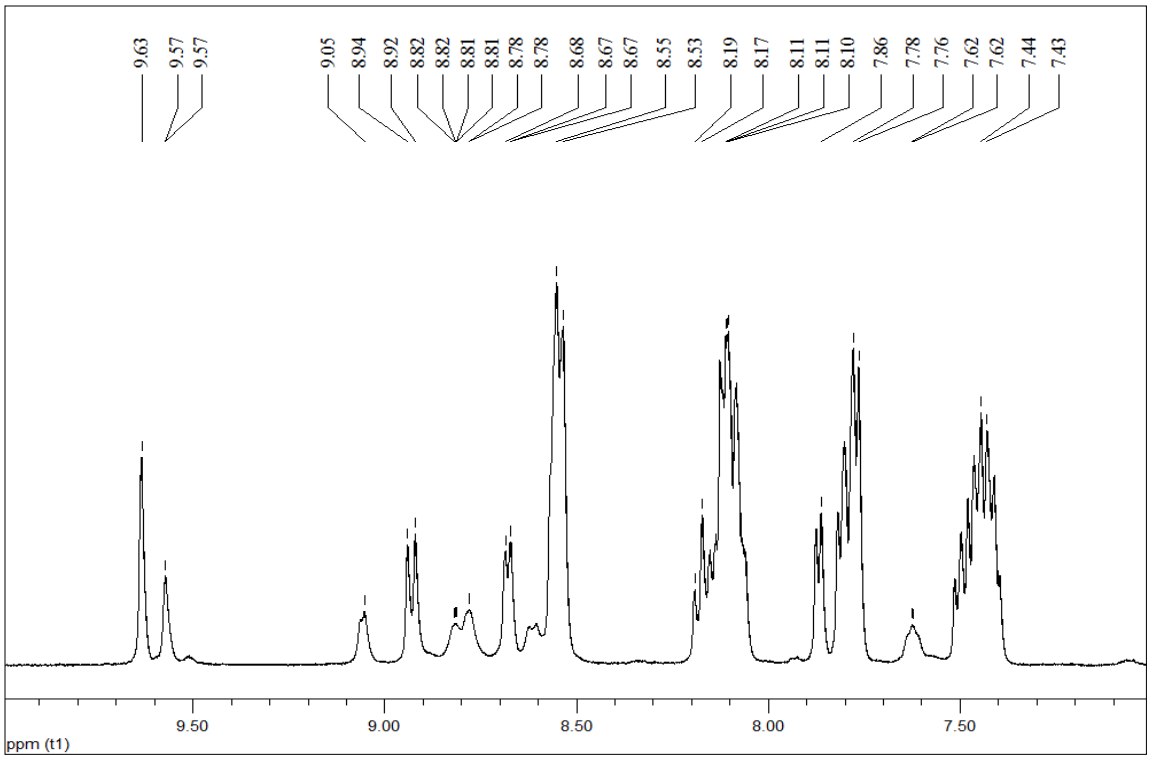

Figure S6. ^{1}H-NMR spectrum (400 MHz) of **[Ru_2L][$(PF_6)_4$]** in CD_3CN.

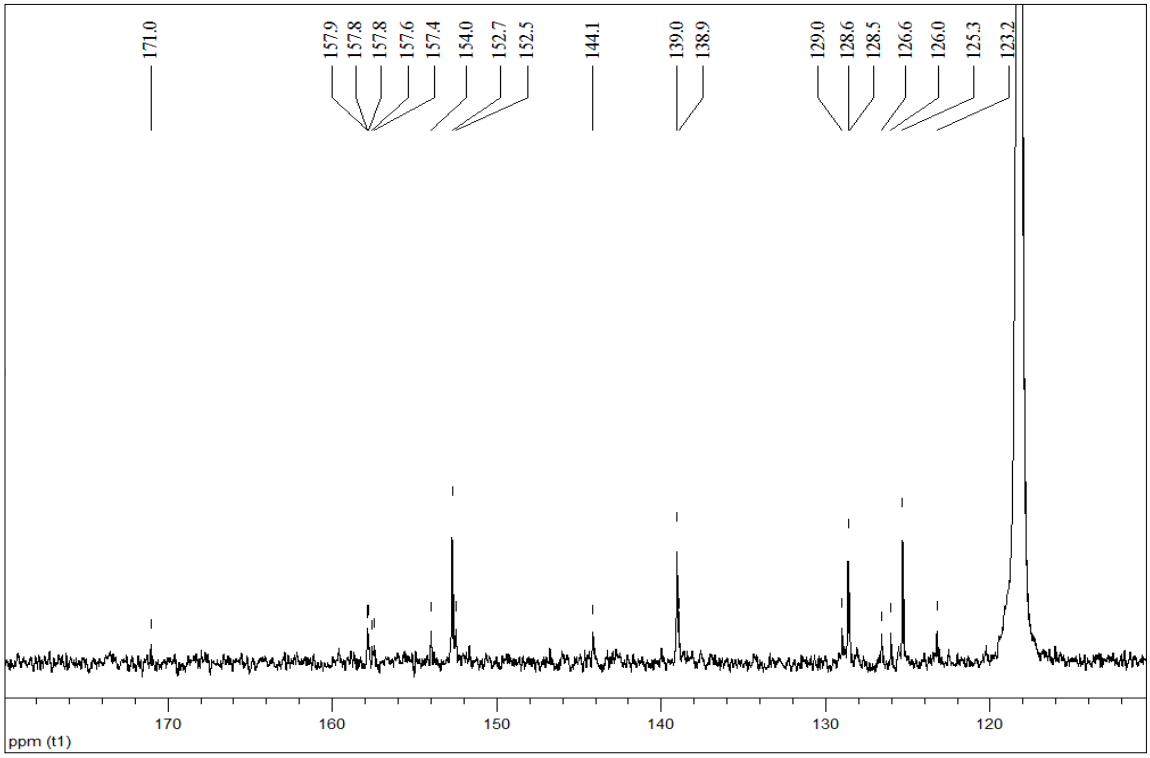

Figure S7. ^{13}C-NMR spectrum (100 MHz) of **[Ru_2L][$(PF_6)_4$]** in CD_3CN.

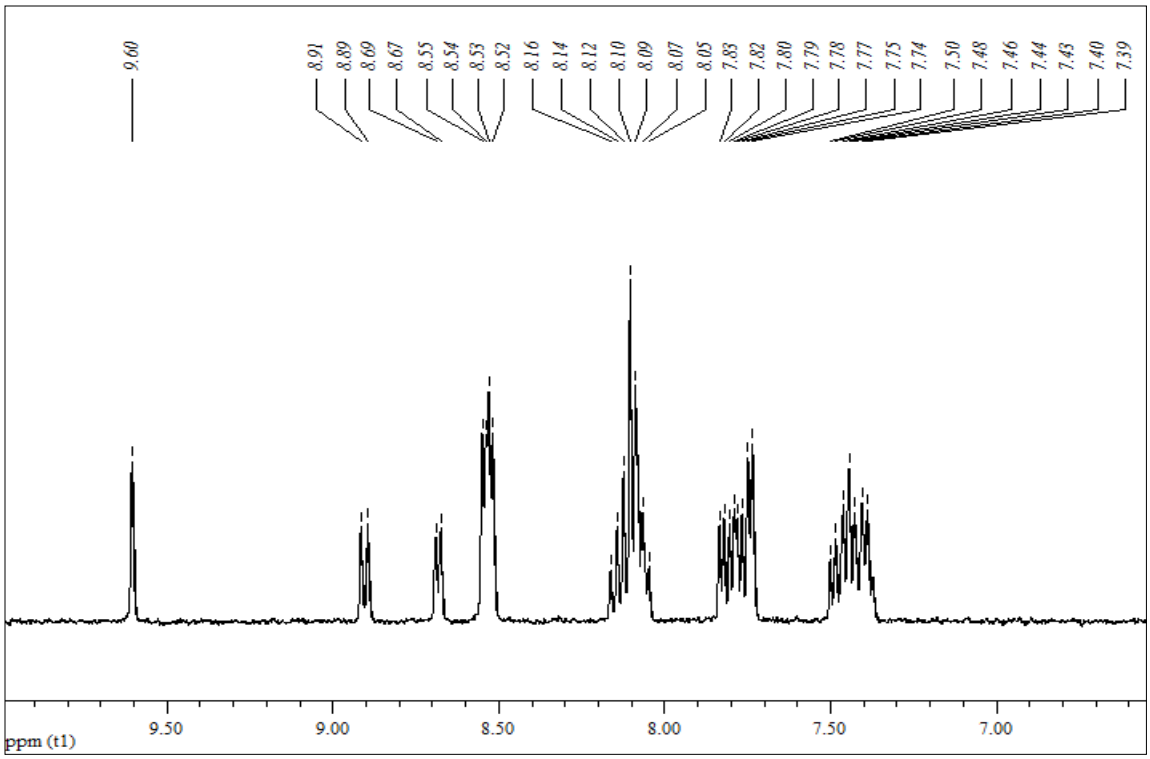

Figure S8. ^{1}H-NMR spectrum (400 MHz) of **[Ru$_3$L][(PF$_6$)$_6$]** in CD_3CN.

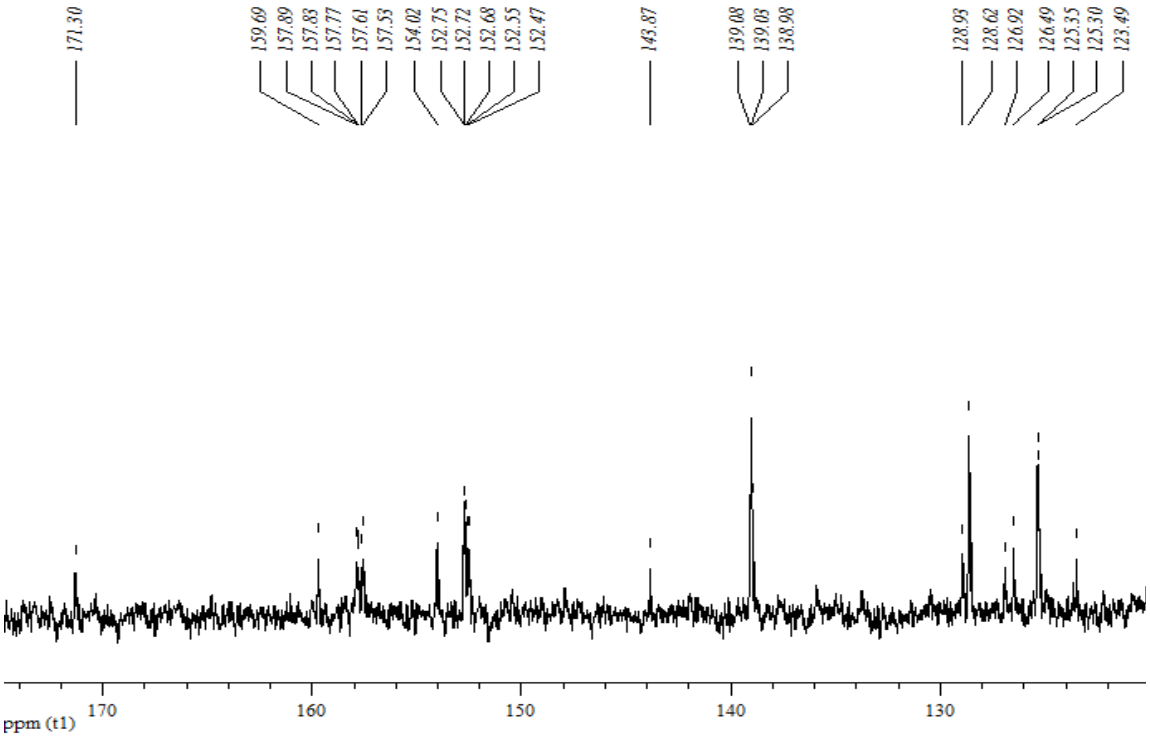

Figure S9. ^{13}C-NMR spectrum (100 MHz) of **[Ru$_3$L][(PF$_6$)$_6$]** in CD_3CN.

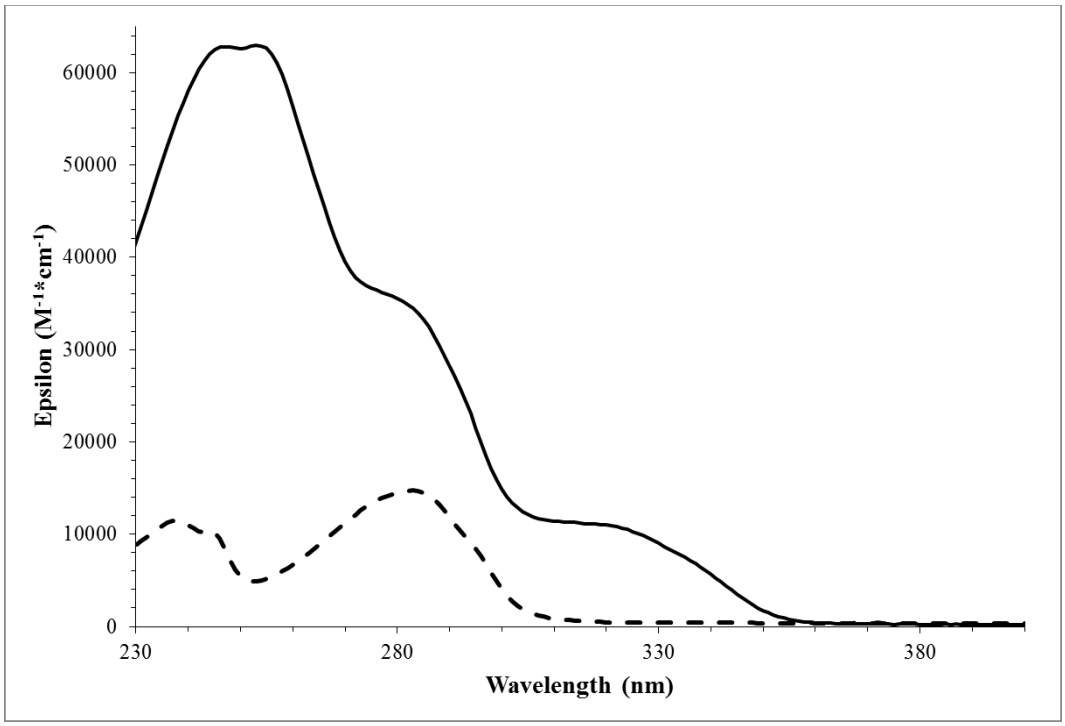

Figure S10 Absorption spectra of ligand **L** (solid) and reference ligand 2,2'-bipyridine (dash) recorded in dichloromethane solution at ambient temperature.

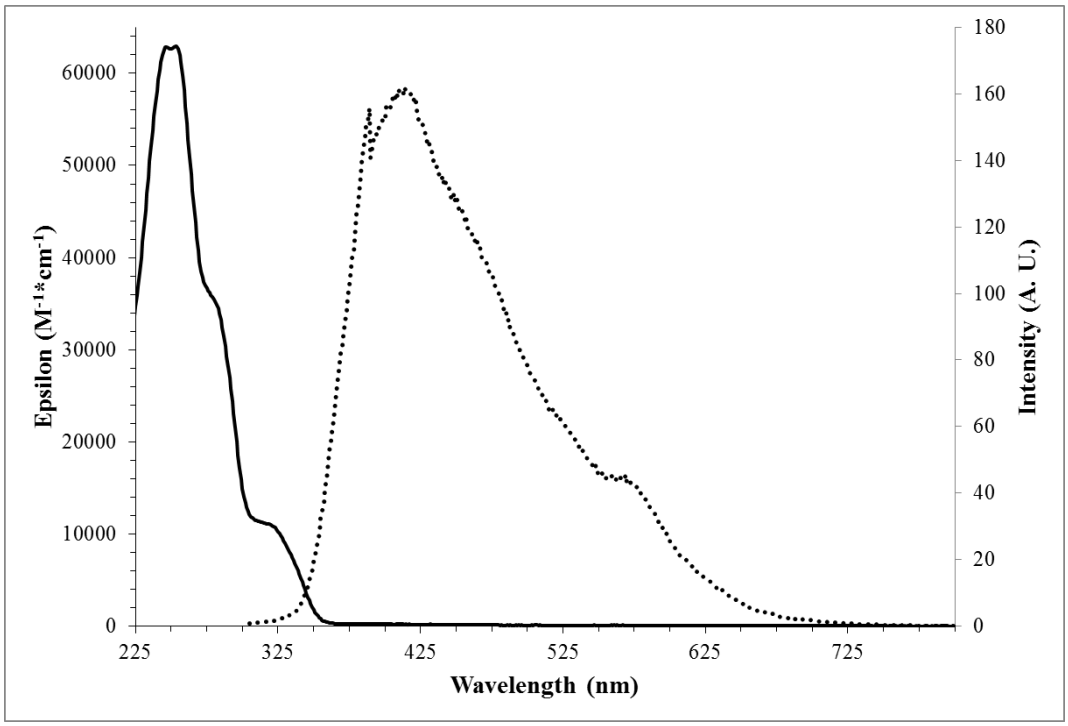

Fig. S11 Comparison of the absorption spectra of ligand **L** (solid line) and its emission spectra (dotted line) recorded in dichloromethane solution at ambient temperature.

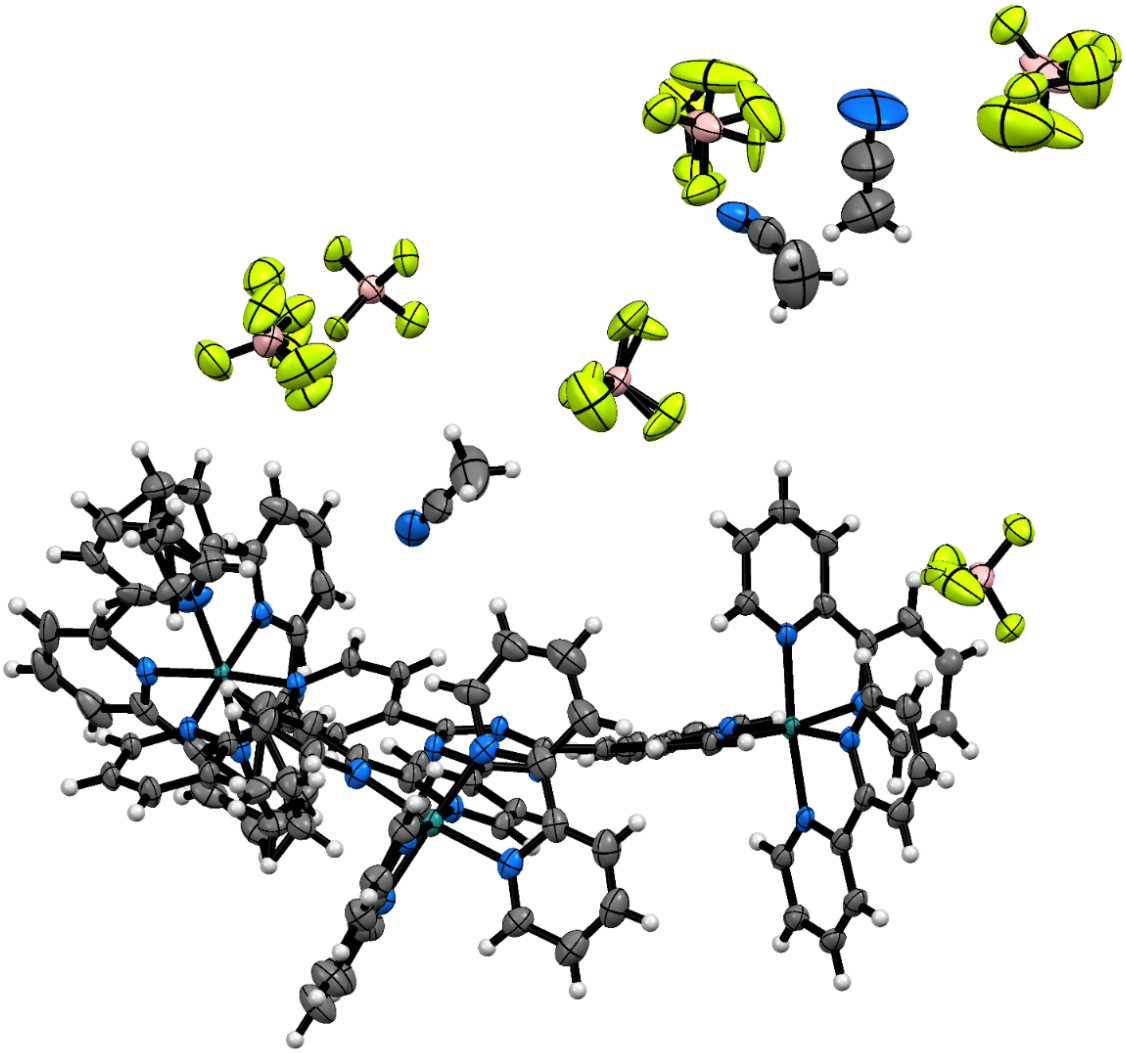

Figure S12. X-Ray structure of **Ru_3L** with the six counter-anions (BF_4, three of them have rotational disorder) and three molecules of solvent (acetonitrile). Thermal ellipsoids are shown with a 30% probability.

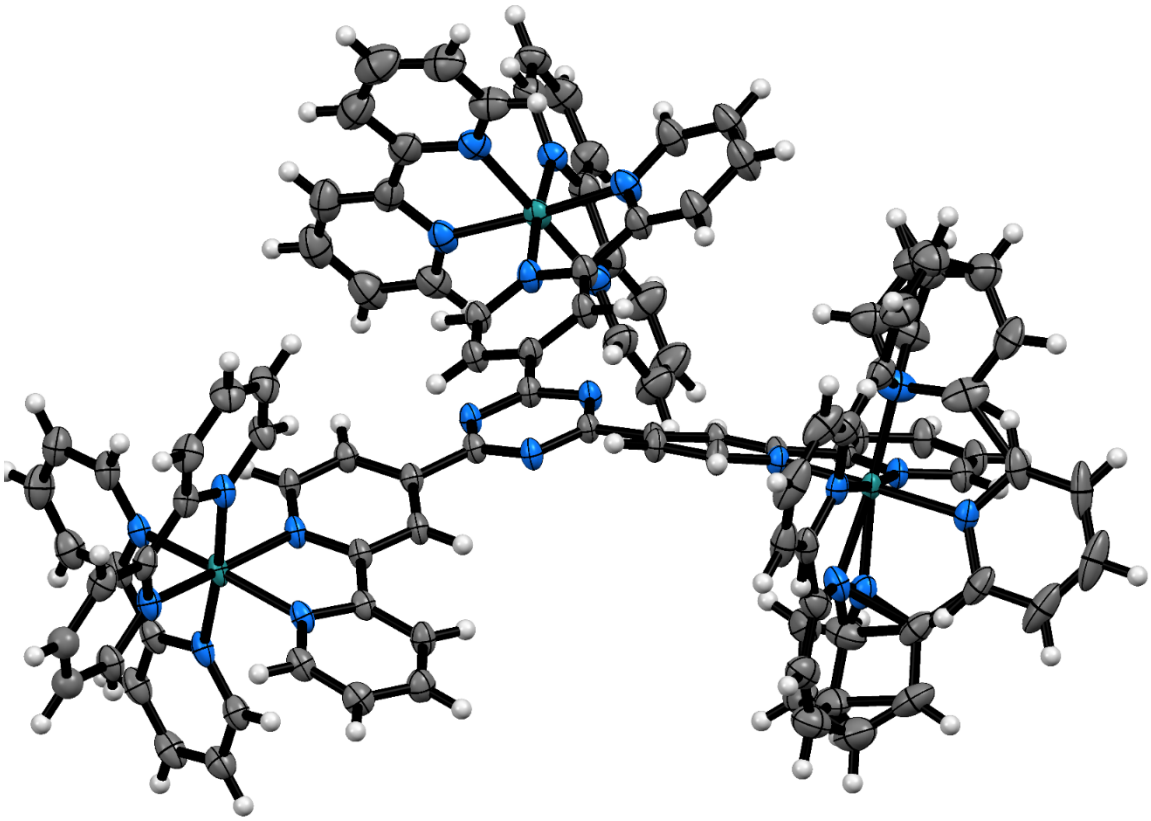

Figure S13. X-Ray structure of **Ru_3L** with emphasis on the disordered ruthenium moiety (right). Thermal ellipsoids are shown with a 30% probability.

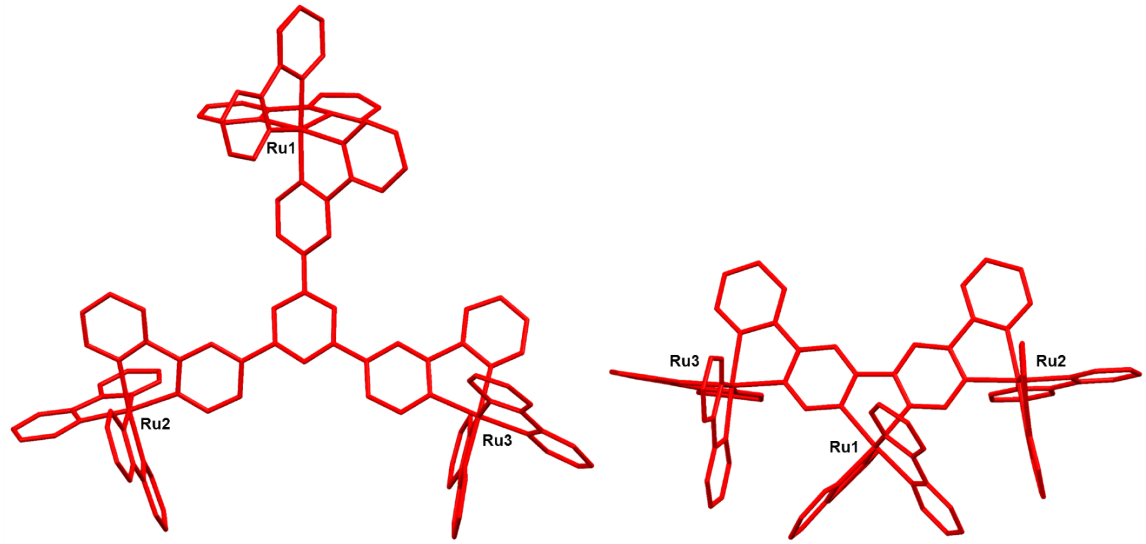

Figure S14. X-Ray crystal structure: Top-view of **Ru_3L** (left) and the reference **triruthenium** species (right). **Ru_3L** metal-to-metal distances: Ru1-Ru2 = 12.77 Å; Ru1-Ru3 = 12.99 Å; Ru2-Ru3 = 13.60 Å. **Triruthenium** metal-to-metal distances: Ru1-Ru2 = 6.11 Å; Ru1-Ru3 = 6.09 Å; Ru2-Ru3 = 11.01 Å.

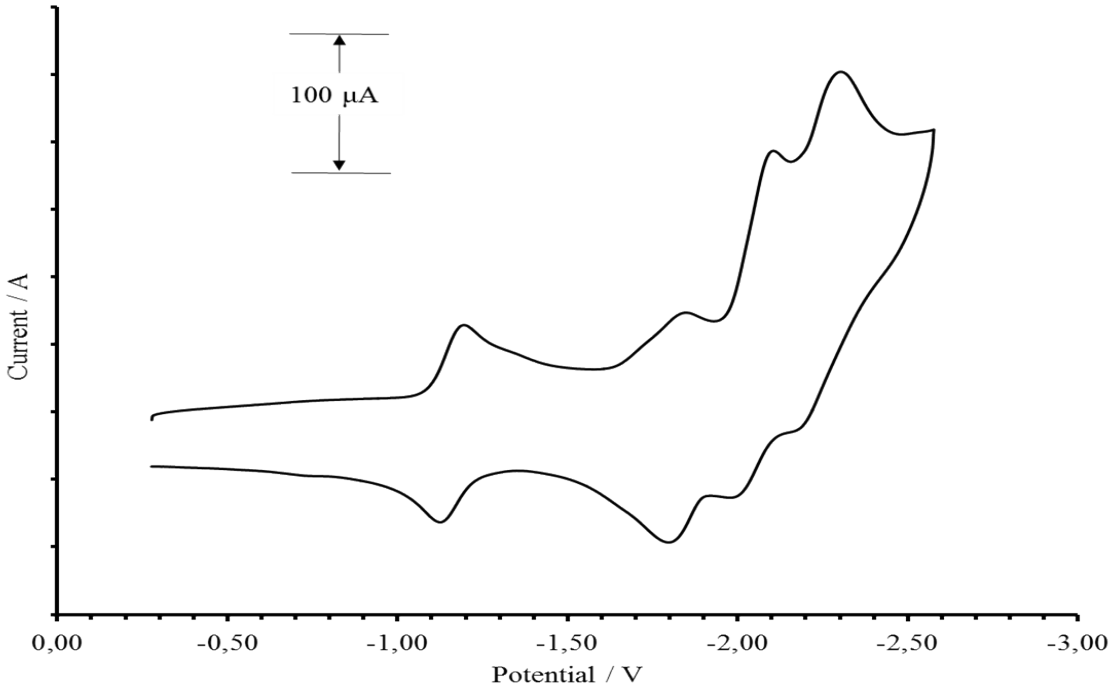

Fig. S15 Cyclic voltammogram of ligand **L** obtained at a scan rate of 500 mV/s. At lower scan rate (25, 50, 100 and 200 mV/s) the second, third and fourth processes are not fully reversible.

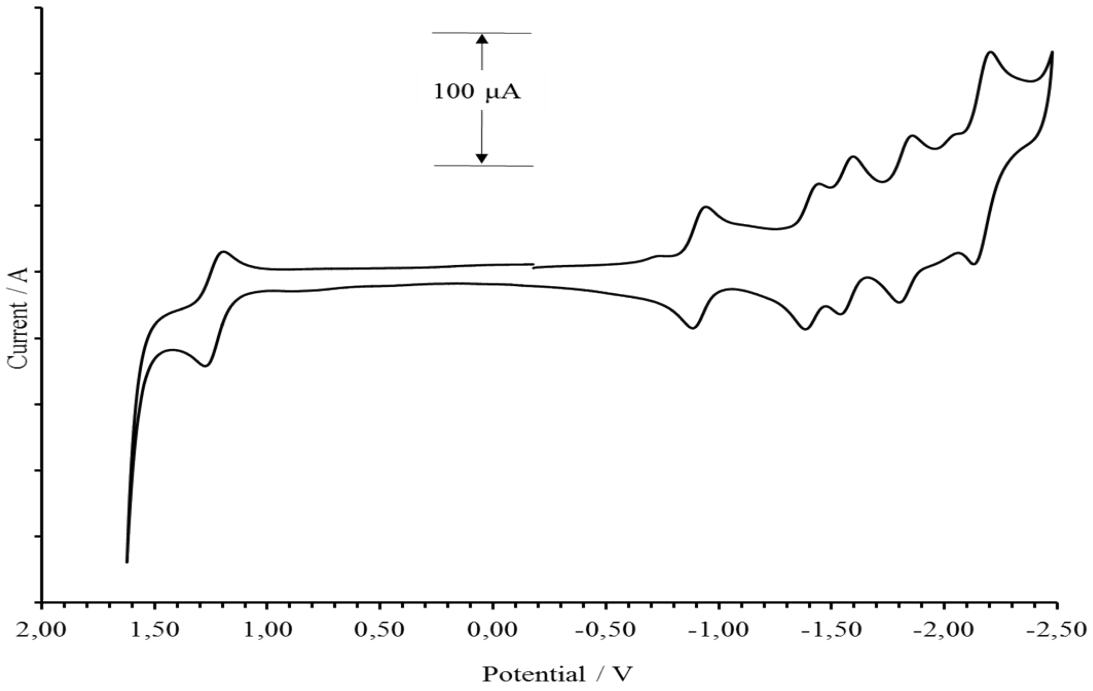

Fig. S16 Cyclic voltammogram of complex **RuL** obtained at a scan rate of 50 mV/s in deaerated DMF, using $TBAPF_6$ as supporting electrolyte.

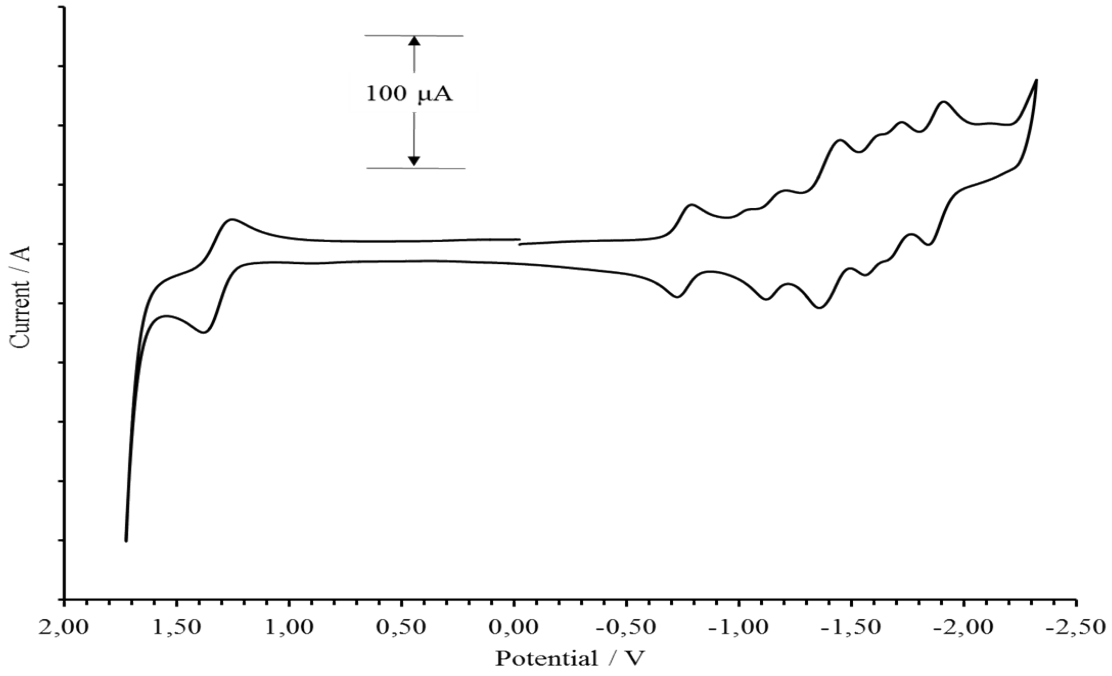

Fig. S17 Cyclic voltammogram of complex **Ru_2L** obtained at a scan rate of 50 mV/s in deaerated DMF, using $TBAPF_6$ as supporting electrolyte.

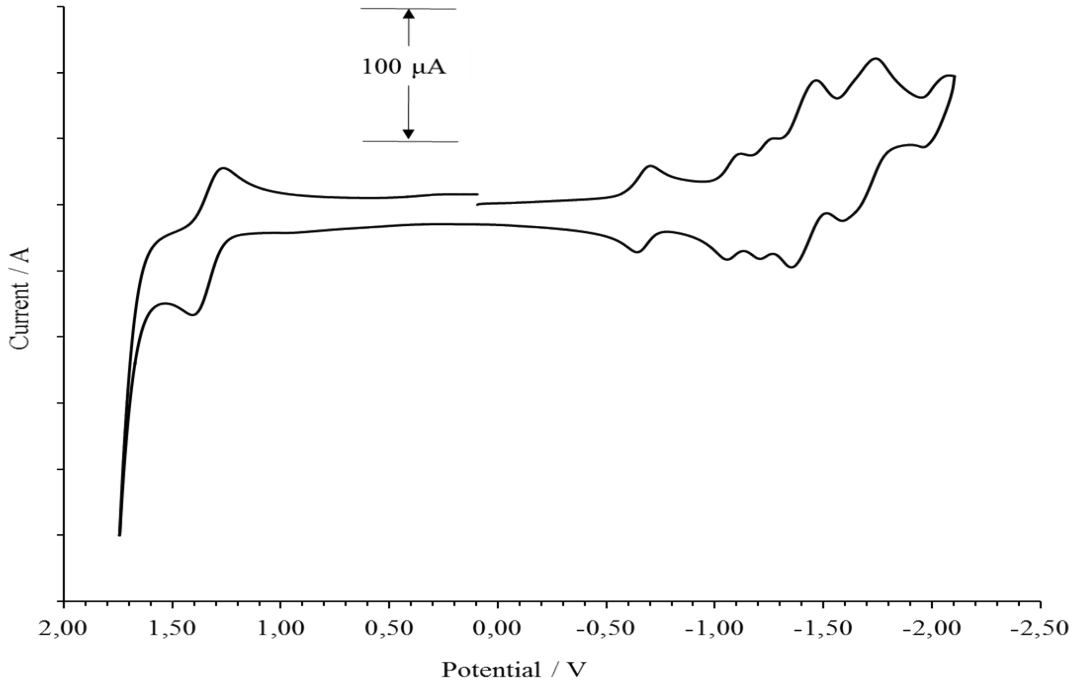

Fig. S18 Cyclic voltammogram of complex **Ru_3L** obtained at a scan rate of 50 mV/s in deaerated DMF, using $TBAPF_6$ as supporting electrolyte.

Table S1. Atomic coordinates for DFT optimization of **RuL** in (*S=0*) PBE0/LANL2DZ CPCM: CH_3CN.

Standard orientation :					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-7.282107	-3.577066	0.102648
2	6	0	-8.770033	-3.563552	0.118540
3	6	0	-6.554284	-2.375243	0.049632
4	6	0	-9.473751	-2.540558	0.783036
5	6	0	-5.151500	-2.419988	0.040275
6	6	0	-10.874735	-2.560209	0.777594
7	6	0	-4.515420	-3.671428	0.084807
8	6	0	-11.537107	-3.598851	0.108116
9	6	0	-5.314399	-4.819940	0.135457
10	6	0	-10.761530	-4.579209	-0.529021
11	6	0	-4.266498	1.126298	-0.123371
12	6	0	-4.361511	-1.173439	-0.018369
13	6	0	-2.324999	-0.104743	-0.057621
14	1	0	-7.056351	-1.417003	-0.006166
15	1	0	-8.940385	-1.760040	1.314166
16	1	0	-3.434899	-3.742633	0.079535
17	1	0	-12.619525	-3.653737	0.078512
18	1	0	-4.859512	-5.804559	0.174293
19	1	0	-11.234830	-5.398894	-1.061308
20	7	0	-6.664561	-4.786477	0.145300
21	7	0	-9.410877	-4.570598	-0.528911
22	7	0	-2.911829	1.111943	-0.114860
23	7	0	-3.010638	-1.269591	-0.010460
24	7	0	-5.024019	0.005758	-0.074216
25	6	0	-0.849971	-0.165472	-0.044493
26	6	0	1.308545	0.908476	-0.041192
27	6	0	-0.191270	-1.401405	-0.013987
28	1	0	1.930270	1.793131	-0.052211
29	6	0	1.205393	-1.441367	-0.000260
30	1	0	-0.781972	-2.308265	0.001394
31	6	0	-6.950376	3.774056	-0.250231
32	6	0	-4.952152	2.432671	-0.191810
33	1	0	-8.031143	3.872858	-0.253844
34	6	0	-4.212061	3.623547	-0.256904
35	6	0	-4.889517	4.853928	-0.315474
36	1	0	-3.129876	3.579819	-0.238751
37	6	0	1.988637	-2.683656	0.031493

38	6	0	1.427001	-3.966505	0.002544
39	6	0	4.155526	-3.594019	0.119016
40	6	0	2.264384	-5.085904	0.033998
41	1	0	0.353429	-4.096528	-0.045875
42	6	0	3.652148	-4.895452	0.093613
43	1	0	5.219533	-3.405828	0.167632
44	1	0	1.842744	-6.084252	0.011992
45	1	0	4.337084	-5.734329	0.119409
46	6	0	-4.131393	6.132393	-0.390364
47	6	0	-2.932271	6.213938	-1.124305
48	6	0	-2.244147	7.433423	-1.175809
49	1	0	-2.557945	5.351655	-1.664984
50	6	0	-3.968350	8.373130	0.217241
51	6	0	-2.769000	8.538992	-0.491749
52	1	0	-1.323576	7.518876	-1.743745
53	1	0	-4.406797	9.202842	0.763621
54	1	0	-2.270601	9.501789	-0.504629
55	7	0	3.346464	-2.506973	0.090444
56	7	0	-6.246391	4.925198	-0.312192
57	1	0	-11.435000	-1.785713	1.290948
58	7	0	1.949429	-0.287601	-0.013178
59	6	0	4.858407	3.332686	1.677545
60	6	0	4.505544	1.994099	1.462013
61	6	0	4.793213	2.256954	-0.858358
62	6	0	5.149724	3.597245	-0.703271
63	6	0	5.184493	4.144788	0.586781
64	1	0	4.881912	3.741058	2.679780
65	1	0	4.752431	1.798754	-1.837201
66	1	0	5.393916	4.190281	-1.576317
67	1	0	5.459464	5.181973	0.740956
68	6	0	4.143411	1.055431	2.533994
69	6	0	4.067986	1.403850	3.888855
70	6	0	3.523304	-1.158943	3.034469
71	6	0	3.710644	0.434961	4.831751
72	1	0	4.281156	2.415417	4.210406
73	6	0	3.433882	-0.868639	4.396596
74	1	0	3.320165	-2.153291	2.659968
75	1	0	3.649112	0.692787	5.882897
76	1	0	3.153048	-1.649594	5.092793
77	7	0	3.872009	-0.222658	2.118399
78	7	0	4.476327	1.467275	0.196657
79	44	0	3.989977	-0.541601	0.074869

80	6	0	6.559166	-1.115946	-1.224857
81	7	0	6.018433	-0.957051	0.024869
82	6	0	7.927793	-1.363674	-1.391995
83	1	0	8.348366	-1.485457	-2.381959
84	6	0	8.755227	-1.452990	-0.268241
85	1	0	9.815877	-1.644161	-0.384757
86	6	0	8.191963	-1.293800	1.005610
87	1	0	8.795456	-1.358046	1.902907
88	6	0	6.822677	-1.046136	1.112362
89	1	0	6.350347	-0.921583	2.077367
90	6	0	5.600501	-1.010702	-2.334183
91	6	0	5.939656	-1.180461	-3.682950
92	6	0	4.949201	-1.064512	-4.663345
93	1	0	6.959557	-1.401664	-3.970956
94	6	0	3.352821	-0.623338	-2.913270
95	6	0	3.633306	-0.781357	-4.271054
96	1	0	5.199531	-1.192924	-5.710251
97	1	0	2.351083	-0.400764	-2.571169
98	1	0	2.835321	-0.683734	-4.997147
99	7	0	4.311243	-0.731656	-1.960764
100	7	0	-4.640475	7.202781	0.272232
101	6	0	-6.354493	2.508521	-0.189544
102	1	0	-6.956356	1.609549	-0.141546
103	6	0	-0.079629	1.009150	-0.060133
104	1	0	-0.558101	1.980013	-0.084170

Table S2. MO composition of **RuL** in (*S=0*) ground state in α-spin.

MO	Energy (eV)	Composition		
		Ruthenium	2,2'-bipyridyl	L1
LUMO+5	-2.074	0	8	92
LUMO+4	-2.500	3	4	94
LUMO+3	-2.608	6	92	2
LUMO+2	-2.712	2	95	4
LUMO+1	-3.091	0	0	100
LUMO	**-3.311**	**4**	**2**	**94**
HOMO	**-6.527**	**76**	**15**	**9**
HOMO-1	-6.694	73	17	10
HOMO-2	-6.705	73	17	10
HOMO-3	-7.108	0	0	100
HOMO-4	-7.116	0	0	100
HOMO-5	-7.336	0	0	100

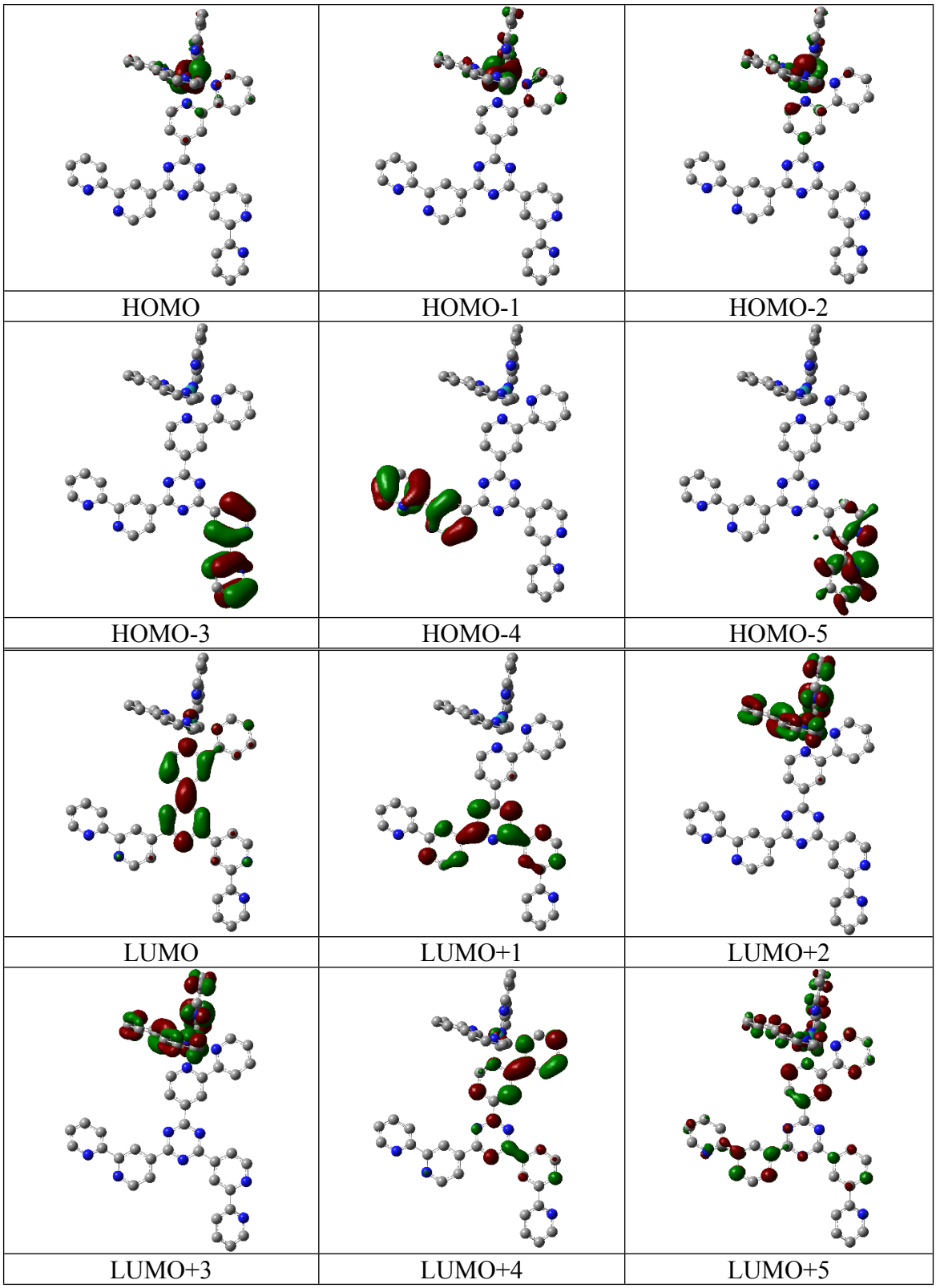

Figure S19. Kohn-Sham molecular orbital diagrams of **RuL** in (*S=0*) ground state.

Table S3. Total energy values for the optimized structure of the first, second and third reduction on complex **RuL** (uPBE0, LANL2DZ, CPCM: Acetonitrile).

RuL	S	2S+1	Total Energy			Experimental
			a. u.	eV	ΔeV	eV
Neutral	0	1	-2843.83755154	-77384.790161925	-	-
1st reduction	1/2	2	-2843.97322085	-77388.481904827	3.69	3.55
2nd reduction	1	3	-2844.07905828	-77391.361884978	2.88	3.05
3rd reduction	3/2	4	-2844.18196269	-77394.162057642	2.80	2.90

Table S4. Spin contamination monitoring for the DFT calculation of **RuL** reduced species.

RuL	S	2S+1	S**2		
			Before annihilation	After annihilation	% change
1st reduction	1/2	2	0.7643	0.7501	2
2nd reduction	1	3	2.0257	2.0004	1
3rd reduction	3/2	4	3.7888	3.7508	1

Table S5. Mulliken spin density values for each of the reduced **RuL** species.

RuL	Mulliken spin density		
	Ruthenium	2,2'-bpy	tris-4-(2,2'-bpy)-1",3",5"-triazine
1st reduction	0.036 (4%)	0.012 (1%)	0.952 (95%)
2nd reduction	0.000 (0%)	0.004 (0%)	0.996 (100%)
3rd reduction	0.036 (4%)	0.914 (91%)	0.050 (5%)

Table S6. Atomic coordinates for DFT optimization of **Ru_2L** in (*S=0*) PBE0/LANL2DZ CPCM: CH_3CN.

Standard orientation :					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.927792	1.365666	-0.070408
2	6	0	-6.202607	-3.301013	-1.339476
3	6	0	-9.392080	-1.468011	1.408110
4	6	0	-6.218415	2.066837	-0.087131
5	6	0	-6.389248	-2.346867	-2.442137
6	6	0	-8.465410	-1.039406	2.465506
7	6	0	-5.875231	-4.651350	-1.518177
8	6	0	-6.221708	-2.669834	-3.795001
9	6	0	-10.699792	-1.911218	1.644227
10	6	0	-8.799724	-0.982812	3.824814

11	6	0	-3.689397	2.011468	-0.103422
12	6	0	-6.354060	3.460844	-0.097042
13	6	0	-2.510402	1.254899	-0.088420
14	6	0	-5.714398	-5.475986	-0.400297
15	6	0	-7.844489	-0.557215	4.753174
16	6	0	-11.503634	-2.295272	0.566253
17	6	0	-6.419352	-1.685800	-4.768782
18	6	0	-7.631924	4.028443	-0.116363
19	6	0	-2.608089	-0.145689	-0.042428
20	6	0	-5.884072	-4.928549	0.879126
21	6	0	-6.568746	-0.194501	4.298818
22	6	0	-10.978712	-2.227169	-0.731840
23	6	0	-8.750801	3.183730	-0.125574
24	6	0	-6.781093	-0.392570	-4.365760
25	6	0	-3.869131	-0.734650	-0.012941
26	6	0	-6.212579	-3.577336	0.997356
27	6	0	-9.668287	-1.780365	-0.907479
28	6	0	-8.555340	1.801813	-0.112593
29	6	0	-6.932823	-0.127192	-3.004126
30	6	0	-6.292108	-0.268535	2.933033
31	6	0	0.047929	3.861176	-0.198927
32	1	0	-5.461673	-6.522679	-0.525533
33	1	0	-8.091310	-0.509233	5.807652
34	1	0	-12.517215	-2.639961	0.736374
35	6	0	-1.195960	1.925305	-0.119725
36	1	0	-6.293713	-1.923794	-5.818894
37	6	0	1.099321	1.814515	-0.123254
38	1	0	-5.747904	-5.060187	-2.512438
39	1	0	-5.939928	-3.672337	-4.090945
40	1	0	-11.090677	-1.960364	2.652483
41	1	0	-9.790191	-1.262739	4.160433
42	1	0	-3.616769	3.090591	-0.141856
43	1	0	-5.480151	4.099727	-0.088340
44	1	0	-1.716867	-0.760194	-0.030217
45	1	0	-5.767262	-5.530773	1.771972
46	1	0	-5.799070	0.141228	4.983187
47	1	0	-11.566457	-2.513762	-1.595506
48	1	0	-9.758446	3.580996	-0.141296
49	1	0	-6.943848	0.399489	-5.086625
50	1	0	-3.981075	-1.809302	0.025645
51	1	0	-6.349848	-3.117171	1.966622
52	1	0	-5.319065	0.000556	2.544552

53	1	0	-9.228512	-1.710414	-1.893080
54	1	0	-9.393385	1.117962	-0.121096
55	1	0	-7.214483	0.856816	-2.653780
56	7	0	-5.012658	-0.003785	-0.023341
57	7	0	-6.370098	-2.775598	-0.084282
58	7	0	-8.887159	-1.406544	0.135173
59	7	0	-7.318081	1.248610	-0.094461
60	7	0	-6.744898	-1.079738	-2.058052
61	7	0	-7.214968	-0.683230	2.030982
62	7	0	1.207437	3.161276	-0.176880
63	44	0	-6.918082	-0.780141	-0.017126
64	7	0	-0.083072	1.155786	-0.095826
65	7	0	-1.173130	3.276801	-0.169195
66	6	0	2.342516	1.020071	-0.086302
67	6	0	4.748266	0.870113	-0.055248
68	6	0	2.293558	-0.378723	-0.026795
69	1	0	5.729321	1.324251	-0.069681
70	6	0	3.482906	-1.111634	0.017958
71	1	0	1.328346	-0.868593	-0.012112
72	6	0	-0.927348	7.502697	-0.301057
73	6	0	0.117935	5.334510	-0.259876
74	1	0	-1.809404	8.134935	-0.296795
75	6	0	1.358782	5.987278	-0.325690
76	6	0	1.396497	7.391834	-0.376800
77	1	0	2.270636	5.402602	-0.314323
78	6	0	3.540762	-2.577839	0.087234
79	6	0	2.414305	-3.409865	0.064186
80	6	0	4.961888	-4.444779	0.252989
81	6	0	2.580024	-4.796221	0.139387
82	1	0	1.420207	-2.988393	-0.012127
83	6	0	3.876180	-5.321618	0.237286
84	1	0	5.976538	-4.811068	0.330939
85	1	0	1.716592	-5.451358	0.122563
86	1	0	4.050303	-6.389000	0.299298
87	6	0	2.696823	8.111636	-0.453015
88	6	0	3.771443	7.576840	-1.189440
89	6	0	4.982681	8.279497	-1.238698
90	1	0	3.657163	6.645571	-1.733069
91	6	0	3.972557	9.959507	0.159076
92	6	0	5.090705	9.496314	-0.550789
93	1	0	5.819548	7.888445	-1.807924
94	1	0	4.014844	10.895685	0.707644

95	1	0	6.008512	10.073395	-0.561625
96	7	0	4.804635	-3.100538	0.179519
97	7	0	0.262114	8.139484	-0.363948
98	1	0	-7.751126	5.105802	-0.124098
99	7	0	4.704331	-0.484952	0.006196
100	6	0	8.999522	1.249138	1.717897
101	6	0	8.033854	0.255610	1.510824
102	6	0	8.448198	0.286970	-0.804882
103	6	0	9.418558	1.279274	-0.658351
104	6	0	9.700517	1.768326	0.624911
105	1	0	9.207035	1.614852	2.715496
106	1	0	8.201008	-0.114791	-1.778210
107	1	0	9.937175	1.653344	-1.532774
108	1	0	10.450115	2.537450	0.772158
109	6	0	7.240610	-0.356489	2.586432
110	6	0	7.332927	0.012602	3.934670
111	6	0	5.604160	-1.966089	3.103576
112	6	0	6.534421	-0.633892	4.883239
113	1	0	8.015304	0.793382	4.245726
114	6	0	5.656306	-1.641511	4.459865
115	1	0	4.942691	-2.740460	2.739078
116	1	0	6.597108	-0.357505	5.929568
117	1	0	5.021253	-2.169377	5.160975
118	7	0	6.376964	-1.341253	2.181692
119	7	0	7.766284	-0.217395	0.252269
120	44	0	6.345103	-1.719822	0.145805
121	6	0	8.294468	-3.535691	-1.089388
122	7	0	7.898560	-3.090534	0.145292
123	6	0	9.358542	-4.436868	-1.224428
124	1	0	9.667430	-4.780831	-2.203349
125	6	0	10.026246	-4.892038	-0.083209
126	1	0	10.851148	-5.589374	-0.174770
127	6	0	9.612485	-4.432960	1.175103
128	1	0	10.100777	-4.760100	2.085083
129	6	0	8.548588	-3.532909	1.249455
130	1	0	8.199400	-3.157462	2.201794
131	6	0	7.524611	-2.997699	-2.219896
132	6	0	7.740818	-3.356993	-3.556713
133	6	0	6.952853	-2.785964	-4.560924
134	1	0	8.510292	-4.072900	-3.816305
135	6	0	5.788023	-1.543757	-2.856122
136	6	0	5.960359	-1.862576	-4.203683

137	1	0	7.110585	-3.055903	-5.598904
138	1	0	5.036115	-0.832241	-2.542711
139	1	0	5.328305	-1.394867	-4.948846
140	7	0	6.550262	-2.095094	-1.880126
141	7	0	2.800145	9.290890	0.212155
142	6	0	-1.053432	6.109425	-0.248757
143	1	0	-2.027460	5.638820	-0.199491
144	6	0	3.597528	1.651130	-0.103771
145	1	0	3.669591	2.730244	-0.150804

Table S7. MO composition of **Ru_2L** in (*S=0*) ground state in α-spin.

MO	Energy (eV)	Composition		
		Ruthenium	2,2'-bipyridyl	L1
LUMO+5	-2.664	6	92	2
LUMO+4	-2.692	5	26	69
LUMO+3	-2.764	2	96	3
LUMO+2	-2.786	0	73	26
LUMO+1	-3.355	3	2	96
LUMO	**-3.492**	**5**	**3**	**93**
HOMO	**-6.589**	**76**	**15**	**8**
HOMO-1	-6.754	76	15	9
HOMO-2	-6.756	73	17	9
HOMO-3	-6.766	73	17	9
HOMO-4	-6.772	73	17	10
HOMO-5	-7.175	72	16	11

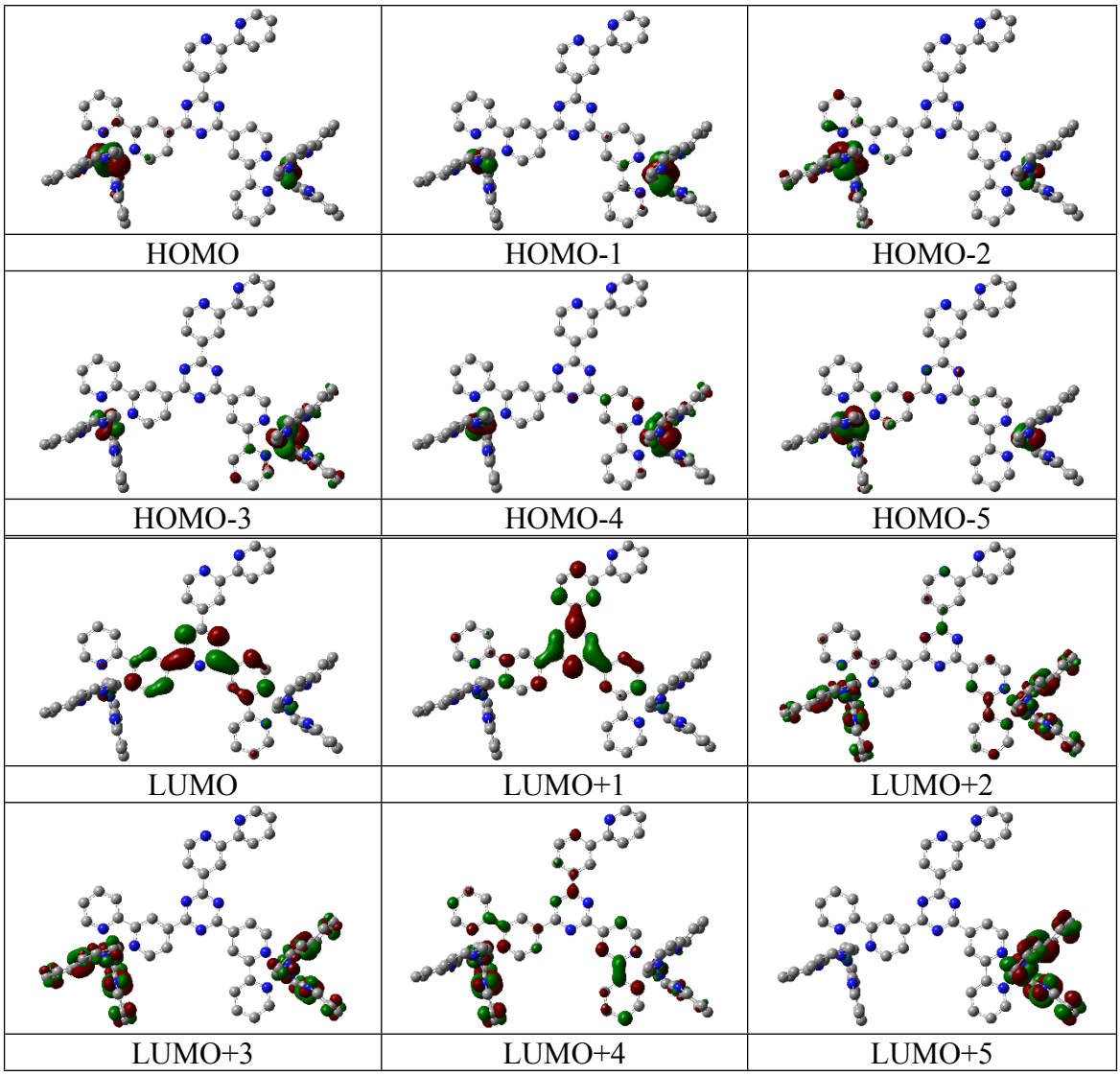

Figure S20. Kohn-Sham molecular orbital diagrams of **Ru_2L** in (*S=0*) ground state.

Table S8. Total energy values for the optimized structure of the first, second and third reduction on complex **Ru_2L** (uPBE0, LANL2DZ, CPCM: Acetonitrile).

Ru_2L	S	2S+1	Total Energy			Experimental
			a. u.	eV	ΔeV	eV
Neutral	0	1	-3927,07362710	-106861,15610299	-	-
1st reduction	1/2	2	-3927,21481519	-106864,99802559	3.84	3.64
2nd reduction	1	3	-3927,33505555	-106868,26993883	3.27	3.25
3rd reduction	1/2	2	-3927,43457354	-106870,97796227	2.94	3.00

Table S9. Spin contamination monitoring for the DFT calculation of **Ru_2L** reduced species.

Ru_2L	S	2S+1	S**2		
			Before annihilation	After annihilation	% change
1st reduction	1/2	2	0.7652	0.7502	2
2nd reduction	1	3	2.0251	2.0004	1
3rd reduction	1/2	2	0.7632	0.7501	2

Table S10. Mulliken spin density values for each of the reduced **Ru_2L** species.

Ru_2L	Mulliken spin density		
	Ruthenium	2,2'-bpy	tris-4-(2,2'-bpy)-1",3",5"-triazine
1st reduction	0.044 (4%)	0.012 (1%)	0.944 (94%)
2nd reduction	0.033 (3%)	0.033 (3%)	0.934 (93%)
3rd reduction	0.018 (2%)	0.863 (86%)	0.119 (12%)

Table S11. Atomic coordinates for DFT optimization of **Ru_3L** in (*S=0*) PBE0/LANL2DZ CPCM: CH_3CN.

Standard orientation :					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.246061	3.872933	-0.049003
2	6	0	-7.940807	2.881238	-1.432467
3	6	0	-7.833579	6.594917	1.270867
4	6	0	-3.201522	5.340950	-0.083743
5	6	0	-7.139345	3.462519	-2.519122
6	6	0	-7.067607	5.972398	2.359956
7	6	0	-8.990010	1.974622	-1.631681
8	6	0	-7.307985	3.145271	-3.873118
9	6	0	-8.825110	7.565105	1.465757
10	6	0	-7.214415	6.308012	3.712155
11	6	0	-2.110921	3.057892	-0.045192
12	6	0	-2.019151	6.092110	-0.076674
13	6	0	-2.256104	1.664731	-0.015025
14	6	0	-9.692554	1.479293	-0.528536
15	6	0	-6.434717	5.657316	4.673450
16	6	0	-9.496077	8.097445	0.360347
17	6	0	-6.491995	3.754720	-4.831415
18	6	0	-2.089742	7.488140	-0.114005
19	6	0	-3.551699	1.121796	0.009451
20	6	0	-9.328013	1.904405	0.756781

21	6	0	-5.519424	4.679693	4.258586
22	6	0	-9.158338	7.644902	-0.922847
23	6	0	-3.348217	8.104467	-0.157608
24	6	0	-5.518782	4.672758	-4.412046
25	6	0	-4.645419	1.982180	0.004080
26	6	0	-8.275775	2.810715	0.895375
27	6	0	-8.164197	6.674784	-1.057170
28	6	0	-4.492716	7.305641	-0.160257
29	6	0	-5.394309	4.949680	-3.049874
30	6	0	-5.414415	4.387209	2.898135
31	6	0	1.216850	0.532014	-0.018677
32	1	0	-10.506669	0.777556	-0.669721
33	1	0	-6.539612	5.908301	5.722818
34	1	0	-10.265161	8.848854	0.497990
35	6	0	-1.068985	0.789141	-0.008402
36	1	0	-6.613727	3.518075	-5.882324
37	6	0	-0.148565	-1.318691	0.016808
38	1	0	-9.261221	1.657556	-2.630659
39	1	0	-8.062722	2.433234	-4.181899
40	1	0	-9.075711	7.903283	2.463104
41	1	0	-7.924025	7.066661	4.017015
42	1	0	-1.114684	3.480255	-0.066665
43	1	0	-1.054569	5.601849	-0.040853
44	1	0	-3.699681	0.049548	0.032634
45	1	0	-9.845192	1.546333	1.638760
46	1	0	-4.896072	4.150732	4.969320
47	1	0	-9.651902	8.030733	-1.806601
48	1	0	-3.448997	9.182647	-0.187756
49	1	0	-4.866057	5.168108	-5.120672
50	1	0	-5.655829	1.598063	0.027054
51	1	0	-7.963782	3.160642	1.870297
52	1	0	-4.722873	3.636549	2.539660
53	1	0	-7.874544	6.303269	-2.030773
54	1	0	-5.481019	7.743697	-0.195342
55	1	0	-4.658735	5.654764	-2.686519
56	7	0	-4.508001	3.332237	-0.022359
57	7	0	-7.591777	3.291310	-0.171676
58	7	0	-7.511315	6.157408	0.012250
59	7	0	-4.427749	5.952248	-0.125642
60	7	0	-6.185647	4.362513	-2.119071
61	7	0	-6.170353	5.014645	1.964050
62	7	0	1.107915	-0.817117	0.001662

63	44	0	-6.059651	4.681566	-0.077076
64	7	0	-1.262709	-0.549768	0.012057
65	7	0	0.154020	1.369318	-0.024606
66	6	0	-0.313256	-2.784387	0.035721
67	6	0	0.607378	-5.011999	0.061290
68	6	0	-1.592625	-3.355226	0.043265
69	1	0	1.445912	-5.694600	0.064660
70	6	0	-1.730486	-4.745701	0.057445
71	1	0	-2.457071	-2.704037	0.038625
72	6	0	4.039850	3.030414	-0.074798
73	6	0	2.568956	1.121345	-0.036326
74	1	0	4.214236	4.097220	-0.095287
75	6	0	3.702258	0.297742	-0.032676
76	6	0	4.976075	0.871769	-0.052740
77	1	0	3.569206	-0.776199	-0.013170
78	6	0	-3.024331	-5.440945	0.067172
79	6	0	-4.265308	-4.792862	0.022543
80	6	0	-4.081621	-7.540811	0.138856
81	6	0	-5.439569	-5.551943	0.038549
82	1	0	-4.322074	-3.712715	-0.025253
83	6	0	-5.345142	-6.949400	0.098658
84	1	0	-3.967807	-8.615268	0.188720
85	1	0	-6.406614	-5.063362	0.004962
86	1	0	-6.228995	-7.575554	0.113541
87	6	0	6.224791	0.098059	-0.048739
88	6	0	6.282172	-1.301345	-0.067849
89	6	0	7.526017	-1.940014	-0.059442
90	1	0	5.374021	-1.890200	-0.090646
91	6	0	8.573006	0.230735	-0.017026
92	6	0	8.690565	-1.159884	-0.032232
93	1	0	7.584779	-3.022321	-0.073660
94	1	0	9.448458	0.865456	0.006931
95	1	0	9.674425	-1.613110	-0.023972
96	7	0	-2.941561	-6.807918	0.124641
97	7	0	5.139567	2.234929	-0.074541
98	1	0	-1.182582	8.081530	-0.108982
99	7	0	-0.630877	-5.568165	0.066008
100	6	0	2.745449	-8.739701	1.803339
101	6	0	1.439599	-8.292261	1.564139
102	6	0	1.731573	-8.572535	-0.753691
103	6	0	3.040266	-9.022977	-0.574893
104	6	0	3.556322	-9.109443	0.725692

105	1	0	3.129587	-8.803207	2.813459
106	1	0	1.299139	-8.488516	-1.741581
107	1	0	3.633680	-9.298666	-1.438219
108	1	0	4.568261	-9.457804	0.898086
109	6	0	0.504991	-7.880027	2.621315
110	6	0	0.825879	-7.851663	3.984739
111	6	0	-1.672485	-7.115806	3.083630
112	6	0	-0.137898	-7.443344	4.912127
113	1	0	1.811918	-8.141800	4.324512
114	6	0	-1.408857	-7.069706	4.453166
115	1	0	-2.641761	-6.839433	2.690590
116	1	0	0.098375	-7.418215	5.969804
117	1	0	-2.185122	-6.748354	5.136974
118	7	0	-0.740826	-7.512527	2.182576
119	7	0	0.943120	-8.212857	0.288596
120	44	0	-1.024523	-7.585847	0.133607
121	6	0	-1.765526	-10.092328	-1.205916
122	7	0	-1.577043	-9.581469	0.052185
123	6	0	-2.110922	-11.436942	-1.394406
124	1	0	-2.255102	-11.834010	-2.391152
125	6	0	-2.267850	-12.271293	-0.283248
126	1	0	-2.535051	-13.313421	-0.416058
127	6	0	-2.074888	-11.739133	0.999234
128	1	0	-2.187211	-12.349147	1.887341
129	6	0	-1.729518	-10.393077	1.127119
130	1	0	-1.575839	-9.946372	2.100066
131	6	0	-1.578066	-9.130327	-2.301368
132	6	0	-1.761265	-9.439592	-3.655411
133	6	0	-1.558881	-8.450633	-4.622990
134	1	0	-2.059591	-10.435528	-3.957038
135	6	0	-1.010175	-6.913856	-2.850152
136	6	0	-1.176289	-7.165837	-4.212554
137	1	0	-1.697457	-8.678276	-5.673751
138	1	0	-0.712762	-5.936115	-2.495435
139	1	0	-1.008714	-6.370038	-4.928167
140	7	0	-1.203306	-7.871075	-1.909790
141	7	0	7.368802	0.853006	-0.024285
142	44	0	7.084526	2.903075	-0.056109
143	6	0	6.625908	4.437335	2.403856
144	6	0	7.048991	2.178952	2.913416
145	6	0	6.468859	4.735372	3.763744
146	6	0	6.905197	2.418452	4.280656

147	1	0	7.279609	1.190805	2.538695
148	6	0	6.609899	3.718766	4.713714
149	1	0	6.238840	5.743686	4.083849
150	1	0	7.023137	1.601747	4.982491
151	1	0	6.491650	3.937517	5.768850
152	6	0	6.544152	5.759606	-1.004847
153	6	0	6.498491	5.426663	1.323979
154	6	0	6.289058	7.123427	-0.855092
155	1	0	6.663516	5.317473	-1.984817
156	6	0	6.244013	6.788154	1.534201
157	6	0	6.138277	7.647830	0.436312
158	1	0	6.213534	7.753021	-1.733390
159	1	0	6.130967	7.178425	2.537558
160	1	0	5.942336	8.703425	0.586069
161	7	0	6.916107	3.162754	1.990625
162	7	0	6.648069	4.923775	0.057239
163	6	0	9.602676	3.486155	-1.450377
164	6	0	9.881802	3.722581	0.873527
165	6	0	10.935018	3.859483	-1.669239
166	6	0	11.216804	4.097082	0.715424
167	1	0	9.433720	3.654570	1.855595
168	6	0	11.753036	4.168459	-0.577947
169	1	0	11.333699	3.911728	-2.674317
170	1	0	11.814614	4.327122	1.589025
171	1	0	12.785819	4.458267	-0.734241
172	6	0	8.659794	3.138878	-2.522971
173	6	0	6.448479	2.509519	-3.022775
174	6	0	8.998914	3.101366	-3.881648
175	6	0	6.728989	2.458961	-4.388925
176	1	0	5.458304	2.288609	-2.647314
177	6	0	8.026782	2.758644	-4.826465
178	1	0	10.006055	3.332845	-4.204282
179	1	0	5.945183	2.189880	-5.086596
180	1	0	8.277263	2.726475	-5.880671
181	7	0	9.086642	3.421314	-0.182156
182	7	0	7.388497	2.842350	-2.104382
183	6	0	2.747364	2.514817	-0.057949
184	1	0	1.893055	3.179776	-0.061358
185	6	0	0.805169	-3.634689	0.044520
186	1	0	1.807823	-3.226432	0.038616

Table S12. MO composition of **Ru_3L** in (*S=0*) ground state in α-spin.

MO	Energy (eV)	Composition		
		Ruthenium	2,2'-bipyridyl	L1
LUMO+5	-2.801	4	85	11
LUMO+4	-2.822	2	96	3
LUMO+3	-2.822	2	96	2
LUMO+2	-2.958	3	25	72
LUMO+1	-3.610	5	3	93
LUMO	**-3.611**	**5**	**6**	**90**
HOMO	**-6.652**	**76**	**16**	**8**
HOMO-1	-6.656	76	15	9
HOMO-2	-6.658	76	18	5
HOMO-3	-6.818	73	21	6
HOMO-4	-6.820	74	20	7
HOMO-5	-6.821	74	18	9

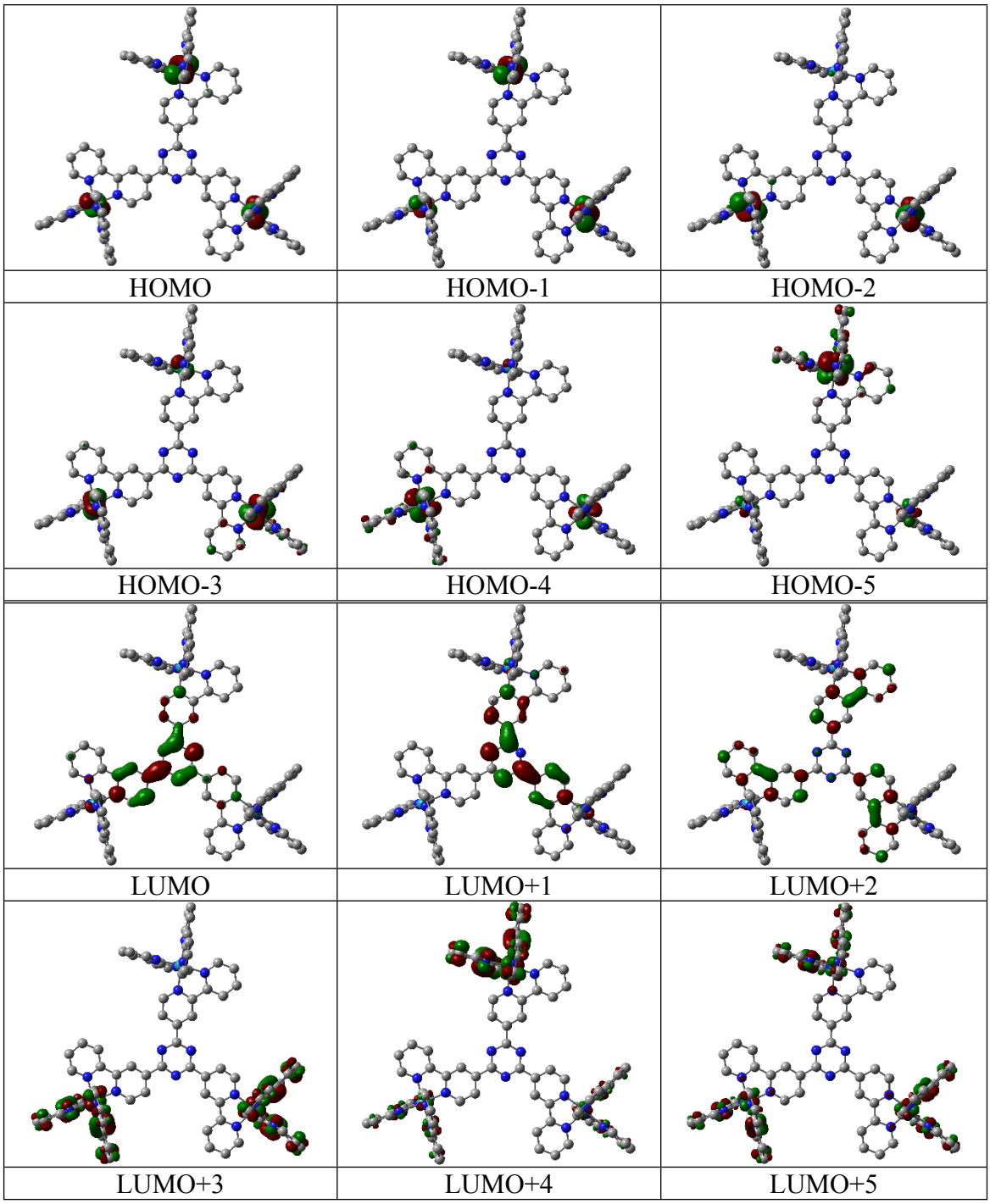

Figure S21. Kohn-Sham molecular orbital diagrams of **Ru_3L** in (*S=0*) ground state.

Table S13. Total energy values for the optimized structure of the first, second and third reduction on complex **Ru_3L** (uPBE0, LANL2DZ, CPCM: Acetonitrile).

Ru_2L	S	2S+1	Total Energy			Experimental
			a. u.	eV	ΔeV	eV
Neutral	0	1	-5010.30553921	-136337.40876873	-	-
1st reduction	1/2	2	-5010.45167636	-136341.38536461	3.98	3.70
2nd reduction	1	3	-5010.57838626	-136344.83331789	3.45	3.29
3rd reduction	3/2	4	-5010.69236501	-136347.93483881	3.10	3.14

Table S14. Spin contamination monitoring for the DFT calculation of **Ru_3L** reduced species.

Ru_3L	S	2S+1	S**2		
			Before annihilation	After annihilation	% change
1st reduction	1/2	2	0.7651	0.7502	2
2nd reduction	1	3	2.0203	2.0003	1
3rd reduction	3/2	4	3.7898	3.7508	1

Table S15. Mulliken spin density values for each of the reduced **Ru_3L** species.

Ru_3L	Mulliken spin density		
	Ruthenium	2,2'-bpy	tris-4-(2,2'-bpy)-1",3",5"-triazine
1st reduction	0.049 (5%)	0.011 (1%)	0.940 (94%)
2nd reduction	0.044 (4%)	0.017 (2%)	0.938 (94%)
3rd reduction	0.033 (3%)	0.058 (6%)	0.909 (91%)