Supplementary Information

Rhodium Amidinate Dimers as Structural and Functional Hubs for Multimetallic Assemblies.

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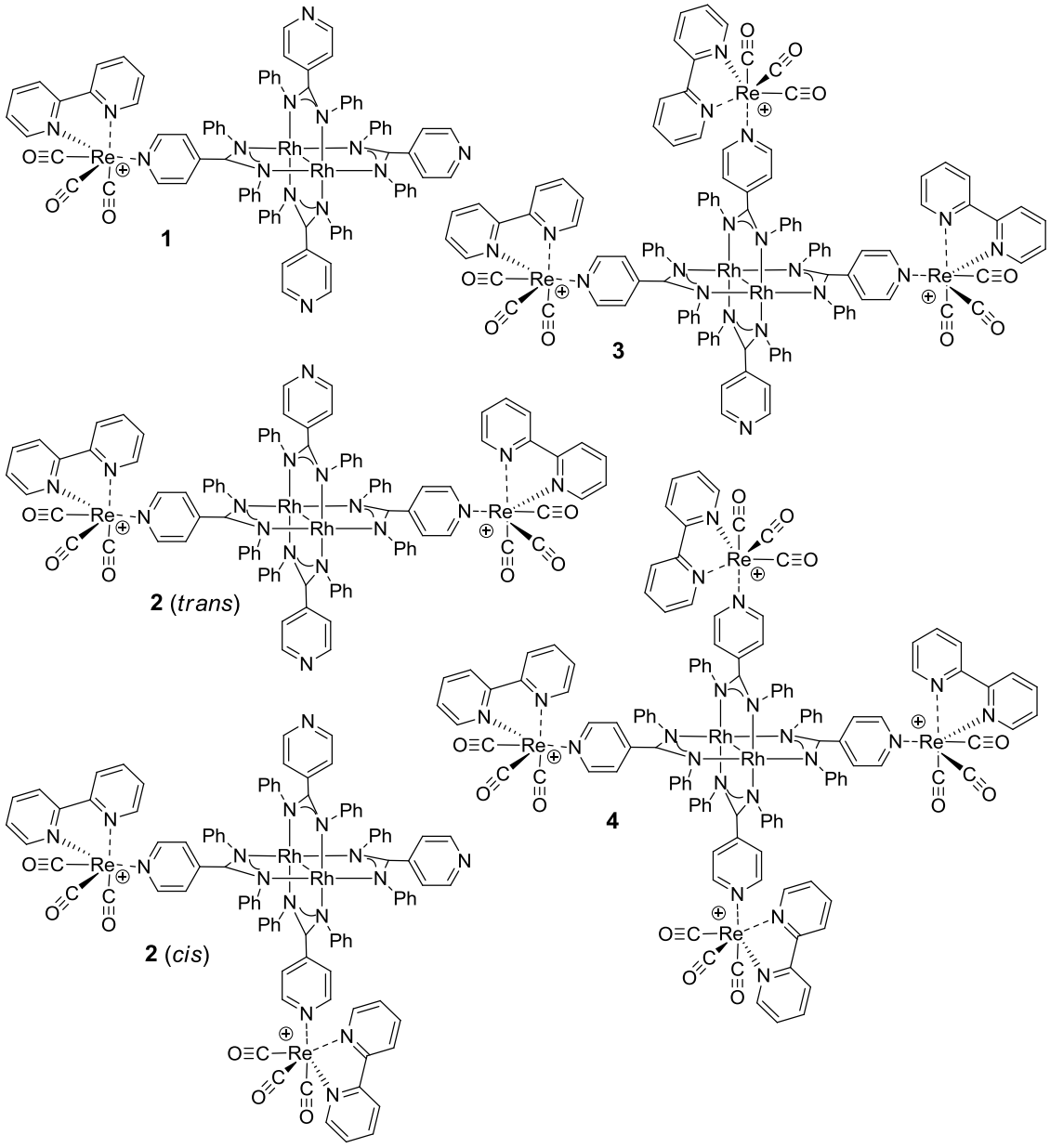
Table S21. Singlet electronic transition obtained from TD-DFT for **5** (G03 opt 3-21G) 31

Chart S1. Rh2 complexes 1 to 4 synthesized in this study (anions omitted).



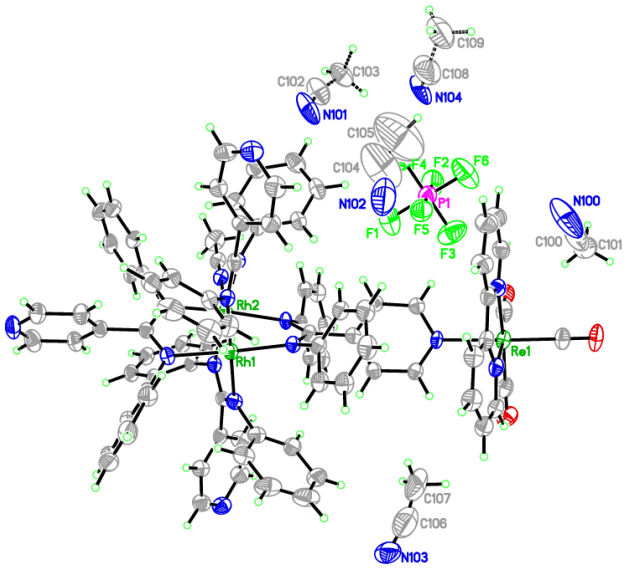


Figure S1. ORTEP view of the asymmetric unit of the X-ray crystal structure of **1** (50% probability displacement ellipsoids); Showing labeling for anion and solvent molecules.

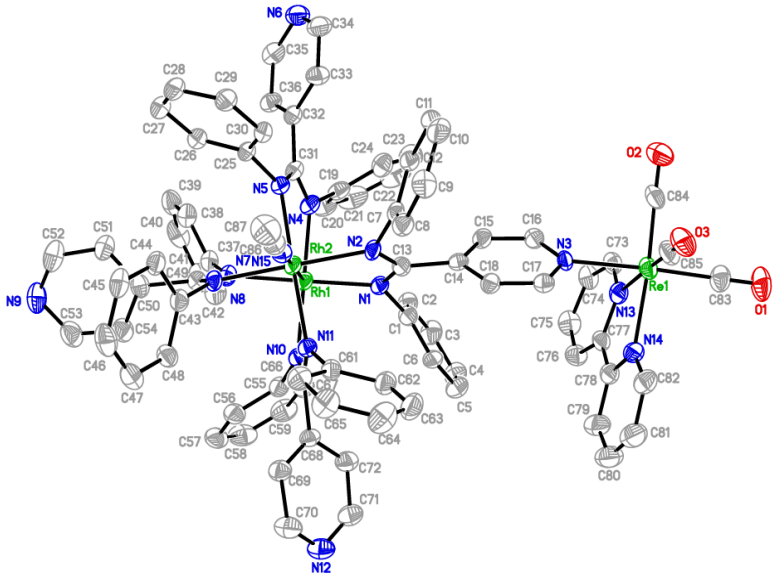


Figure S2. ORTEP view and labeling of the X-ray crystal structure of **1** (50% probability displacement ellipsoids; hydrogen atoms, anion and solvent molecules removed for the sake of clarity).

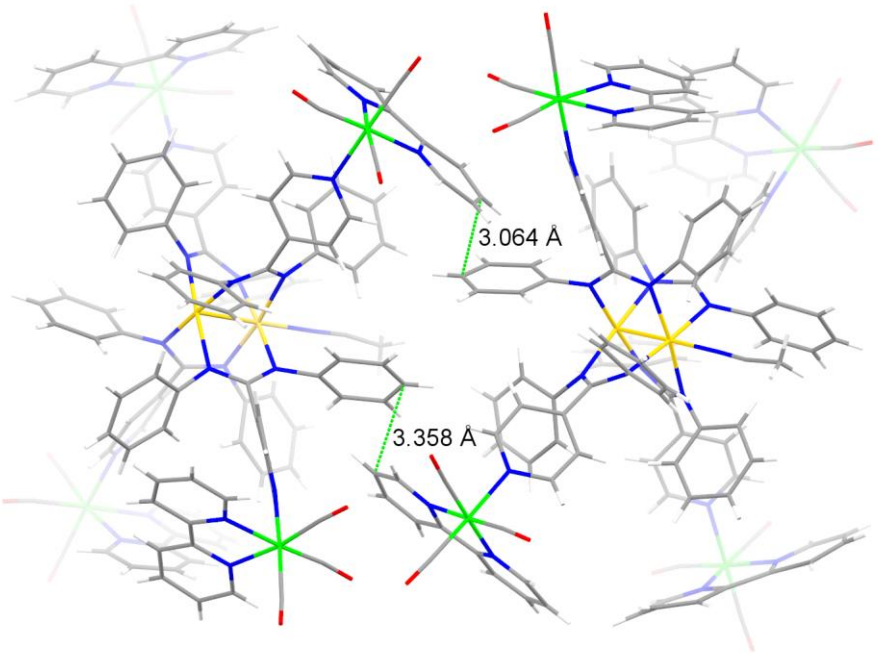


Figure S3. Wireframe view of **4** showing the π stacking interactions between adjacent molecules; cocrystallised solvent and anions are omitted for the sake of clarity.

Table S1. Unadjusted computed IR CO bands for **1**, **4** and **8**.

complex	CO stretches (cm^{-1})		
1	2037.49	2047.73	2118.25
4	2029.82	2033.79	2124.73
	2029.9	2055.88	2125.11
8	2041.15	2053.05	2122.7

Table S2. UV-vis absorption bands data of **1** to **5** and **8** in dichloromethane

Band assignment	Complex λ_{exp} (nm); (ε ($M^{-1}cm^{-1}$))					
	1	**2**	**3**	**4**	**5**	**8**
^{1}Ph($\pi \rightarrow \pi^*$) Re ^{1}MLCT	305 (50k)	307 (60k)	308 (71k)	310 (82k)	298 (40k)	306 (15k)
^{1}Bpy ($\pi \rightarrow \pi^*$)	320 (38k)	320 (49k)	320 (63k)	320 (75k)	—	321 (14k)
Re ^{1}MLCT	344s (25k)	344s (30k)	344s (36k)	344s (42k)	—	358 (4.8k)
Rh_2 ^1M_2LCT	507; 541*; 571 (2k; 2k; 1.5k)	586 (1.7k)	595 (2.0k)	603 (2.5k)	541 (4.9k)	—
$^1Rh_2$ ($\pi^* \rightarrow \sigma^*$)	835 (2.2k)	833 (2.3k)	832 (2.3k)	831 (2.4k)	837 (2.2k)	—
$^1Rh_2$ ($\delta^* \rightarrow \sigma^*$)	992 (60)	994 (50)	989 (100)	991 (50)	993 (60)	—
$^1Rh_2$ ($\delta^* \rightarrow \sigma^*$)	1095 (40)	1095 (70)	1089 (70)	1084 (60)	1101 (100)	—

*: calculated as being a $^1LM_2CT$

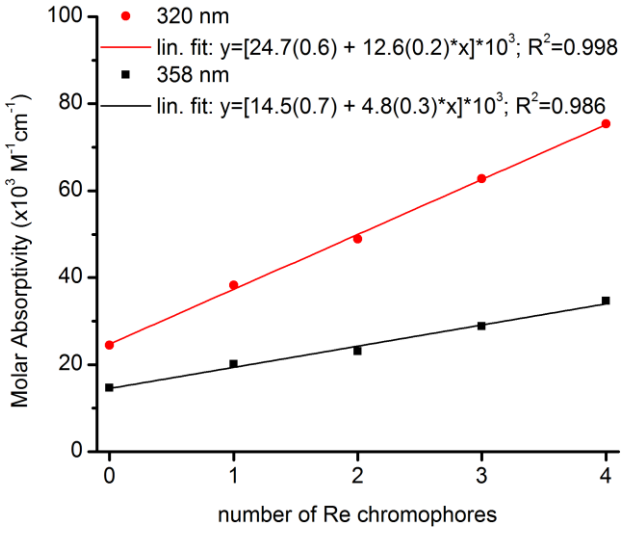


Figure S4. Molar absorptivity at specific wavelengths for complexes **1** to **4** in function of the number of rhenium chromophores (in dichloromethane).

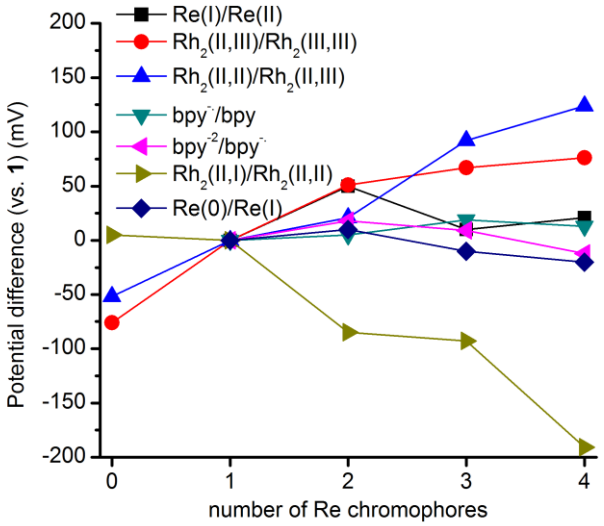


Figure S5. Variation in potential in function of the number of Re chromophores, all redox couples are referenced vs. **1** redox couple (in acetonitrile).

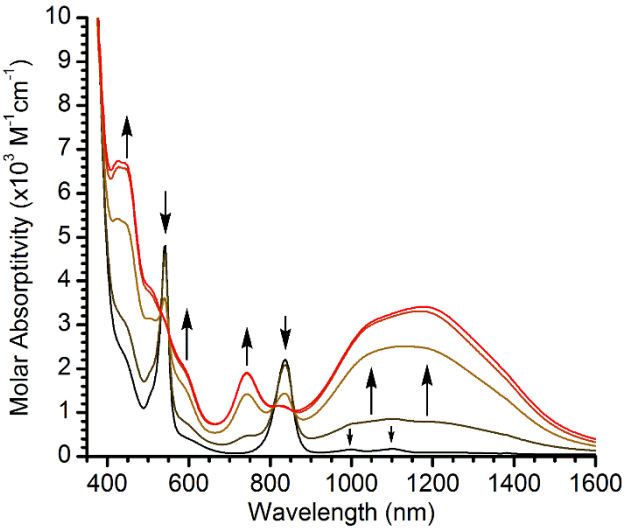


Figure S6. Spectral changes of **5** during chemical oxidation in DCM (using *meta*-chloroperoxybenzoic acid). Black line: starting material, red final oxidized product.

Chart S2. Frontier MO orbital diagrams of **1**; rb3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[$NCN_{amidinate}$, $N_{py\text{-}Re}$, CO], 3-21G[C_{aryl},H, N_{py}] with CPCM (DCM).

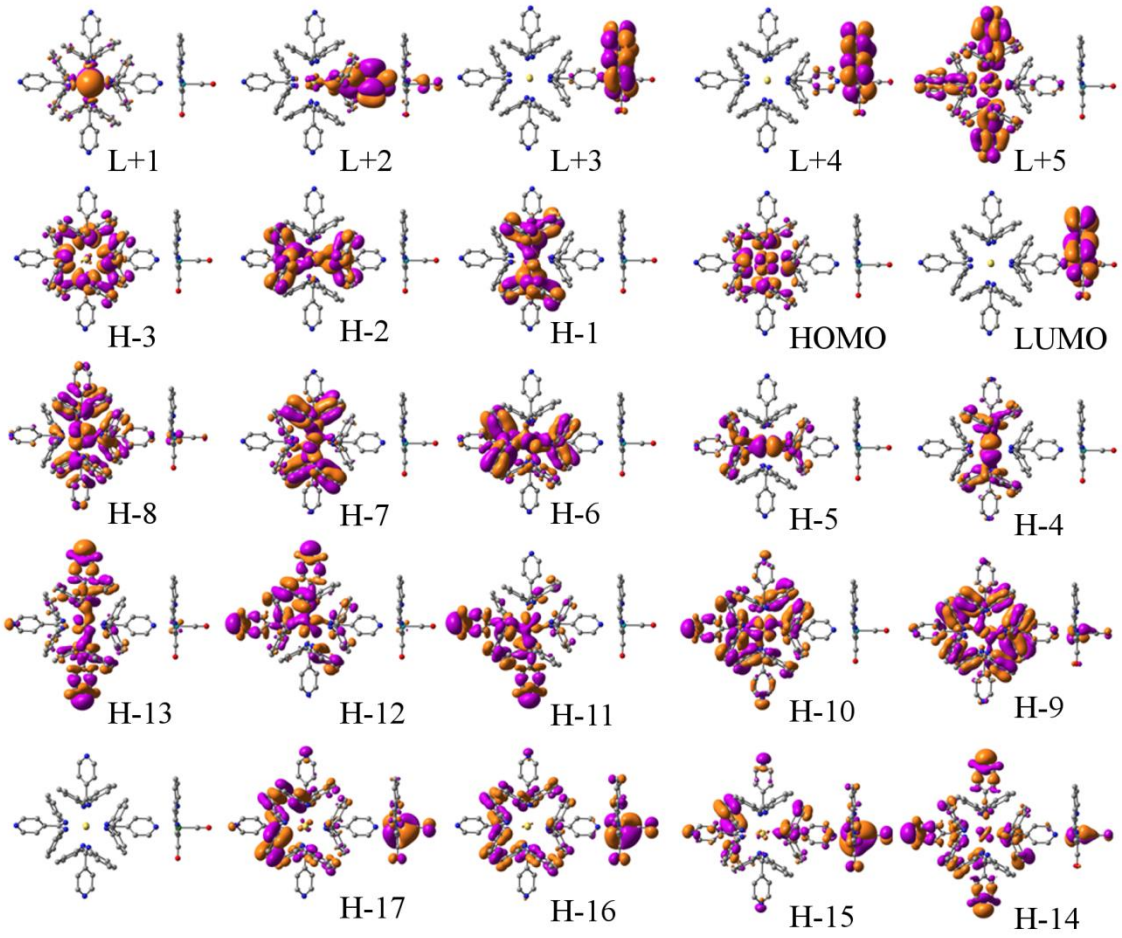


Chart S3. Selected MO orbital diagrams of **4**; rb3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[$NCN_{amidinate}$, $N_{py\text{-}Re}$, CO], 3-21G[C_{aryl},H, N_{py}] with CPCM (DCM).

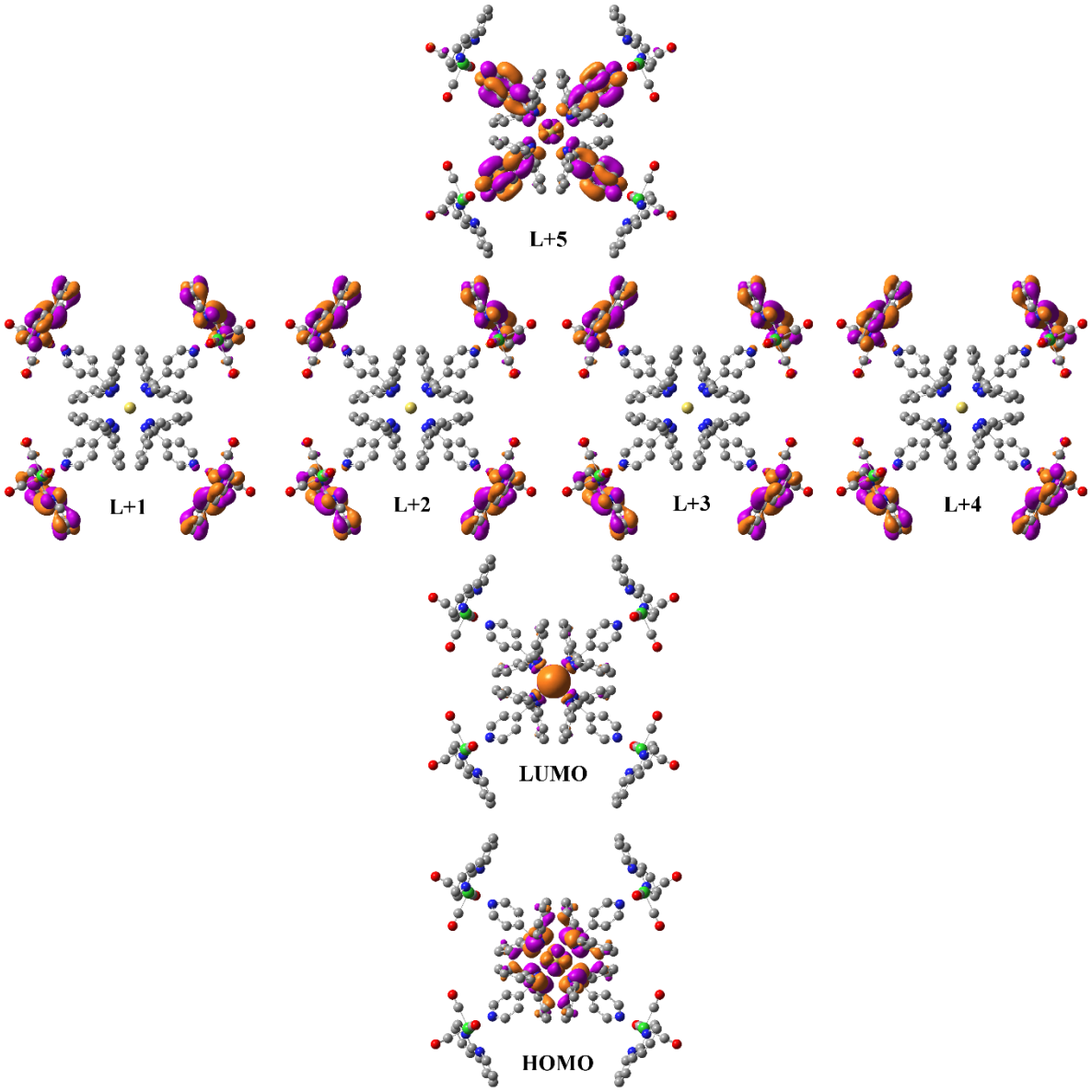


Chart S4. Selected MO orbital diagrams of **5+MeCN**; rb3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$,, CO], 3-21G[C_{aryl},H, N_{py}] with CPCM (DCM).

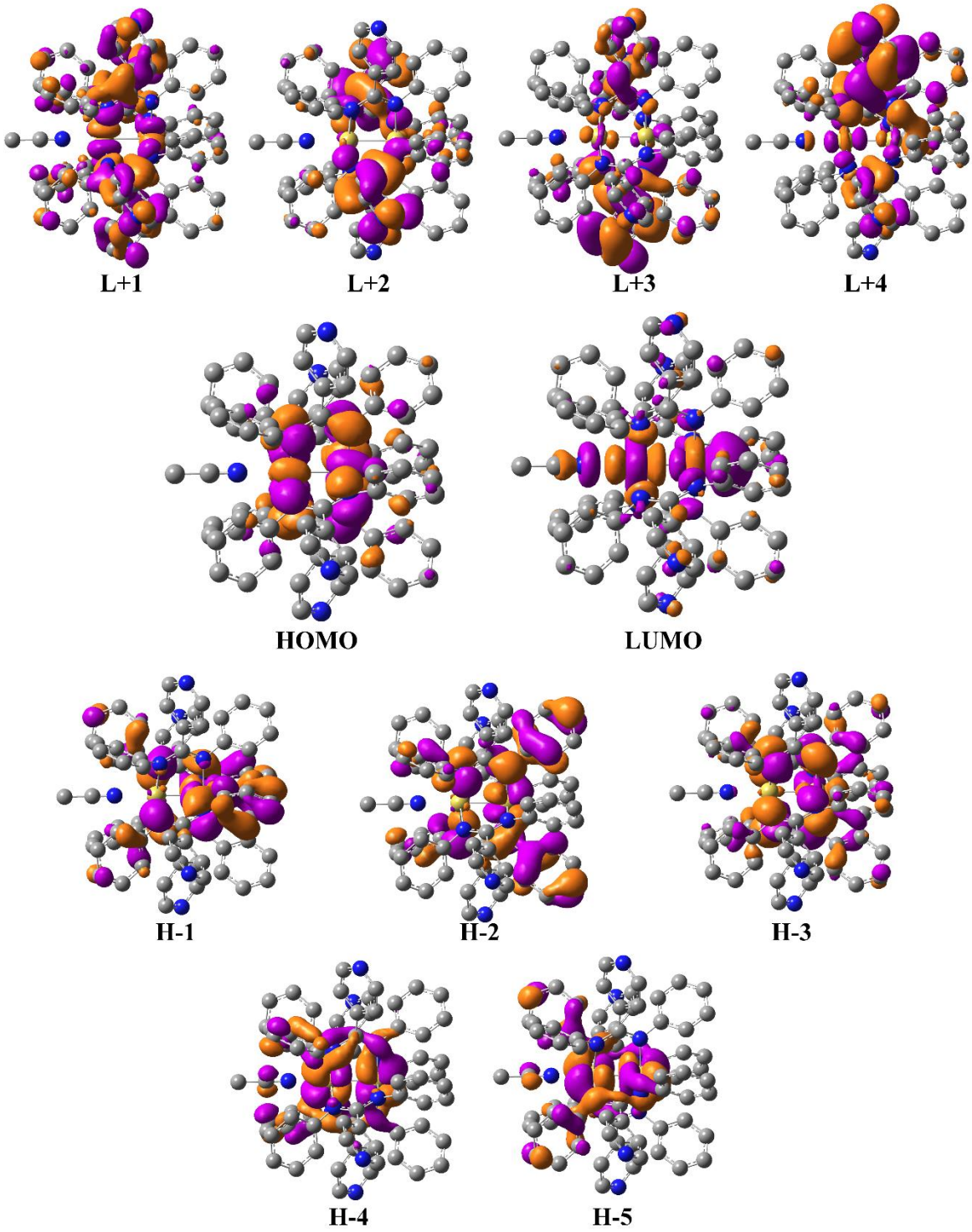


Chart S5. Total electron spin density of (**5**+**MeCN**)$^{+}$; ub3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$,, CO], 3-21G[C_{aryl},H, N_{py}] with CPCM (DCM).(isovalue = 0.0004)

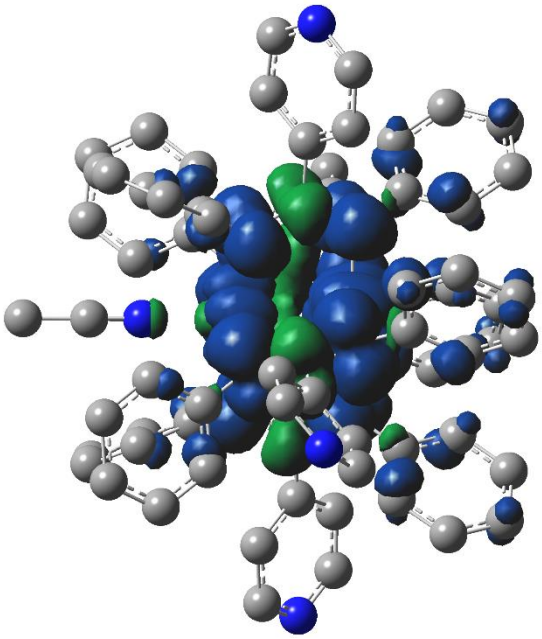


Table S3. Optimized atomic coordinates obtained from DFT for **1** singlet ground state (b3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[C,H,N]) E= -4568.16047523 Hartree.

Atom	x /Å	y /Å	z /Å
Re	7.078802	-0.737771	-0.520865
Rh	-2.128412	0.089657	1.196838
Rh	-2.26695	-0.095151	-1.213186
N	-0.026209	0.199741	0.986602
N	-0.197107	-0.50194	-1.227753
N	4.840888	-0.527855	-0.378956
N	-1.998888	-2.005471	1.259991
N	-2.664081	-2.133652	-0.956861
N	-2.73604	-7.024916	0.581298
N	-4.206622	-0.034485	1.242314
N	-4.298425	0.323679	-1.045233
N	-9.220253	0.501257	0.348602
N	-2.253694	2.169909	0.967069
N	-1.851684	1.963471	-1.306971
N	-1.714751	7.028831	-0.579177
N	7.101634	-0.133936	1.592768
N	7.114132	1.460802	-0.536085
O	10.16261	-0.922482	-0.624425
O	6.867258	-3.777567	-0.028324
O	6.914804	-1.111247	-3.580848
C	0.722662	0.903156	1.963132
C	0.732199	0.45229	3.294359
H	0.204324	-0.460381	3.547171
C	1.418787	1.164247	4.278
H	1.413813	0.796838	5.300278
C	2.107213	2.337227	3.958936
H	2.628415	2.895128	4.731055
C	2.100737	2.793325	2.639282
H	2.615458	3.714224	2.377807
C	1.41271	2.088413	1.651556
H	1.388471	2.46182	0.633222
C	0.336453	-1.293207	-2.280186
C	0.281716	-0.824228	-3.602735
H	-0.127755	0.160122	-3.799471
C	0.761805	-1.611245	-4.650216
H	0.718019	-1.228963	-5.665915
C	1.30125	-2.8753	-4.401443
H	1.672542	-3.484369	-5.219505
C	1.352204	-3.350596	-3.089554
H	1.759309	-4.336311	-2.882923
C	0.868436	-2.57141	-2.038554
H	0.886996	-2.953942	-1.023424
C	0.532528	-0.197787	-0.157685
C	2.035479	-0.313031	-0.236717
C	2.753284	-1.084673	0.684171
H	2.239106	-1.623518	1.472207
C	4.132506	-1.170511	0.576056
H	4.700572	-1.777763	1.270532
C	4.145145	0.216061	-1.267495
H	4.724105	0.716359	-2.034495
C	2.765415	0.344157	-1.233866
H	2.26184	0.949485	-1.979235
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C	-1.717953	-2.299436	3.663113
H	-2.616713	-1.712859	3.818252
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C	0.131965	-3.582471	4.565867
H	0.675778	-3.978219	5.417974
C	0.552504	-3.867492	3.26464
H	1.427256	-4.491073	3.100071
C	-0.147527	-3.364801	2.168524
H	0.181401	-3.597614	1.16127
C	-3.422277	-2.776336	-1.971661
C	-4.701009	-3.300924	-1.718566
H	-5.101916	-3.258838	-0.711761
C	-5.447803	-3.876066	-2.745409
H	-6.430665	-4.284054	-2.528003
C	-4.942039	-3.925427	-4.046463
H	-5.526774	-4.37161	-4.844633
C	-3.675532	-3.400033	-4.307293
H	-3.264924	-3.442016	-5.312039
C	-2.919193	-2.830634	-3.28168
H	-1.927358	-2.442919	-3.485501
C	-2.382759	-2.730783	0.202386
C	-2.506137	-4.227373	0.328747
C	-1.871592	-5.090317	-0.571761
H	-1.281098	-4.700232	-1.393568
C	-2.013782	-6.466434	-0.397826
H	-1.522944	-7.154796	-1.083255
C	-3.345912	-6.191616	1.433175
H	-3.933959	-6.657976	2.221206
C	-3.260417	-4.801685	1.357673
H	-3.772338	-4.179429	2.083663
C	-4.802192	-0.573777	2.413753
C	-5.521895	-1.780693	2.385152
H	-5.666082	-2.289318	1.438166
C	-6.057555	-2.316204	3.55518
H	-6.621506	-3.243433	3.509808
C	-5.871181	-1.6695	4.779146
H	-6.288501	-2.088784	5.689216
C	-5.151049	-0.474533	4.817085
H	-5.011619	0.04747	5.759461
C	-4.620826	0.072578	3.647331
H	-4.085649	1.014683	3.679422
C	-4.926417	0.949093	-2.155459
C	-4.96797	0.28911	-3.394494
H	-4.581127	-0.720594	-3.472141
C	-5.527357	0.915015	-4.509993
H	-5.562314	0.383328	-5.456541
C	-6.054968	2.203483	-4.411166
H	-6.495394	2.684712	-5.278714
C	-6.018748	2.864459	-3.18119
H	-6.432048	3.864726	-3.088545
C	-5.45276	2.249191	-2.065969
H	-5.423605	2.767938	-1.113966
C	-4.914312	0.192399	0.132257
C	-6.414483	0.30038	0.208698
C	-7.236817	-0.482053	-0.609093
H	-6.808797	-1.182369	-1.317872
C	-8.619986	-0.347079	-0.495138
H	-9.278452	-0.951392	-1.116101
C	-8.4248	1.249551	1.122931
H	-8.925937	1.936693	1.801957

Atom	x /Å	y /Å	z /Å
C	-7.031952	1.185885	1.09848
H	-6.440816	1.812555	1.757479
C	-2.801943	2.90967	2.047509
C	-3.996723	3.638259	1.917777
H	-4.492508	3.677327	0.954073
C	-4.54099	4.309456	3.01153
H	-5.461024	4.873551	2.888852
C	-3.915366	4.254745	4.25914
H	-4.343697	4.775296	5.10982
C	-2.732918	3.526273	4.398431
H	-2.230797	3.482515	5.36075
C	-2.178152	2.859755	3.304977
H	-1.249863	2.30993	3.412629
C	-1.205752	2.43839	-2.474658
C	0.06864	3.03351	-2.433125
H	0.544852	3.196103	-1.471844
C	0.705964	3.435475	-3.606406
H	1.68216	3.910044	-3.549985
C	0.097149	3.237496	-4.847756
H	0.594271	3.551437	-5.760193
C	-1.164469	2.64169	-4.898729
H	-1.658493	2.494563	-5.854784
C	-1.812442	2.24671	-3.727743
H	-2.801609	1.805269	-3.77375
C	-2.010641	2.727608	-0.221182
C	-1.91276	4.226913	-0.341748
C	-2.671376	4.928793	-1.284538
H	-3.352348	4.406876	-1.948112

Atom	x /Å	y /Å	z /Å
C	-2.539325	6.315474	-1.356253
H	-3.125727	6.880524	-2.078067
C	-0.992353	6.348187	0.319073
H	-0.328184	6.940089	0.946485
C	-1.055756	4.965256	0.482063
H	-0.452884	4.472813	1.237277
C	7.159922	-0.998278	2.625814
H	7.226548	-2.04791	2.365992
C	7.145968	-0.587964	3.952896
H	7.198659	-1.326861	4.74404
C	7.06551	0.775212	4.229023
H	7.04867	1.135457	5.252049
C	7.01732	1.674277	3.168677
H	6.965755	2.736829	3.367903
C	7.043105	1.200022	1.853852
C	7.05209	2.086396	0.670661
C	7.038979	3.481831	0.755823
H	6.985975	3.972276	1.719238
C	7.102965	4.246584	-0.404422
H	7.096914	5.329781	-0.345912
C	7.185408	3.597924	-1.634785
H	7.250507	4.149191	-2.565693
C	7.186752	2.208857	-1.655556
H	7.254316	1.664113	-2.589557
C	9.008245	-0.858722	-0.590943
C	6.957336	-2.643398	-0.249791
C	6.98299	-1.00891	-2.428492

Table S4. Optimized atomic coordinates obtained from DFT for **4** singlet ground state (b3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[C,H,N]) E= -7311.41466425 Hartree.

Atom	x /Å	y /Å	z /Å
Rh	0	0	1.209872
Rh	0	0	-1.209872
Re	7.298783	-5.651819	-0.639793
Re	7.298783	5.651819	0.639793
Re	-7.298783	-5.651819	0.639793
Re	-7.298783	5.651819	-0.639793
N	1.286141	-1.661263	1.126552
N	1.663169	1.278094	1.133364
N	-1.663169	-1.278094	1.133364
N	-1.286141	1.661263	1.126552
N	1.663169	-1.278094	-1.133364
N	1.286141	1.661263	-1.126552
N	-1.286141	-1.661263	-1.126552
N	-1.663169	1.278094	-1.133364
C	1.946649	-1.927169	-0.002284
C	1.260821	-2.586382	2.20303
C	1.946649	1.927169	0.002284
C	2.571642	1.234023	2.226674
C	-1.946649	-1.927169	0.002284
C	-2.571642	-1.234023	2.226674
C	-1.946649	1.927169	-0.002284
C	-1.260821	2.586382	2.20303
C	2.571642	-1.234023	-2.226674
C	1.260821	2.586382	-2.20303
C	-1.260821	-2.586382	-2.20303

Atom	x /Å	y /Å	z /Å
C	-2.571642	1.234023	-2.226674
C	3.062691	-2.948968	-0.001639
C	1.560217	-2.149035	3.504262
C	0.878956	-3.926098	2.012687
C	3.062691	2.948968	0.001639
C	3.899377	0.799582	2.069187
C	2.122488	1.57459	3.512998
C	-3.062691	-2.948968	0.001639
C	-3.899377	-0.799582	2.069187
C	-2.122488	-1.57459	3.512998
C	-3.062691	2.948968	-0.001639
C	-1.560217	2.149035	3.504262
C	-0.878956	3.926098	2.012687
C	3.899377	-0.799582	-2.069187
C	2.122488	-1.57459	-3.512998
C	1.560217	2.149035	-3.504262
C	0.878956	3.926098	-2.012687
C	-1.560217	-2.149035	-3.504262
C	-0.878956	-3.926098	-2.012687
C	-2.122488	1.57459	-3.512998
C	-3.899377	0.799582	-2.069187
C	3.125506	-3.973462	-0.953257
C	4.118228	-2.864136	0.914236
H	1.866531	-1.120481	3.661365
C	1.48483	-3.032815	4.581704

Atom	x /Å	y /Å	z /Å
C	0.814514	-4.806331	3.093057
H	0.632535	-4.270017	1.013095
C	3.125506	3.973462	0.953257
C	4.118228	2.864136	-0.914236
H	4.254475	0.52209	1.082147
C	4.760267	0.734356	3.165056
C	2.985663	1.496373	4.607428
H	1.102806	1.919143	3.645006
C	-3.125506	-3.973462	0.953257
C	-4.118228	-2.864136	-0.914236
H	-4.254475	-0.52209	1.082147
C	-4.760267	-0.734356	3.165056
C	-2.985663	-1.496373	4.607428
H	-1.102806	-1.919143	3.645006
C	-3.125506	3.973462	-0.953257
C	-4.118228	2.864136	0.914236
H	-1.866531	1.120481	3.661365
C	-1.48483	3.032815	4.581704
C	-0.814514	4.806331	3.093057
H	-0.632535	4.270017	1.013095
H	4.254475	-0.52209	-1.082147
C	4.760267	-0.734356	-3.165056
C	2.985663	-1.496373	-4.607428
H	1.102806	-1.919143	-3.645006
H	1.866531	1.120481	-3.661365
C	1.48483	3.032815	-4.581704
C	0.814514	4.806331	-3.093057
H	0.632535	4.270017	-1.013095
H	-1.866531	-1.120481	-3.661365
C	-1.48483	-3.032815	-4.581704
C	-0.814514	-4.806331	-3.093057
H	-0.632535	-4.270017	-1.013095
H	-1.102806	1.919143	-3.645006
C	-2.985663	1.496373	-4.607428
C	-4.760267	0.734356	-3.165056
H	-4.254475	0.52209	-1.082147
H	2.332047	-4.107529	-1.679377
C	4.240748	-4.799159	-1.001118
C	5.20208	-3.723336	0.79322
H	4.119174	-2.109714	1.692192
H	1.727401	-2.679465	5.579451
C	1.112598	-4.364446	4.383806
H	0.522966	-5.839633	2.926636
H	2.332047	4.107529	1.679377
C	4.240748	4.799159	1.001118
C	5.20208	3.723336	-0.79322
H	4.119174	2.109714	-1.692192
H	5.787852	0.412289	3.021673
C	4.308055	1.08018	4.440766
H	2.624828	1.776167	5.592606
H	-2.332047	-4.107529	1.679377
C	-4.240748	-4.799159	1.001118
C	-5.20208	-3.723336	-0.79322
H	-4.119174	-2.109714	-1.692192
H	-5.787852	-0.412289	3.021673
C	-4.308055	-1.08018	4.440766
H	-2.624828	-1.776167	5.592606
H	-2.332047	4.107529	-1.679377
C	-4.240748	4.799159	-1.001118
C	-5.20208	3.723336	0.79322
H	-4.119174	2.109714	1.692192
H	-1.727401	2.679465	5.579451

Atom	x /Å	y /Å	z /Å
C	-1.112598	4.364446	4.383806
H	-0.522966	5.839633	2.926636
H	5.787852	-0.412289	-3.021673
C	4.308055	-1.08018	-4.440766
H	2.624828	-1.776167	-5.592606
H	1.727401	2.679465	-5.579451
C	1.112598	4.364446	-4.383806
H	0.522966	5.839633	-2.926636
H	-1.727401	-2.679465	-5.579451
C	-1.112598	-4.364446	-4.383806
H	-0.522966	-5.839633	-2.926636
H	-2.624828	1.776167	-5.592606
C	-4.308055	1.08018	-4.440766
H	-5.787852	0.412289	-3.021673
N	5.29769	-4.664189	-0.170615
H	4.316408	-5.572793	-1.755907
H	6.045096	-3.641392	1.468883
H	1.055448	-5.048045	5.224729
N	5.29769	4.664189	0.170615
H	4.316408	5.572793	1.755907
H	6.045096	3.641392	-1.468883
H	4.978777	1.030675	5.292291
N	-5.29769	-4.664189	0.170615
H	-4.316408	-5.572793	1.755907
H	-6.045096	-3.641392	-1.468883
H	-4.978777	-1.030675	5.292291
N	-5.29769	4.664189	-0.170615
H	-4.316408	5.572793	-1.755907
H	-6.045096	3.641392	1.468883
H	-1.055448	5.048045	5.224729
H	4.978777	-1.030675	-5.292291
H	1.055448	5.048045	-5.224729
H	-1.055448	-5.048045	-5.224729
H	-4.978777	1.030675	-5.292291
C	9.005758	-6.474363	-1.037747
C	6.956252	-5.457977	-2.526581
C	8.12858	-3.912808	-0.615902
N	7.515542	-6.119564	1.499933
N	6.335572	-7.610606	-0.365518
C	9.005758	6.474363	1.037747
C	6.956252	5.457977	2.526581
C	8.12858	3.912808	0.615902
N	7.515542	6.119564	-1.499933
N	6.335572	7.610606	0.365518
C	-9.005758	-6.474363	1.037747
C	-6.956252	-5.457977	2.526581
C	-8.12858	-3.912808	0.615902
N	-7.515542	-6.119564	-1.499933
N	-6.335572	-7.610606	0.365518
C	-9.005758	6.474363	-1.037747
C	-6.956252	5.457977	-2.526581
C	-8.12858	3.912808	-0.615902
N	-7.515542	6.119564	1.499933
N	-6.335572	7.610606	-0.365518
O	10.022195	-6.968383	-1.269509
O	6.705745	-5.383404	-3.656287
O	8.606247	-2.858236	-0.54341
C	8.191377	-5.349419	2.377946
C	6.992199	-7.300754	1.929266
C	6.335653	-8.127555	0.893919
C	5.810717	-8.341634	-1.370125
O	10.022195	6.968383	1.269509

Atom	x /Å	y /Å	z /Å
O	6.705745	5.383404	3.656287
O	8.606247	2.858236	0.54341
C	8.191377	5.349419	-2.377946
C	6.992199	7.300754	-1.929266
C	6.335653	8.127555	-0.893919
C	5.810717	8.341634	1.370125
O	-10.022195	-6.968383	1.269509
O	-6.705745	-5.383404	3.656287
O	-8.606247	-2.858236	0.54341
C	-8.191377	-5.349419	-2.377946
C	-6.992199	-7.300754	-1.929266
C	-6.335653	-8.127555	-0.893919
C	-5.810717	-8.341634	1.370125
O	-10.022195	6.968383	-1.269509
O	-6.705745	5.383404	-3.656287
O	-8.606247	2.858236	-0.54341
C	-6.992199	7.300754	1.929266
C	-8.191377	5.349419	2.377946
C	-5.810717	8.341634	-1.370125
C	-6.335653	8.127555	0.893919
H	8.614773	-4.433906	1.982025
C	8.365826	-5.700466	3.710714
C	7.127052	-7.703995	3.261214
C	5.786197	-9.386694	1.15288
C	5.259199	-9.602035	-1.17676
H	5.857618	-7.899371	-2.357994
H	8.614773	4.433906	-1.982025
C	8.365826	5.700466	-3.710714
C	7.127052	7.703995	-3.261214
C	5.786197	9.386694	-1.15288
C	5.259199	9.602035	1.17676
H	5.857618	7.899371	2.357994
H	-8.614773	-4.433906	-1.982025
C	-8.365826	-5.700466	-3.710714
C	-7.127052	-7.703995	-3.261214
C	-5.786197	-9.386694	-1.15288
C	-5.259199	-9.602035	1.17676
H	-5.857618	-7.899371	2.357994
C	-7.127052	7.703995	3.261214

Atom	x /Å	y /Å	z /Å
C	-8.365826	5.700466	3.710714
H	-8.614773	4.433906	1.982025
H	-5.857618	7.899371	-2.357994
C	-5.259199	9.602035	-1.17676
C	-5.786197	9.386694	1.15288
H	8.928954	-5.049288	4.369282
C	7.818033	-6.899535	4.162183
H	6.712032	-8.646286	3.594803
H	5.794368	-9.794501	2.155462
C	5.24389	-10.133	0.111241
H	4.866264	-10.152425	-2.023822
H	8.928954	5.049288	-4.369282
C	7.818033	6.899535	-4.162183
H	6.712032	8.646286	-3.594803
H	5.794368	9.794501	-2.155462
C	5.24389	10.133	-0.111241
H	4.866264	10.152425	2.023822
H	-8.928954	-5.049288	-4.369282
C	-7.818033	-6.899535	-4.162183
H	-6.712032	-8.646286	-3.594803
H	-5.794368	-9.794501	-2.155462
C	-5.24389	-10.133	-0.111241
H	-4.866264	-10.152425	2.023822
H	-6.712032	8.646286	3.594803
C	-7.818033	6.899535	4.162183
H	-8.928954	5.049288	4.369282
H	-4.866264	10.152425	-2.023822
C	-5.24389	10.133	0.111241
H	-5.794368	9.794501	2.155462
H	7.937236	-7.212229	5.194078
H	4.830619	-11.117595	0.302652
H	7.937236	7.212229	-5.194078
H	4.830619	11.117595	-0.302652
H	-7.937236	-7.212229	-5.194078
H	-4.830619	-11.117595	-0.302652
H	-7.937236	7.212229	5.194078
H	-4.830619	11.117595	0.302652

Table S5. Optimized atomic coordinates obtained from DFT for **5** singlet ground state (b3lyp/LanL2DZ(f)[Rh] 6-31G**[C,H,N]) E= -3653.66095020 Hartree.

Atom	x /Å	y /Å	z /Å
Rh	0	0	1.211702
Rh	0	0	-1.211702
N	0.266446	2.078908	1.128826
N	-0.266446	2.078908	-1.128826
C	-0.788251	4.971969	0.901036
H	-1.415107	4.460227	1.623349
C	0	4.248163	0
C	0.788251	4.971969	-0.901036
H	1.415107	4.460227	-1.623349
C	0.755482	6.365035	-0.853827
H	1.367828	6.946213	-1.540969
C	-0.755482	6.365035	0.853827
H	-1.367828	6.946213	1.540969
N	0	7.06734	0
C	0	2.740564	0
C	-0.923522	2.700898	-2.221369

Atom	x /Å	y /Å	z /Å
C	-0.364231	2.616008	-3.507214
H	0.597092	2.131456	-3.634136
C	-1.025206	3.168745	-4.604974
H	-0.569812	3.101203	-5.589011
C	-2.251567	3.815998	-4.443951
H	-2.761357	4.248855	-5.299175
C	-2.814051	3.904336	-3.168659
H	-3.766964	4.406718	-3.027526
C	-2.163206	3.346436	-2.069511
H	-2.608447	3.411253	-1.082767
C	0.923522	2.700898	2.221369
C	0.364231	2.616008	3.507214
H	-0.597092	2.131456	3.634136
C	1.025206	3.168745	4.604974
H	0.569812	3.101203	5.589011
C	2.251567	3.815998	4.443951

Atom	x /Å	y /Å	z /Å
H	2.761357	4.248855	5.299175
C	2.814051	3.904336	3.168659
H	3.766964	4.406718	3.027526
C	2.163206	3.346436	2.069511
H	2.608447	3.411253	1.082767
N	2.078908	-0.266446	1.128826
N	2.078908	0.266446	-1.128826
C	4.971969	0.788251	0.901036
H	4.460227	1.415107	1.623349
C	4.248163	0	0
C	4.971969	-0.788251	-0.901036
H	4.460227	-1.415107	-1.623349
C	6.365035	-0.755482	-0.853827
H	6.946213	-1.367828	-1.540969
C	6.365035	0.755482	0.853827
H	6.946213	1.367828	1.540969
N	7.06734	0	0
C	2.740564	0	0
C	2.700898	0.923522	-2.221369
C	2.616008	0.364231	-3.507214
H	2.131456	-0.597092	-3.634136
C	3.168745	1.025206	-4.604974
H	3.101203	0.569812	-5.589011
C	3.815998	2.251567	-4.443951
H	4.248855	2.761357	-5.299175
C	3.904336	2.814051	-3.168659
H	4.406718	3.766964	-3.027526
C	*3.346436*	2.163206	-2.069511
H	3.411253	2.608447	-1.082767
C	2.700898	-0.923522	2.221369
C	2.616008	-0.364231	3.507214
H	2.131456	0.597092	3.634136
C	3.168745	-1.025206	4.604974
H	3.101203	-0.569812	5.589011
C	3.815998	-2.251567	4.443951
H	4.248855	-2.761357	5.299175
C	3.904336	-2.814051	3.168659
H	4.406718	-3.766964	3.027526
C	3.346436	-2.163206	2.069511
H	3.411253	-2.608447	1.082767
N	-0.266446	-2.078908	1.128826
N	0.266446	-2.078908	-1.128826
C	0.788251	-4.971969	0.901036
H	1.415107	-4.460227	1.623349
C	0	-4.248163	0
C	-0.788251	-4.971969	-0.901036
H	-1.415107	-4.460227	-1.623349
C	-0.755482	-6.365035	-0.853827
H	-1.367828	-6.946213	-1.540969
C	0.755482	-6.365035	0.853827
H	1.367828	-6.946213	1.540969
N	0	-7.06734	0
C	0	-2.740564	0
C	0.923522	-2.700898	-2.221369
C	0.364231	-2.616008	-3.507214
H	-0.597092	-2.131456	-3.634136
C	1.025206	-3.168745	-4.604974
H	0.569812	-3.101203	-5.589011
C	2.251567	-3.815998	-4.443951
H	2.761357	-4.248855	-5.299175
C	2.814051	-3.904336	-3.168659
H	3.766964	-4.406718	-3.027526
C	2.163206	-3.346436	-2.069511
H	2.608447	-3.411253	-1.082767
C	-0.923522	-2.700898	2.221369
C	-0.364231	-2.616008	3.507214
H	0.597092	-2.131456	3.634136
C	-1.025206	-3.168745	4.604974
H	-0.569812	-3.101203	5.589011
C	-2.251567	-3.815998	4.443951
H	-2.761357	-4.248855	5.299175
C	-2.814051	-3.904336	3.168659
H	-3.766964	-4.406718	3.027526
C	-2.163206	-3.346436	2.069511
H	-2.608447	-3.411253	1.082767
N	-2.078908	0.266446	1.128826
N	-2.078908	-0.266446	-1.128826
C	-4.971969	-0.788251	0.901036
H	-4.460227	-1.415107	1.623349
C	-4.248163	0	0
C	-4.971969	0.788251	-0.901036
H	-4.460227	1.415107	-1.623349
C	-6.365035	0.755482	-0.853827
H	-6.946213	1.367828	-1.540969
C	-6.365035	-0.755482	0.853827
H	-6.946213	-1.367828	1.540969
N	-7.06734	0	0
C	-2.740564	0	0
C	-2.700898	-0.923522	-2.221369
C	-2.616008	-0.364231	-3.507214
H	-2.131456	0.597092	-3.634136
C	-3.168745	-1.025206	-4.604974
H	-3.101203	-0.569812	-5.589011
C	-3.815998	-2.251567	-4.443951
H	-4.248855	-2.761357	-5.299175
C	-3.904336	-2.814051	-3.168659
H	-4.406718	-3.766964	-3.027526
C	-3.346436	-2.163206	-2.069511
H	-3.411253	-2.608447	-1.082767
C	-2.700898	0.923522	2.221369
C	-2.616008	0.364231	3.507214
H	-2.131456	-0.597092	3.634136
C	-3.168745	1.025206	4.604974
H	-3.101203	0.569812	5.589011
C	-3.815998	2.251567	4.443951
H	-4.248855	2.761357	5.299175
C	-3.904336	2.814051	3.168659
H	-4.406718	3.766964	3.027526
C	-3.346436	2.163206	2.069511
H	-3.411253	2.608447	1.082767

Table S6. Optimized atomic coordinates obtained from DFT for **5+MeCN** singlet ground state (b3lyp/LanL2DZ(f)[Rh] 6-31G**[C,H,N]) E= -3786.42119891 Hartree.

Atom	x /Å	y /Å	z /Å
Rh	0.013651	-0.018687	1.157388
Rh	-0.019378	0.023767	-1.296967
N	1.860457	-1.072118	0.98443
N	1.999092	-0.529353	-1.272581
N	6.452314	-2.888348	-0.412961
N	-1.047989	-1.865072	1.008779
N	-0.571307	-1.995235	-1.263671
N	-2.925044	-6.441968	-0.358561
N	-1.8313	1.044541	1.071851
N	-2.03668	0.57546	-1.196543
N	-6.450631	2.927925	-0.134513
N	1.070298	1.827023	1.046813
N	0.534101	2.040489	-1.205806
N	2.893961	6.461714	-0.190667
C	2.278625	-1.948269	2.027079
C	2.806719	-1.437597	3.223165
H	2.924646	-0.364945	3.32689
C	3.200191	-2.297366	4.24878
H	3.631837	-1.883604	5.156872
C	3.072743	-3.681614	4.105018
H	3.387585	-4.348435	4.902126
C	2.553977	-4.198164	2.917129
H	2.461689	-5.272556	2.784322
C	2.157483	-3.339851	1.890251
H	1.757716	-3.741782	0.965698
C	2.806221	-0.173907	-2.384228
C	3.901786	0.69766	-2.254377
H	4.164192	1.076464	-1.272572
C	4.649443	1.07564	-3.368918
H	5.496085	1.744818	-3.242723
C	4.312672	0.60464	-4.639336
H	4.894042	0.901723	-5.506799
C	3.22164	-0.25522	-4.779009
H	2.952132	-0.638705	-5.759172
C	2.474149	-0.642389	-3.666281
H	1.63789	-1.322098	-3.779916
C	2.529648	-1.062724	-0.173137
C	3.901245	-1.692149	-0.247726
C	4.954205	-1.273504	0.572579
H	4.811263	-0.479916	1.297059
C	6.196159	-1.893894	0.446256
H	7.028526	-1.574494	1.071028
C	5.437412	-3.285816	-1.190762
H	5.654933	-4.095411	-1.88518
C	4.161056	-2.725889	-1.153889
H	3.384351	-3.084483	-1.820403
C	-1.901896	-2.281019	2.070936
C	-1.368179	-2.828547	3.247889
H	-0.295108	-2.965173	3.320682
C	-2.206002	-3.21761	4.293255
H	-1.774967	-3.662838	5.186565
C	-3.591289	-3.067302	4.187884
H	-4.241378	-3.378515	5.000083
C	-4.131192	-2.530261	3.018616
H	-5.207166	-2.420269	2.915491
C	-3.2946	-2.137876	1.972607
H	-3.714645	-1.723269	1.062921
C	-0.249981	-2.799633	-2.387518
C	0.622775	-3.89722	-2.285776
H	1.030077	-4.162252	-1.316085
C	0.96615	-4.643155	-3.412624
H	1.636974	-5.491457	-3.308164

Atom	x /Å	y /Å	z /Å
C	0.45854	-4.302535	-4.66782
H	0.728642	-4.882554	-5.544952
C	-0.402754	-3.209403	-4.779684
H	-0.814369	-2.936939	-5.747545
C	-0.755361	-2.463628	-3.654402
H	-1.436448	-1.625731	-3.745962
C	-1.074716	-2.528756	-0.151704
C	-1.712501	-3.897141	-0.214731
C	-1.274853	-4.956768	0.586822
H	-0.459608	-4.82178	1.288385
C	-1.904387	-6.195231	0.472146
H	-1.570402	-7.03259	1.082467
C	-3.340748	-5.420763	-1.11839
H	-4.17167	-5.630606	-1.789575
C	-2.774002	-4.147173	-1.091071
H	-3.148779	-3.365023	-1.742106
C	-2.202354	1.902704	2.146835
C	-2.676529	1.371619	3.356032
H	-2.791743	0.297409	3.445172
C	-3.021442	2.213086	4.41343
H	-3.4056	1.783658	5.335171
C	-2.90074	3.599297	4.287738
H	-3.177182	4.251888	5.110441
C	-2.436911	4.136815	3.08634
H	-2.349975	5.213356	2.968111
C	-2.087286	3.296736	2.028413
H	-1.728838	3.714878	1.094328
C	-2.87682	0.257594	-2.294827
C	-3.975112	-0.609757	-2.15974
H	-4.212797	-1.015937	-1.182557
C	-4.757001	-0.948914	-3.263267
H	-5.605043	-1.615511	-3.132861
C	-4.452732	-0.442451	-4.528209
H	-5.060843	-0.709226	-5.387139
C	-3.359291	0.41348	-4.673335
H	-3.11471	0.824302	-5.64895
C	-2.577474	0.761766	-3.571439
H	-1.739659	1.439059	-3.688555
C	-2.532697	1.077157	-0.066402
C	-3.901924	1.716004	-0.081238
C	-4.927902	1.287813	0.767879
H	-4.763819	0.481354	1.473338
C	-6.170017	1.916586	0.696849
H	-6.981609	1.58996	1.344792
C	-5.461158	3.335	-0.939701
H	-5.698115	4.158775	-1.610673
C	-4.187505	2.768175	-0.958049
H	-3.432374	3.136275	-1.643839
C	1.953643	2.199367	2.100371
C	1.450111	2.653219	3.329115
H	0.377319	2.74981	3.45084
C	2.316552	3.001076	4.365079
H	1.908079	3.370481	5.302279
C	3.700334	2.902777	4.198749
H	4.372027	3.181663	5.005099
C	4.21013	2.458281	2.978106
H	5.284023	2.388652	2.828455
C	3.345313	2.105923	1.9411
H	3.741871	1.762914	0.991795
C	0.182145	2.882869	-2.292003
C	-0.683211	3.978931	-2.128985
H	-1.060225	4.214266	-1.139689

Atom	x /Å	y /Å	z /Å
C	-1.056944	4.762028	-3.2204
H	-1.721251	5.608273	-3.068456
C	-0.587882	4.461264	-4.500519
H	-0.881629	5.070332	-5.34992
C	0.265816	3.370116	-4.673247
H	0.647877	3.128245	-5.661146
C	0.648654	2.587111	-3.583714
H	1.323935	1.751048	-3.722667
C	1.066554	2.5338	-0.088602
C	1.69764	3.906377	-0.115363
C	1.289081	4.925449	0.751577
H	0.504431	4.753117	1.479349
C	1.909042	6.171262	0.668629
H	1.597472	6.977677	1.330295
C	3.282234	5.478772	-1.012946
H	4.084532	5.723745	-1.706689
C	2.721844	4.202177	-1.021411
H	3.073358	3.452714	-1.721993
C	0.058275	-0.18206	4.485456
N	0.042905	-0.082288	3.334583
C	0.078142	-0.333566	5.931711
H	0.04251	0.646288	6.415077
H	-0.785497	-0.924881	6.248899
H	0.994152	-0.850851	6.231005

Table S7. Optimized atomic coordinates obtained from DFT for (**5+MeCN)**$^{+}$ doublet ground state (b3lyp/LanL2DZ(f)[Rh] 6-31G**[C,H,N]) E= -3786.22305851 Hartree.

Atom	x /Å	y /Å	z /Å
Rh	0.014461	-0.005428	1.1604031
Rh	-0.016304	0.0061251	-1.2903551
N	2.0506412	-0.522931	1.0018701
N	2.0402422	0.0261211	-1.2553991
N	6.9670375	-1.0198287	-0.382362
N	-0.509023	-2.0435651	1.0257211
N	0.004614	-2.0504321	-1.2400201
N	-1.0393228	-6.9681544	-0.316654
N	-2.0231401	0.5186021	1.0577851
N	-2.0713452	-0.0157899	-1.2024671
N	-6.9717504	1.0395709	-0.198923
N	0.5337371	2.0303462	1.0337831
N	-0.0371289	2.0613943	-1.2177931
N	1.0222488	6.9707506	-0.26636
C	2.7094979	-1.2108804	2.0713842
C	3.0763092	-0.535877	3.2434933
H	2.8858783	0.5281054	3.3228233
C	3.7106469	-1.2217933	4.2795184
H	4.016292	-0.6801169	5.1704924
C	3.9829883	-2.587563	4.1659683
H	4.4849043	-3.115193	4.9707694
C	3.6229539	-3.2628533	2.9993633
H	3.8441788	-4.3204278	2.8909772
C	2.9885962	-2.580352	1.9600592
H	2.7193731	-3.1029645	1.0486031
C	2.7335763	0.5490237	-2.3864332
C	3.5473686	1.6882792	-2.2710552
H	3.6878825	2.14845	-1.2991701
C	4.1768517	2.224219	-3.3931982
H	4.8092105	3.1002588	-3.2847262
C	3.9972636	1.6408683	-4.6493453
H	4.4895294	2.0585884	-5.5216134
C	3.1853583	0.5120578	-4.7704353
H	3.0475123	0.0413941	-5.7392014
C	2.5553172	-0.032753	-3.6505023
H	1.9416434	-0.9199108	-3.7480913
C	2.7033186	-0.3367283	-0.148105
C	4.1921202	-0.5684812	-0.22167
C	5.0870407	0.1317081	0.5939051
H	4.7345141	0.8615088	1.3134281
C	6.4520843	-0.1258136	0.4694811
H	7.1659904	0.414058	1.0881491
C	6.1038142	-1.6879281	-1.1561171
H	6.5365318	-2.411991	-1.8433171
C	4.7221785	-1.4984813	-1.1221181
H	4.0764373	-2.0612551	-1.7869051
C	-1.1938774	-2.6896818	2.1051012
C	-0.511997	-3.0643552	3.2705883
H	0.5560714	-2.8919753	3.3369133
C	-1.1966043	-3.6836149	4.3166694
H	-0.6503639	-3.9944	5.2029964
C	-2.5678019	-3.9338322	4.2191343
H	-3.0945959	-4.4241152	5.0316204
C	-3.2499272	-3.5672688	3.0585273
H	-4.3120427	-3.7717937	2.9624893
C	-2.568668	-2.9476221	2.0097392
H	-3.0965445	-2.6721001	1.1033481
C	0.5106927	-2.7538552	-2.3725732
C	1.6515831	-3.5665015	-2.2663722
H	2.1260319	-3.6975504	-1.2999961
C	2.1708309	-4.2067275	-3.3903112
H	3.0483328	-4.8382393	-3.2888952
C	1.5689472	-4.0388883	-4.6392973
H	1.9737773	-4.5393612	-5.5129724
C	0.4384767	-3.2279581	-4.7513693
H	-0.0462761	-3.0990381	-5.7143994
C	-0.0896911	-2.587291	-3.6294973
H	-0.9783029	-1.9745712	-3.7197393
C	-0.3428213	-2.7044865	-0.122684
C	-0.5789133	-4.1932421	-0.182356
C	0.137167	-5.0849646	0.6228271
H	0.8840748	-4.73004	1.3233651
C	-0.1254237	-6.4502072	0.5119301
H	0.426708	-7.1616433	1.1225771
C	-1.7232261	-6.107936	-1.0798871
H	-2.463431	-6.5430466	-1.7481091
C	-1.5302564	-4.7265343	-1.0582321
H	-2.1075732	-4.0833221	-1.7129101
C	-2.6458008	1.2172094	2.1417312
C	-2.9794551	0.552965	3.3293833

Atom	x /Å	y /Å	z /Å
H	-2.7937462	-0.5118605	3.4094873
C	-3.5763288	1.2500312	4.3798494
H	-3.8516669	0.7182467	5.2862424
C	-3.8457731	2.6159118	4.2641963
H	-4.3180361	3.1523188	5.0810424
C	-3.5209258	3.2805382	3.0810793
H	-3.7405197	4.3383378	2.9715453
C	-2.9229471	2.587159	2.0280012
H	-2.6807031	3.1011596	1.1042921
C	-2.7949102	-0.5323295	-2.3174052
C	-3.6065515	-1.671354	-2.1859781
H	-3.7203585	-2.1370008	-1.2131931
C	-4.2674016	-2.2003087	-3.2933102
H	-4.8974674	-3.0763755	-3.1723752
C	-4.1224815	-1.609653	-4.5504903
H	-4.6393193	-2.021858	-5.4110914
C	-3.3133162	-0.4806895	-4.6875563
H	-3.2021042	-0.0044636	-5.6570234
C	-2.6513921	0.0567153	-3.5825413
H	-2.0405893	0.9444981	-3.6920013
C	-2.7052415	0.3428184	-0.07686
C	-4.1945852	0.5803264	-0.110905
C	-5.0705166	-0.120865	0.7242171
H	-4.702018	-0.8542288	1.4319841
C	-6.4375732	0.1408707	0.6359681
H	-7.1368113	-0.3995329	1.2707071
C	-6.1266331	1.7085822	-0.9916901
H	-6.5746787	2.4366752	-1.6646571
C	-4.7451404	1.5154255	-0.9936651
H	-4.1153282	2.0794573	-1.6724491
C	1.2392654	2.6653448	2.1058962
C	0.586208	2.9941871	3.3011453
H	-0.4744755	2.7932102	3.3968733
C	1.2889282	3.6051078	4.3396414

Atom	x /Å	y /Å	z /Å
H	0.7653197	3.8773159	5.2517564
C	2.6494079	3.8924882	4.2049763
H	3.1900519	4.3754411	5.0127244
C	3.3029333	3.5710768	3.0147573
H	4.3562548	3.8040258	2.8905902
C	2.6040121	2.9594412	1.9731582
H	3.1095306	2.7204152	1.0438201
C	-0.5732945	2.7758534	-2.3293832
C	-1.712345	3.5853187	-2.1854131
H	-2.1620288	3.7058236	-1.2060031
C	-2.2615438	4.2360188	-3.2888752
H	-3.1372606	4.8646256	-3.1581972
C	-1.6916181	4.0826847	-4.5546013
H	-2.1195671	4.5915956	-5.4122354
C	-0.5628476	3.2754834	-4.7041003
H	-0.1024038	3.1579555	-5.6804194
C	-0.0050168	2.6240153	-3.6029713
H	0.8822021	2.0143365	-3.7225263
C	0.3373934	2.7041356	-0.102351
C	0.5706883	4.1936663	-0.15085
C	-0.131382	5.0753917	0.6773481
H	-0.8619898	4.7112821	1.3902651
C	0.1265247	6.4422283	0.5753481
H	-0.4143859	7.1461194	1.2044821
C	1.6919842	6.1199832	-1.0524451
H	2.4174131	6.5636258	-1.7311881
C	1.5023965	4.7380405	-1.0409761
H	2.0660693	4.1029983	-1.7152471
C	0.0727279	-0.0925381	4.4782084
N	0.046297	-0.032956	3.3255353
C	0.1143147	-0.1858452	5.9284075
H	-0.1974825	0.7617435	6.3752725
H	-0.5570689	-0.9820059	6.2620505
H	1.1333793	-0.4191782	6.2493425

Table S8. Singlet electronic transitions obtained from TD-DFT for **1** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[$C_{amidinate}$,N,CO], 3-21G[C_{aryl},H] with CPCM (DCM).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
1316.5	0	A	HOMO->L+1 (83%)
761.9	0.0001	A	HOMO->LUMO (100%)
748.4	0.009	A	H-4->L+1 (72%)
745.8	0.0091	A	H-5->L+1 (72%)
659.4	0.0017	A	H-1->L+1 (88%)
641.8	0.0028	A	H-2->L+1 (87%)
625.5	0.0092	A	HOMO->L+2 (89%)
543.8	0	A	H-1->LUMO (100%)
542.0	0.0067	A	H-3->L+1 (98%)
533.3	0.0001	A	H-2->LUMO (97%)
509.8	0.0165	A	HOMO->L+5 (76%)
482.1	0.0001	A	H-12->L+1 (12%), H-8->L+1 (56%)
469.7	0.0001	A	H-3->LUMO (97%)
462.2	0.0002	A	HOMO->L+3 (97%)
456.8	0.0097	A	H-1->L+2 (98%)
455.4	0.0172	A	H-2->L+2 (86%)
449.3	0.0002	A	HOMO->L+4 (32%), HOMO->L+11 (34%)
442.9	0	A	H-4->LUMO (99%)
442.2	0	A	HOMO->L+4 (67%), HOMO->L+11 (20%)
440.6	0.0008	A	H-5->LUMO (99%)
427.8	0.0013	A	HOMO->L+7 (93%)
424.4	0.0066	A	HOMO->L+8 (91%)
407.4	0.0701	A	H-7->L+1 (67%), H-6->L+1 (12%), H-4->L+1 (12%)
406.6	0.0005	A	HOMO->L+6 (66%), HOMO->L+9 (15%), HOMO->L+11 (12%)
405.8	0.0029	A	H-3->L+2 (81%)
404.1	0.0849	A	H-7->L+1 (13%), H-6->L+1 (63%), H-5->L+1 (10%)
395.2	0.0045	A	H-4->L+2 (80%)
393.8	0.0195	A	H-5->L+2 (87%)
387.5	0.0004	A	H-10->L+1 (77%)
383.8	0.0041	A	H-17->LUMO (41%), H-16->LUMO (45%)
383.5	0.0002	A	HOMO->L+6 (24%), HOMO->L+9 (71%)
380.8	0.0409	A	H-15->LUMO (14%), H-9->LUMO (18%), H-8->LUMO (24%), H-6->LUMO (21%)
374.3	0.0217	A	H-1->L+3 (27%), H-1->L+5 (61%)
373.9	0.0158	A	HOMO->L+12 (46%)
373.6	0.0011	A	H-7->LUMO (92%)
372.9	0.0197	A	H-15->LUMO (17%), H-6->LUMO (68%)
371.1	0.005	A	H-1->L+3 (72%), H-1->L+5 (23%)
368.2	0.0168	A	H-2->L+3 (42%), H-2->L+5 (41%)
365.8	0.011	A	H-2->L+3 (52%), H-2->L+5 (34%)
365.4	0.0048	A	H-26->LUMO (20%), H-15->LUMO (11%), H-8->LUMO (49%)
364.9	0.0065	A	H-12->L+1 (32%), H-11->L+1 (25%), H-8->L+1 (27%)
361.8	0.0125	A	H-26->LUMO (52%), H-8->LUMO (17%)
360.2	0.0002	A	H-1->L+4 (98%)
358.5	0.0008	A	H-9->L+1 (73%)
356.9	0.0077	A	H-28->L+1 (15%), H-13->L+1 (56%)
356.4	0.0171	A	H-12->L+1 (25%), H-11->L+1 (24%)
355.9	0.0017	A	H-2->L+4 (91%)
353.6	0.001	A	HOMO->L+10 (95%)
351.6	0.0074	A	H-15->LUMO (16%), H-9->LUMO (67%)
349.6	0.0033	A	H-4->L+5 (55%)

Table S9. Singlet electronic transitions obtained from TD-DFT for **4** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[$C_{amidinate}$,N,CO], 3-21G[C_{aryl},H] with CPCM (DCM).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
1288.1	0	A	HOMO->LUMO (83%)
744.2	0.0092	B2	H-6->LUMO (13%), H-5->LUMO (68%)
743.7	0.0097	B3	H-7->LUMO (14%), H-4->LUMO (69%)
659.4	0.0013	B3	H-2->LUMO (89%)
658.6	0.0015	B2	H-1->LUMO (87%)
619.3	0.015	B1	HOMO->L+1 (38%), HOMO->L+5 (54%)
605.2	0	A	HOMO->L+2 (97%)
604.5	0.0004	B3	HOMO->L+4 (99%)
604.4	0	B2	HOMO->L+3 (99%)
595.7	0.0065	B1	HOMO->L+1 (62%), HOMO->L+5 (34%)
556.1	0	A	HOMO->L+6 (95%)
547.0	0.0062	B1	H-3->LUMO (98%)
543.4	0.0035	B2	HOMO->L+7 (95%)
542.6	0.003	B3	HOMO->L+8 (95%)
475.1	0	B1	H-21->LUMO (40%), H-17->LUMO (26%), H-8->LUMO (17%)
465.7	0.0027	B3	H-2->L+2 (30%), H-1->L+1 (65%)
465.5	0.0002	B2	H-2->L+1 (47%), H-1->L+2 (47%)
464.8	0.0013	B1	H-2->L+3 (39%), H-1->L+4 (58%)
464.8	0	A	H-2->L+4 (39%), H-1->L+3 (58%)
461.5	0.0026	B2	H-2->L+1 (47%), H-1->L+2 (50%)
461.3	0.001	B3	H-2->L+2 (68%), H-1->L+1 (29%)
460.7	0	A	H-2->L+4 (59%), H-1->L+3 (40%)
460.7	0.0002	B1	H-2->L+3 (59%), H-1->L+4 (40%)
447.3	0	A	HOMO->L+17 (25%), HOMO->L+21 (16%), HOMO->L+26 (29%)
443.3	0.0194	B3	H-1->L+5 (86%)
442.8	0.0136	B2	H-2->L+5 (85%)
431.3	0.038	B1	H-2->L+7 (31%), H-1->L+8 (32%), HOMO->L+25 (19%)
428.8	0.003	B2	H-1->L+6 (89%)
428.5	0	A	H-3->L+5 (11%), H-2->L+8 (38%), H-1->L+7 (45%)
428.2	0.0018	B3	H-2->L+6 (90%)

Table S10. Singlet and triplet electronic transitions obtained from TD-DFT for **5** from singlet ground state; G03 b3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (DCM).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
2210.8	0	^{3}B2	HOMO(A)->LUMO(A) (64%), HOMO(B)->LUMO(B) (64%)
1335.5	0	^{1}B2	HOMO->LUMO (82%)
1075.8	0	^{3}E	H-4(A)->LUMO(A) (55%), H-4(B)->LUMO(B) (55%)
1075.8	0	^{3}E	H-4(A)->LUMO(A) (55%), H-4(B)->LUMO(B) (55%)
749.6	0.0088	^{1}E	H-4->LUMO (75%)
749.6	0.0088	^{1}E	H-5->LUMO (75%)
702.5	0	^{3}E	H-1(A)->LUMO(A) (47%), H-1(B)->LUMO(B) (47%)
702.5	0	^{3}E	H-1(A)->LUMO(A) (47%), H-1(B)->LUMO(B) (47%)
650.6	0.0019	^{1}E	H-1->LUMO (90%)
650.6	0.0019	^{1}E	H-2->LUMO (90%)
547.7	0.0117	^{1}A2	H-3->LUMO (95%)
540.4	0.0231	^{1}A2	HOMO->L+1 (81%)
485.0	0	^{1}B1	H-11->LUMO (21%), H-8->LUMO (69%)
445.3	0	^{1}A1	HOMO->L+5 (70%), HOMO->L+10 (10%)
438.7	0	^{1}B2	HOMO->L+2 (97%)
427.7	0.0051	^{1}E	HOMO->L+3 (96%)
427.7	0.0051	^{1}E	HOMO->L+4 (96%)
403.3	0.0688	^{1}E	H-6->LUMO (81%), H-4->LUMO (10%)
403.3	0.0688	^{1}E	H-7->LUMO (81%), H-5->LUMO (10%)
385.3	0	^{1}B2	H-10->LUMO (88%)
380.7	0.0476	^{1}E	H-1->L+1 (85%)
380.7	0.0476	^{1}E	H-2->L+1 (85%)
366.8	0.0129	^{1}A2	HOMO->L+1 (10%), HOMO->L+9 (51%)
362.9	0.0016	^{1}E	H-4->L+1 (69%)
362.9	0.0016	^{1}E	H-5->L+1 (69%)
361.5	0	^{1}B1	H-11->LUMO (75%), H-8->LUMO (24%)
356.9	0.0167	^{1}E	H-25->LUMO (15%), H-13->LUMO (62%)
356.9	0.0167	^{1}E	H-26->LUMO (15%), H-14->LUMO (62%)
356.7	0	^{1}A1	H-9->LUMO (95%)
351.4	0	^{1}B2	H-3->L+1 (63%), H-2->L+4 (16%), H-1->L+3 (16%)
348.4	0.0001	^{1}A2	H-12->LUMO (43%), H-2->L+4 (13%), H-1->L+3 (13%), HOMO->L+9 (10%)
347.8	0.002	^{1}E	H-1->L+2 (89%)
347.8	0.002	^{1}E	H-2->L+2 (89%)
339.4	0.0035	^{1}E	H-34->LUMO (12%), H-32->LUMO (41%), H-20->LUMO (10%), H-4->L+5 (10%)
339.4	0.0034	^{1}E	H-33->LUMO (12%), H-31->LUMO (41%), H-21->LUMO (10%), H-5->L+5 (10%)
339.1	0	^{1}B2	H-3->L+1 (32%), H-2->L+4 (32%), H-1->L+3 (32%)
338.2	0	^{1}E	H-2->L+3 (38%), H-1->L+4 (31%), HOMO->L+6 (30%)
338.1	0	^{1}E	H-2->L+3 (45%), H-1->L+4 (53%)
337.8	0	^{1}B1	H-2->L+3 (15%), H-1->L+4 (15%), HOMO->L+6 (67%)
337.8	0.2295	^{1}A2	H-12->LUMO (30%), H-2->L+4 (27%), H-1->L+3 (27%)
334.4	0	^{1}B1	H-15->LUMO (98%)
333.6	0.0115	^{1}E	HOMO->L+7 (95%)
333.5	0.0115	^{1}E	HOMO->L+8 (95%)
332.0	0	^{1}B2	H-19->LUMO (13%), H-16->LUMO (85%)
329.5	0.0127	^{1}E	H-17->LUMO (89%)
329.5	0.0127	^{1}E	H-18->LUMO (89%)
328.6	0	^{1}A1	HOMO->L+5 (22%), HOMO->L+10 (62%)
324.3	0.0002	^{1}E	H-20->LUMO (79%)
324.3	0.0002	^{1}E	H-21->LUMO (79%)
322.8	0	^{1}B1	HOMO->L+11 (97%)
320.9	0.0002	^{1}A2	H-24->LUMO (20%), H-22->LUMO (70%)
318.3	0	^{1}A1	H-23->LUMO (95%)
316.7	0	^{1}A2	H-3->L+2 (78%)

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
316.2	0.0534	^{1}E	H-3->L+3 (10%), H-2->L+5 (41%), HOMO->L+12 (31%)
316.2	0.0535	^{1}E	H-3->L+4 (10%), H-1->L+5 (41%), HOMO->L+13 (31%)
316.1	0	^{1}B2	H-19->LUMO (82%), H-16->LUMO (14%)
314.8	0.0367	^{1}E	H-3->L+3 (15%), H-2->L+5 (41%), HOMO->L+12 (28%)
314.8	0.0366	^{1}E	H-3->L+4 (15%), H-1->L+5 (41%), HOMO->L+13 (28%)
311.8	0.0278	^{1}E	H-4->L+2 (15%), H-3->L+3 (44%), HOMO->L+12 (32%)
311.8	0.0278	^{1}E	H-5->L+2 (15%), H-3->L+4 (44%), HOMO->L+13 (32%)
310.6	0.0001	^{1}E	H-25->LUMO (28%), H-5->L+2 (23%), H-4->L+5 (21%)
310.6	0.0001	^{1}E	H-26->LUMO (28%), H-5->L+5 (21%), H-4->L+2 (24%)
310.5	0.0267	^{1}A2	H-24->LUMO (53%), HOMO->L+21 (13%)
310.1	0.0119	^{1}E	H-5->L+2 (55%), H-3->L+4 (20%)
310.1	0.0119	^{1}E	H-26->LUMO (10%), H-4->L+2 (54%), H-3->L+3 (20%)
306.7	0	^{1}B2	HOMO->L+14 (31%), HOMO->L+15 (65%)
306.4	0.2702	^{1}A2	H-24->LUMO (25%), H-22->LUMO (10%), HOMO->L+9 (15%), HOMO->L+21 (25%)
306.1	0.001	^{1}E	H-32->LUMO (13%), H-25->LUMO (35%), H-4->L+5 (20%)
306.1	0.001	^{1}E	H-31->LUMO (13%), H-26->LUMO (36%), H-5->L+5 (20%)
305.7	0	^{1}E	H-5->L+3 (48%), H-4->L+4 (48%)
305.1	0	^{1}A1	H-8->L+1 (37%), H-5->L+3 (13%), H-4->L+4 (14%), HOMO->L+10 (16%)
304.5	0.0002	^{1}E	H-5->L+4 (34%), H-4->L+3 (61%)
304.5	0	^{1}E	H-5->L+4 (51%), H-4->L+3 (24%), HOMO->L+14 (16%)
303.9	0	^{1}B2	H-5->L+4 (12%), H-4->L+3 (12%), HOMO->L+14 (50%), HOMO->L+15 (24%)
302.5	0	^{1}E	H-8->L+1 (17%), H-5->L+3 (33%), H-4->L+4 (33%)
300.4	0	^{1}B1	HOMO->L+16 (95%)
297.9	0.0015	^{1}E	HOMO->L+17 (96%)
297.9	0.0015	^{1}E	HOMO->L+18 (96%)
294.9	0	^{1}B1	H-3->L+5 (89%)
291.1	0.0007	^{1}E	HOMO->L+19 (93%)
291.1	0.0007	^{1}E	HOMO->L+20 (93%)
288.6	0.0296	^{1}E	H-6->L+1 (73%)
288.6	0.0296	^{1}E	H-7->L+1 (73%)
288.2	0	^{1}A1	HOMO->L+22 (96%)
287.1	0	?Sym	H-29->LUMO (98%)

Table S11. Singlet electronic transitions obtained from TD-DFT for **5+MeCN** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (MeCN).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
740.2	0	A	HOMO->LUMO (86%)
587.9	0.0117	A	HOMO->L+1 (82%)
555.9	0.0045	A	H-4->LUMO (56%), H-2->LUMO (27%)
555.6	0.0045	A	H-5->LUMO (56%), H-1->LUMO (27%)
467.9	0.0092	A	HOMO->L+5 (69%)
456.0	0.0031	A	H-5->LUMO (26%), H-1->LUMO (61%)
455.0	0.0031	A	H-4->LUMO (26%), H-2->LUMO (61%)
437.6	0.0007	A	HOMO->L+3 (53%), HOMO->L+4 (34%)
436.7	0.0052	A	HOMO->L+2 (88%)
434.6	0.0047	A	HOMO->L+3 (37%), HOMO->L+4 (59%)
410.4	0.0064	A	H-3->LUMO (96%)
401.8	0.011	A	H-4->L+1 (15%), H-2->L+1 (36%), H-1->L+1 (34%)
401.6	0.0118	A	H-5->L+1 (14%), H-2->L+1 (34%), H-1->L+1 (36%)
381.3	0.0204	A	H-5->L+1 (25%), H-4->L+1 (30%), H-1->L+1 (17%)
381.2	0.0204	A	H-5->L+1 (31%), H-4->L+1 (25%), H-2->L+1 (18%)
377.6	0	A	H-8->LUMO (80%)
372.8	0.0112	A	HOMO->L+1 (10%), HOMO->L+9 (35%), HOMO->L+10 (26%)
364.9	0	A	H-3->L+1 (88%)
352.2	0.0001	A	HOMO->L+6 (97%)
348.1	0.0112	A	HOMO->L+7 (72%)
347.9	0.0111	A	HOMO->L+8 (73%)
346.4	0.0031	A	H-1->L+3 (23%), H-1->L+4 (39%), HOMO->L+7 (14%)
346.2	0.0125	A	H-2->L+3 (38%), H-2->L+4 (21%), HOMO->L+8 (11%)
345.7	0.0346	A	H-1->L+2 (62%)
344.4	0.0067	A	H-2->L+3 (27%), H-2->L+4 (26%), H-1->L+2 (13%)
343.3	0.0124	A	H-2->L+3 (16%), HOMO->L+5 (12%), HOMO->L+9 (16%), HOMO->L+10 (21%)
342.7	0.0021	A	H-5->L+5 (13%), H-1->L+5 (43%)
342.4	0.0037	A	H-4->L+5 (10%), H-2->L+4 (20%), H-2->L+5 (36%)
341.4	0.0001	A	H-2->L+2 (93%)
340.5	0	A	H-1->L+3 (62%), H-1->L+4 (34%)

Table S12. Doublet electronic transitions obtained from TD-DFT for (**5**+**MeCN**)$^+$ from doublet ground state; G03 ub3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (MeCN).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
1436.7	0.0293	A	HOMO(B)->LUMO(B) (83%)
1432.2	0.0286	A	H-1(B)->LUMO(B) (83%)
1037.8	0	A	H-2(B)->LUMO(B) (94%)
952.7	0.0144	A	H-11(B)->LUMO(B) (38%), H-3(B)->LUMO(B) (36%), H-1(B)->LUMO(B) (13%)
951.7	0.0143	A	H-12(B)->LUMO(B) (37%), H-4(B)->LUMO(B) (36%), HOMO(B)->LUMO(B) (13%)
738.4	0.0004	A	HOMO(A)->LUMO(A) (85%)
738.2	0.0036	A	H-19(B)->LUMO(B) (13%), H-16(B)->LUMO(B) (23%), H-6(B)->LUMO(B) (37%)
660.4	0.0072	A	H-11(B)->LUMO(B) (31%), H-3(B)->LUMO(B) (59%)
657.1	0.0072	A	H-12(B)->LUMO(B) (31%), H-4(B)->LUMO(B) (58%)
649.1	0.0001	A	H-30(B)->LUMO(B) (15%), H-18(B)->LUMO(B) (19%), H-7(B)->LUMO(B) (23%), H-5(B)->LUMO(B) (33%)
599.9	0.0001	A	H-19(A)->LUMO(A) (14%), H-4(A)->LUMO(A) (11%), H-11(B)->L+1(B) (27%), H-3(B)->L+1(B) (13%)
599.0	0.0001	A	H-20(A)->LUMO(A) (14%), H-5(A)->LUMO(A) (11%), H-12(B)->L+1(B) (27%), H-4(B)->L+1(B) (14%)
585.2	0.0285	A	H-10(B)->LUMO(B) (44%), H-9(B)->LUMO(B) (14%), H-6(B)->LUMO(B) (25%)
581.8	0.0005	A	H-7(B)->LUMO(B) (19%), H-5(B)->LUMO(B) (61%)
564.4	0.0053	A	H-24(B)->LUMO(B) (18%), H-8(B)->LUMO(B) (60%)
562.9	0.0052	A	H-25(B)->LUMO(B) (18%), H-10(B)->LUMO(B) (17%), H-9(B)->LUMO(B) (41%)
554.1	0.0025	A	H-19(B)->LUMO(B) (31%), H-16(B)->LUMO(B) (20%), H-6(B)->LUMO(B) (31%)
541.0	0.0027	A	HOMO(B)->L+1(B) (74%)
539.7	0.0027	A	H-1(B)->L+1(B) (74%)
529.4	0.001	A	H-16(B)->LUMO(B) (32%), H-13(B)->LUMO(B) (49%)
524.0	0.0026	A	HOMO(A)->L+1(A) (67%)
520.2	0.0003	A	H-14(B)->LUMO(B) (67%)
519.7	0.0003	A	H-20(B)->LUMO(B) (10%), H-15(B)->LUMO(B) (66%)
515.1	0.0001	A	H-17(B)->LUMO(B) (71%), H-14(B)->LUMO(B) (10%)
509.5	0.0022	A	H-33(A)->LUMO(A) (17%), HOMO(A)->L+1(A) (12%), H-30(B)->L+1(B) (19%), H-2(B)->L+1(B) (24%)
508.8	0.0056	A	H-1(A)->LUMO(A) (24%), H-20(B)->LUMO(B) (29%)
508.5	0.0076	A	H-2(A)->LUMO(A) (30%), H-1(A)->LUMO(A) (11%), H-21(B)->LUMO(B) (18%)
507.3	0.0066	A	H-2(A)->LUMO(A) (16%), H-1(A)->LUMO(A) (24%), H-20(B)->LUMO(B) (19%)
507.1	0.0037	A	H-2(A)->LUMO(A) (12%), H-1(A)->LUMO(A) (11%), H-21(B)->LUMO(B) (23%), H-20(B)->LUMO(B) (14%)
506.5	0.0007	A	H-21(B)->LUMO(B) (17%), H-18(B)->LUMO(B) (34%), H-7(B)->LUMO(B) (27%)

Table S13. Energy and contribution of MO obtained from DFT for **1** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[$C_{amidinate}$,N,CO], 3-21G[C_{aryl},H] with CPCM (DCM).

MO	eV	Symm.	Rh2	Amidinate	Pyridine	Phenyl	Carbonyl	Bipyridine	Re
L+20	-0.35	A	0.0194344	0.0820708	0.128642	0.628221497	0.08569367	0.0543856	0.0015399
L+19	-0.36	A	0.0057015	0.0162625	0.0354408	0.121163705	0.48536743	0.3282585	0.0078047
L+18	-0.43	A	0.0517297	0.1473281	0.1970809	0.521290594	0.05707049	0.0062981	0.0192005
L+17	-0.46	A	0.0750002	0.0192995	0.305868	0.495266091	0.02890778	0.0738336	0.0018172
L+16	-0.48	A	0.044834	0.0098528	0.1009752	0.383565946	0.17297216	0.2827723	0.0050366
L+15	-0.5	A	0.0424728	0.025355	0.3407043	0.182469983	0.16843925	0.2363143	0.0042403
L+14	-0.63	A	0.0187055	0.0136314	0.8004695	0.166241544	0.00036243	0.0004223	0.000163
L+13	-0.64	A	0.0293005	0.0144472	0.7584878	0.196819853	0.00061288	0.0002447	7.69E-05
L+12	-0.73	A	0.1422747	0.134705	0.282412	0.417116167	0.01410345	0.0021277	0.007256
L+11	-0.95	A	0.2526385	0.1344561	0.2138726	0.393201373	0.00338339	0.001609	0.0008428
L+10	-1.15	A	0.0010007	0.0025232	0.029349	0.003255846	0.6520407	0.0658941	0.2459228
L+9	-1.36	A	0.01186	0.0106307	0.5471662	0.052313035	0.238374	0.0454764	0.0941757
L+8	-1.41	A	0.019475	0.2375883	0.6130528	0.11908028	0.00714775	0.0007835	0.0028783
L+7	-1.42	A	0.0340343	0.2187435	0.6138984	0.132399529	0.0005673	0.0001624	0.000191
L+6	-1.51	A	0.0041875	0.003848	0.3118003	0.021512294	0.43584956	0.0404758	0.1823276
L+5	-1.64	A	0.150884	0.2001756	0.4551971	0.190767	0.00157481	0.0007684	0.0006367
L+4	-1.86	A	0.0001953	0.0001601	0.028202	0.001085725	0.03135213	0.9363769	0.0026412
L+3	-1.97	A	0.0013992	0.0032257	0.0191353	0.002054683	0.02689811	0.934079	0.0132142
L+2	-2.38	A	0.030743	0.1002773	0.753674	0.05095446	0.03202995	0.017457	0.0148702
L+1	-2.8	A	0.83099	0.0756485	0.0037943	0.089480783	4.96E-05	6.64E-06	3.06E-05
LUMO	-3.02	A	4.49E-05	0.0001178	0.0079127	6.91E-05	0.04258955	0.9224173	0.0268459
HOMO	-4.95	A	0.3741408	0.4636251	0.0045965	0.157614593	-4.87E-07	1.79E-06	1.56E-05
H-1	-5.59	A	0.0793107	0.4656124	0.0169273	0.438055405	3.18E-05	5.58E-06	5.32E-05
H-2	-5.66	A	0.0832046	0.4687463	0.0169483	0.431058315	4.30E-06	7.37E-06	3.36E-05
H-3	-5.97	A	0.0287479	0.6360135	0.0111532	0.324060637	2.77E-06	5.55E-06	2.19E-05
H-4	-6.11	A	0.7124772	0.0664973	0.0234683	0.197562028	1.29E-07	1.64E-07	1.10E-06
H-5	-6.14	A	0.7376467	0.0601164	0.0206295	0.179959269	0.00050469	9.68E-05	0.0010485
H-6	-6.62	A	0.2288387	0.1315617	0.0328369	0.606343408	0.00011062	3.23E-05	0.0002818
H-7	-6.63	A	0.2300476	0.1303078	0.0253857	0.614154993	2.98E-05	4.88E-06	6.70E-05
H-8	-6.69	A	0.3949537	0.1820253	0.1051149	0.297117883	0.00575583	0.001441	0.013582
H-9	-6.81	A	0.0565166	0.054783	0.0908673	0.73935074	0.01582069	0.0043289	0.0383331
H-10	-6.86	A	0.2105435	0.0299184	0.1714591	0.585022277	0.00080896	0.0002261	0.0020235
H-11	-6.91	A	0.124843	0.1078281	0.462423	0.299182638	0.00152247	0.0004407	0.0037556
H-12	-6.92	A	0.1979769	0.08135	0.3246339	0.386186472	0.00261804	0.0007563	0.0064844
H-13	-6.95	A	0.1096867	0.1141189	0.5217674	0.241307663	0.00346275	0.0010391	0.0086246
H-14	-7.02	A	0.0285271	0.0403911	0.5213811	0.292389745	0.03057455	0.0096214	0.0771057
H-15	-7.03	A	0.0083804	0.0206687	0.11523	0.282337811	0.14869826	0.0492896	0.3753929
H-16	-7.04	A	0.0036224	0.0050514	0.0215359	0.405309837	0.15092454	0.0411395	0.3724087
H-17	-7.05	A	0.0097802	0.0082246	0.039245	0.508620266	0.1163553	0.0310999	0.2866764
H-18	-7.07	A	0.0401511	0.0378646	0.088729	0.825565331	0.00213994	0.0004784	0.0050782
H-19	-7.11	A	0.020626	0.0329592	0.061915	0.882194892	0.00062654	0.0001321	0.001543
H-20	-7.14	A	0.016244	0.0129619	0.0392117	0.861887281	0.01791889	0.0060611	0.0457195

Table S14. Energy and contribution of MO obtained from DFT for **4** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh,Re] 6-31G**[$C_{amidinate}$,N,CO], 3-21G[C_{aryl},H] with CPCM (DCM).

MO	eV	Symm.	Rh2	Amidinate	Pyridine	Phenyl	Carbonyl	Bipyridine	Re
L+20	-1.98	B2	0.00235636	0.00295604	0.521938024	0.0235484	0.24354125	0.09207424	0.11359866
L+19	-1.98	B3	0.0029142	0.0047791	0.51659074	0.02626197	0.23958508	0.09711126	0.11274482
L+18	-1.98	A	0.00598489	0.00398147	0.519510684	0.03010031	0.23275614	0.09813247	0.10952644
L+17	-2.02	B1	0.03689657	0.02209411	0.501675017	0.08878983	0.15141982	0.12434079	0.07478378
L+16	-2.19	B2	0.00014659	0.00027042	0.066212746	0.00220242	0.03996026	0.88919819	0.00201134
L+15	-2.19	B3	0.00039432	0.00038614	0.069574822	0.00287091	0.04038592	0.88421903	0.002173
L+14	-2.19	A	0.00087882	0.0004527	0.070418569	0.00333107	0.04043342	0.88235942	0.00212305
L+13	-2.19	B1	0.00262377	0.00169409	0.086721096	0.00827159	0.0418657	0.85625483	0.00255811
L+12	-2.31	B2	5.89E-05	0.00033477	0.012262795	0.00022214	0.03329585	0.93899812	0.01482143
L+11	-2.31	A	0.00022651	0.00028282	0.011955492	0.00036533	0.03326794	0.93925815	0.01465718
L+10	-2.31	B3	0.00013787	0.00040469	0.012767508	0.00030824	0.03334421	0.93820632	0.01483435
L+9	-2.31	B1	0.00037876	0.00048447	0.014178209	0.00077078	0.03336825	0.93623043	0.01459798
L+8	-2.86	B2	0.01123472	0.1231015	0.771162435	0.04240836	0.02911413	0.00771294	0.01527324
L+7	-2.86	B3	0.01103936	0.12409097	0.769229448	0.04379492	0.02888642	0.0073474	0.01560044
L+6	-2.92	B1	0.02052902	0.11893454	0.759372746	0.04861777	0.02831028	0.00902652	0.01522139
L+5	-2.99	A	0.07719252	0.11572028	0.678164299	0.07942933	0.02483964	0.01070081	0.01392506
L+4	-3.36	B2	0.0001572	0.00070967	0.014025619	0.00029649	0.04340949	0.9122479	0.02913378
L+3	-3.36	B3	0.00013944	0.00074324	0.013823365	0.00023818	0.04344043	0.91239949	0.02920563
L+2	-3.36	B1	0.00032945	0.00097571	0.015586796	0.00036185	0.04309059	0.91062509	0.02903559
L+1	-3.37	A	0.00069786	0.00115424	0.017142873	0.00075467	0.04274	0.90848879	0.02901044
LUMO	-3.54	B1	0.83355163	0.07678144	0.003898906	0.08558248	5.33E-05	0.00010281	2.46E-05
HOMO	-5.7	B1	0.36487615	0.46237885	0.004692492	0.16797367	-8.45E-07	3.79E-06	8.06E-05
H-1	-6.32	B3	0.07584434	0.45158245	0.015978666	0.45600403	0.00015019	5.39E-05	0.00039341
H-2	-6.33	B2	0.07717421	0.44987674	0.015555666	0.45704221	8.43E-05	2.26E-05	0.00025407
H-3	-6.67	A	0.02681963	0.60570368	0.011381472	0.35593263	2.93E-05	2.71E-05	0.00014948
H-4	-6.86	B2	0.66252452	0.06705666	0.02082436	0.23644694	0.00360846	0.00100472	0.00854208
H-5	-6.87	B3	0.6749495	0.06737592	0.020369073	0.22449007	0.00356904	0.00091699	0.00834131
H-6	-7.29	B3	0.24916797	0.08938659	0.028609918	0.49308701	0.03618452	0.01188013	0.09167253
H-7	-7.29	B2	0.25423788	0.08573923	0.030537531	0.46386741	0.0425571	0.01451945	0.10855039
H-8	-7.3	A	0.07265082	0.04988509	0.086769894	0.1631425	0.16180761	0.05431771	0.41142986
H-9	-7.33	B1	0.00987432	0.01413722	0.074925688	0.18978696	0.18250364	0.0624928	0.46628995
H-10	-7.39	B3	0.0152273	0.03318998	0.029200596	0.10951208	0.21022365	0.0686195	0.53400241
H-11	-7.39	B2	0.01655563	0.03305181	0.026873123	0.11177247	0.21049753	0.06775642	0.53347977
H-12	-7.4	A	0.00725549	0.00293276	0.009523763	0.0010843	0.25984947	0.07367411	0.64569309
H-13	-7.4	B1	0.00221661	0.00064703	0.009896219	0.0107573	0.25888499	0.07376314	0.64384911
H-14	-7.41	B3	0.00176665	0.0074176	0.016847001	0.0269055	0.24764849	0.07646241	0.62294159
H-15	-7.41	B2	0.00636152	0.01172503	0.016702069	0.04495574	0.24036714	0.07452956	0.6053427
H-16	-7.55	B1	0.13508633	0.02906013	0.018561804	0.65784384	0.04035789	0.0147806	0.10433543
H-17	-7.56	A	0.21379329	0.11657828	0.038543032	0.29562011	0.0850689	0.02937819	0.22101446
H-18	-7.56	B1	0.16372265	0.02152963	0.019935459	0.68959469	0.02706831	0.00814107	0.06998586
H-19	-7.63	B2	8.99E-05	0.00081185	0.002072728	0.00256671	0.29255166	0.01717302	0.6847192
H-20	-7.63	B3	5.50E-05	0.00045267	0.002103017	0.00245271	0.29273859	0.01720555	0.68500326

Table S15. Energy and contribution of MO obtained from DFT for **5** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (MeCN).

MO	eV	Symmetry	Rh_2	Amidinate	Pyridine	Phenyl
L+20	0.15	E	0.015713441	0.012772817	0.16568267	0.80584137
L+19	0.15	E	0.015713441	0.012772817	0.16568267	0.80584137
L+18	0.06	E	0.004646881	0.017466638	0.026402086	0.951484069
L+17	0.06	E	0.004646861	0.017466616	0.026402083	0.951476048
L+16	0.05	A1	0.051228509	0.019805942	0.206602544	0.72235907
L+15	-0.01	A2	0.059954048	0.077202161	0.025244866	0.83759612
L+14	-0.02	A2	0.058551307	0.024464481	0.228900428	0.688083684
L+13	-0.13	E	0.018877574	0.102768624	0.129141652	0.749213764
L+12	-0.13	E	0.018877574	0.102768624	0.129141652	0.749213764
L+11	-0.24	A1	0.085269855	0.000179186	0.010789811	0.903743553
L+10	-0.25	B1	0.10800799	0.061761386	0.708960353	0.121257959
L+9	-0.39	B2	0.146958324	0.064960909	0.374794169	0.413276404
L+8	-0.44	E	0.008676587	0.011968574	0.842317499	0.137043713
L+7	-0.44	E	0.008676587	0.011968574	0.842317499	0.137043713
L+6	-0.47	A1	0.030855476	0.012026022	0.759354052	0.197753039
L+5	-0.75	B1	0.237125599	0.126500818	0.221636276	0.414745213
L+4	-1.17	E	0.017836727	0.224898633	0.639019462	0.118247387
L+3	-1.17	E	0.017836727	0.224898633	0.639019462	0.118247387
L+2	-1.25	A2	0.037873434	0.193645343	0.628859262	0.139614983
L+1	-1.48	B2	0.177630959	0.18817182	0.432349508	0.201840961
LUMO	-2.55	A2	0.833011703	0.075015421	0.002489532	0.089482333
HOMO	-4.69	B1	0.377764044	0.463880048	0.004477915	0.15387836
H-1	-5.38	E	0.080746172	0.475035928	0.016750818	0.427464978
H-2	-5.38	E	0.080746172	0.475035928	0.016750818	0.427464978
H-3	-5.7	A1	0.025604292	0.652872673	0.010553731	0.310966384
H-4	-5.87	E	0.742820961	0.060024915	0.021206581	0.175953333
H-5	-5.87	E	0.742820961	0.060024915	0.021206581	0.175953333
H-6	-6.4	E	0.205735878	0.134481799	0.025365266	0.634412298
H-7	-6.4	E	0.205735878	0.134481799	0.025365266	0.634412298
H-8	-6.44	B2	0.479172115	0.197964629	0.107344085	0.215479927
H-9	-6.58	A2	0.046683423	0.058473136	0.099778045	0.795053821
H-10	-6.64	B1	0.243827207	0.012937611	0.098011267	0.645204689
H-11	-6.69	B2	0.318164175	0.014253246	0.031173105	0.636423614
H-12	-6.74	A1	0.096536038	0.114339548	0.48696894	0.302165309
H-13	-6.74	E	0.007754875	0.21883729	0.599247017	0.174144349
H-14	-6.74	E	0.007754707	0.218838707	0.599247031	0.174144265
H-15	-6.83	B2	0.008352089	0.002944627	0.012257658	0.976425291
H-16	-6.84	B1	0.001967835	0.001326899	0.221180139	0.775503541
H-17	-6.89	E	0.016481413	0.035339913	0.060445718	0.887734236
H-18	-6.89	E	0.016481415	0.035339911	0.060446674	0.887734236
H-19	-6.92	B1	0.031344572	0.009093424	0.706763597	0.25279544
H-20	-6.94	E	0.006351297	0.008955412	0.060066319	0.924627604

Table S16. Energy and contribution of MO obtained from DFT for **5+MeCN** from singlet ground state; G03 rb3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (MeCN).

MO	eV	Symmetry	Rh_2	Amidinate	Pyridine	Phenyl	MeCN
L+20	0.26	A	0.033909726	0.057268115	0.140641519	0.76236896	0.005814501
L+19	0.24	A	0.018301083	0.045885893	0.186114311	0.72018471	0.029514927
L+18	0.23	A	0.018229018	0.040171797	0.167304608	0.74436691	0.029922697
L+17	0.2	A	0.004821305	0.014224817	0.061355198	0.90500508	0.014583255
L+16	0.2	A	0.004874958	0.014799751	0.060400625	0.90505497	0.014871295
L+15	0.15	A	0.042545454	0.015087419	0.215156965	0.71996925	0.007240666
L+14	0.08	A	0.046537206	0.035414481	0.03442041	0.87669714	0.00692257
L+13	0.03	A	0.019819754	0.075193633	0.057042347	0.80496562	0.042981996
L+12	0.02	A	0.019438637	0.07897997	0.062852664	0.79521123	0.043512064
L+11	-0.02	A	0.054442941	0.009088332	0.067454941	0.86705657	0.001967891
L+10	-0.16	A	0.120789993	0.057069857	0.379824748	0.44060857	0.001709649
L+9	-0.34	A	0.087867461	0.048841331	0.667047485	0.19616358	8.29E-05
L+8	-0.4	A	0.005494026	0.009342837	0.815164013	0.16870522	0.001293002
L+7	-0.4	A	0.005883149	0.008843146	0.815524764	0.16844558	0.001306789
L+6	-0.44	A	0.024298941	0.00969661	0.745542063	0.21921629	0.001247274
L+5	-0.76	A	0.24298153	0.150246654	0.218575259	0.38756664	0.000625
L+4	-1.03	A	0.072667158	0.16845616	0.641909872	0.11214878	0.0048234
L+3	-1.04	A	0.040073147	0.183552935	0.663786469	0.11001472	0.002568493
L+2	-1.05	A	0.016308849	0.192853254	0.680053411	0.10997917	0.000798132
L+1	-1.41	A	0.21721745	0.167455539	0.408034975	0.20717393	0.000121458
LUMO	-1.64	A	0.699998469	0.081627228	0.069447823	0.10997211	0.038956117
HOMO	-4.5	A	0.4173868	0.460796519	0.005224656	0.11658509	7.78E-06
H-1	-5.23	A	0.212272802	0.442206847	0.015240178	0.32921312	0.001083721
H-2	-5.23	A	0.217354519	0.43703488	0.014599602	0.32987506	0.001121191
H-3	-5.53	A	0.034776687	0.725977977	0.007722226	0.22968641	0.001838226
H-4	-5.65	A	0.732677511	0.115453063	0.015190538	0.12341732	0.013256033
H-5	-5.65	A	0.737297453	0.113406789	0.01537188	0.12056443	0.013367153
H-6	-6.21	A	0.086078351	0.152565765	0.030424221	0.7226721	0.008250038
H-7	-6.22	A	0.095111798	0.150754078	0.03150472	0.71452921	0.008097775
H-8	-6.27	A	0.675347412	0.187268443	0.049687259	0.08742666	0.000264732
H-9	-6.32	A	0.35251183	0.085982256	0.099778045	0.45243421	0.040979752
H-10	-6.48	A	0.130161837	0.062603706	0.098011267	0.69099446	0.003033741
H-11	-6.49	A	0.119267476	0.032023708	0.031173105	0.76423026	7.16E-05
H-12	-6.57	A	0.072382681	0.275318107	0.48696894	0.45307508	0.002297685
H-13	-6.57	A	0.041219527	0.332890545	0.599247017	0.39926491	0.002655078
H-14	-6.59	A	0.128325358	0.157066697	0.599247031	0.56650522	0.001047154
H-15	-6.74	A	0.003114459	0.004404087	0.012257658	0.93870615	0.002465831
H-16	-6.75	A	0.008871692	0.011302279	0.221180139	0.87078968	0.007639807
H-17	-6.75	A	0.009156069	0.016407003	0.060445718	0.81821813	0.014199655
H-18	-6.76	A	0.010118388	0.005361708	0.060446674	0.90926668	0.005337267
H-19	-6.82	A	0.007016483	0.025453538	0.706763597	0.9057315	0.001204305
H-20	-6.82	A	0.006639686	0.026511042	0.060066319	0.91803117	0.001420748

Table S17. Energy and contribution of the α MO obtained from DFT (**5**+**MeCN**)$^+$ from doublet ground state; G03 ub3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (MeCN).

MO	eV	Symm	Rh_2	Amidinate	Pyridine	Phenyl	MeCN
L+20	-0.21	A	0.013421664	0.016900313	0.005063642	0.718910007	0.075519216
L+19	-0.21	A	0.014003453	0.014472337	0.005248493	0.712435948	0.07688535
L+18	-0.24	A	0.009693354	0.043649748	0.00582362	0.825001351	0.021111115
L+17	-0.24	A	0.010568529	0.049547508	0.005384554	0.801278147	0.024128774
L+16	-0.28	A	0.037503402	0.008963413	0.001021876	0.634062023	0.005667031
L+15	-0.31	A	0.066051525	0.266163005	0.038610532	0.548313712	0.003228111
L+14	-0.39	A	0.038576197	0.057893348	0.044623864	0.863014732	0.005285268
L+13	-0.45	A	0.02062526	0.091310691	0.010640365	0.712993096	0.067519879
L+12	-0.45	A	0.019617439	0.098396307	0.010272755	0.696292852	0.062428352
L+11	-0.48	A	0.056840522	0.008377562	0.049802479	0.862380897	0.001460039
L+10	-0.64	A	0.044031891	0.034715318	0.038474335	0.172049906	0.001306354
L+9	-0.74	A	0.006518612	0.011921398	0.003781962	0.240155978	0.004023366
L+8	-0.74	A	0.006359348	0.011044465	0.003660627	0.241164327	0.003688839
L+7	-0.8	A	0.033982611	0.012802931	0.012625149	0.328194658	0.001613552
L+6	-0.9	A	0.194211054	0.191648684	0.145671765	0.183331532	0.000127227
L+5	-1.53	A	0.044088209	0.254266492	0.033150646	0.122722644	0.002058669
L+4	-1.54	A	0.11876725	0.270307245	0.057258238	0.180609051	0.000716405
L+3	-1.54	A	0.178035388	0.258523348	0.08635714	0.214152504	0.001053456
L+2	-1.56	A	0.06983801	0.271594995	0.036517855	0.145451286	0.00185667
L+1	-2.19	A	0.332493137	0.237040754	0.075320176	0.199251283	0.000105271
LUMO	-2.82	A	0.747531014	0.101486695	0.309755416	0.078374448	0.053076492
HOMO	-5.79	A	0.277611227	0.517307375	0.150502423	0.200446356	1.02E-05
H-1	-6.18	A	0.067493778	0.391956286	0.057014151	0.51448014	0.000617317
H-2	-6.18	A	0.067483553	0.393805793	0.057102253	0.512209242	0.000609857
H-3	-6.5	A	0.029430814	0.581356854	0.01996802	0.37545926	0.000650176
H-4	-6.66	A	0.104708278	0.100636322	0.048333533	0.731808169	0.001216244
H-5	-6.67	A	0.107222846	0.099049737	0.049416738	0.73077124	0.00121918
H-6	-6.93	A	0.034383546	0.039443248	0.001329095	0.811836317	0.011408049
H-7	-7	A	0.027625843	0.038071389	0.005794051	0.786498916	0.000256912
H-8	-7.03	A	0.033267985	0.061573542	0.022680888	0.113436206	0.00292966
H-9	-7.05	A	0.011446236	0.063508369	0.002282802	0.119905443	0.001136314
H-10	-7.05	A	0.01311985	0.059752643	0.003194034	0.125964457	0.001234598
H-11	-7.08	A	0.020083021	0.009966253	0.008915931	0.123305206	6.77E-05
H-12	-7.13	A	0.010292563	0.004102617	0.006044935	0.891790373	0.000990242
H-13	-7.15	A	0.064158863	0.014236724	0.033317984	0.829898837	0.013772136
H-14	-7.15	A	0.122760249	0.018339747	0.06391525	0.741872451	0.02155956
H-15	-7.16	A	0.134195225	0.017108703	0.076392546	0.76144392	0.005915171
H-16	-7.17	A	0.31383792	0.037082842	0.176402135	0.56887917	0.016055705
H-17	-7.18	A	0.234437539	0.03368439	0.133433622	0.661550815	0.011255746
H-18	-7.25	A	0.058464375	0.062391704	0.047932211	0.819382287	0.007709307
H-19	-7.3	A	0.34378232	0.023139549	0.17939991	0.568256792	0.011557418
H-20	-7.3	A	0.347081983	0.023017715	0.181311921	0.563543171	0.011865451

Table S18. Energy and contribution of the β MO obtained from DFT (**5+MeCN**)$^+$ from doublet ground state; G03 ub3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (MeCN).

MO	eV	Symm	Rh_2	Amidinate	Pyridine	Phenyl	MeCN
L+21	-0.2	A	0.008471009	0.014028834	0.017844996	0.173868857	0.722085287
L+20	-0.2	A	0.0086192	0.013935549	0.013769429	0.175913565	0.72257501
L+19	-0.23	A	0.005553889	0.013705554	0.05352167	0.104072169	0.805103221
L+18	-0.23	A	0.005894659	0.012910323	0.056311454	0.110890194	0.801754069
L+17	-0.25	A	0.038583978	0.080428934	0.221246491	0.086074009	0.601519567
L+16	-0.28	A	0.035547557	0.038751048	0.009925086	0.30621377	0.639294049
L+15	-0.39	A	-0.006074629	0.041044148	0.056238246	0.032889513	0.864513575
L+14	-0.44	A	0.010128857	0.02058044	0.089346867	0.105516493	0.715545742
L+13	-0.45	A	0.009485652	0.019645532	0.095940546	0.120102359	0.700183967
L+12	-0.47	A	0.007077827	0.05589005	0.008943566	0.072950627	0.860273603
L+11	-0.63	A	0.004347496	0.052537198	0.037655777	0.726757702	0.18158954
L+10	-0.74	A	0.002822637	0.006669692	0.012011258	0.742087289	0.235296476
L+9	-0.74	A	0.002787356	0.006505339	0.011127185	0.742671182	0.236086657
L+8	-0.8	A	0.020935427	0.033303701	0.013281166	0.630631098	0.321165901
L+7	-0.84	A	0.045927272	0.166829241	0.137733788	0.481739011	0.213579858
L+6	-1.48	A	0.159713786	0.304133447	0.237019145	0.1464047	0.312254294
L+5	-1.51	A	0.008048308	0.041585712	0.239410402	0.594465223	0.122312854
L+4	-1.52	A	0.011064201	0.024665349	0.267979203	0.58335507	0.122649184
L+3	-1.53	A	0.010359847	0.031407046	0.26078974	0.581576816	0.124253459
L+2	-2.14	A	0.2626029	0.33378282	0.228976762	0.232918246	0.204211144
L+1	-2.71	A	0.417764397	0.749996761	0.098165744	0.02023628	0.08149661
LUMO	-4.21	A	0.132557993	0.440150763	0.450272969	0.005812042	0.103751289
HOMO	-5.98	A	0.009451582	0.068941585	0.481122767	0.018672006	0.430765485
H-1	-5.98	A	0.009545382	0.06965676	0.476520606	0.018202583	0.435121456
H-2	-6.24	A	0.006940685	0.031883202	0.687248168	0.008185359	0.271833294
H-3	-6.64	A	0.077319568	0.149354864	0.101683712	0.061209697	0.686511595
H-4	-6.65	A	0.079255703	0.153482234	0.099736704	0.061184734	0.684312306
H-5	-6.92	A	0.037794137	0.04116332	0.043927096	0.103317842	0.799972059
H-6	-6.95	A	0.095052215	0.179606967	0.117770353	0.156410007	0.545785151
H-7	-7.02	A	0.016196467	0.048627372	0.05722232	0.706480123	0.184236513
H-8	-7.02	A	0.028280902	0.04965522	0.111067615	0.679563098	0.155851662
H-9	-7.03	A	0.024605635	0.075777022	0.08924209	0.589557356	0.242130767
H-10	-7.03	A	0.010936372	0.109091637	0.035013948	0.408093319	0.44654828
H-11	-7.07	A	0.220077604	0.546919467	0.042244824	0.10629509	0.284620772
H-12	-7.08	A	0.213009487	0.532608659	0.042303755	0.116918508	0.288772859
H-13	-7.1	A	0.012344423	0.050565344	0.010927549	0.516969714	0.421425021
H-14	-7.14	A	0.007447275	0.015096124	0.013297319	0.079995567	0.881421305
H-15	-7.15	A	0.014101463	0.022801225	0.020629891	0.103443826	0.836378062
H-16	-7.16	A	0.10011709	0.221845837	0.055108516	0.125815371	0.59684359
H-17	-7.16	A	0.015578335	0.038569245	0.015265575	0.073734164	0.865491855
H-18	-7.23	A	0.018984924	0.072138613	0.071604222	0.168172522	0.681625765
H-19	-7.26	A	0.25030067	0.270680065	0.050901074	0.117093535	0.561017569

Table S19. Singlet electronic transition obtained from TD-DFT for **5** from singlet ground state; G09 rb3lyp/LanL2DZ(f)[Rh] 6-31G**[$NCN_{amidinate}$], 3-21G[C_{aryl},H, N_{py}] with CPCM (DCM).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
1056.4	0	B	HOMO->LUMO (99%)
706.1	0.0075	E	H-5->LUMO (38%), H-4->LUMO (50%)
706.1	0.0075	E	H-5->LUMO (50%), H-4->LUMO (38%)
573.3	0.0025	E	H-2->LUMO (91%)
573.3	0.0025	E	H-1->LUMO (91%)
543.8	0.0311	A	HOMO->L+1 (85%)
486.5	0.005	A	H-3->LUMO (99%)
446.6	0	B	H-11->LUMO (11%), H-6->LUMO (87%)
445.0	0	B	HOMO->L+2 (99%)
436.8	0.0054	E	HOMO->L+3 (98%)

Table S20. Singlet electronic transition obtained from TD-DFT for **5** from singlet ground state; G09 rb3lyp/LanL2DZ(f)[Rh] 6-31G**[C,H,N]) with CPCM (DCM).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
1056.3	0	B	HOMO->LUMO (98%)
711.3	0.0082	E	H-4->LUMO (85%)
711.3	0.0082	E	H-5->LUMO (85%)
578.1	0.0027	E	H-2->LUMO (91%)
578.1	0.0027	E	H-1->LUMO (91%)
550.3	0.0313	A	HOMO->L+1 (85%)
487.3	0.0064	A	H-3->LUMO (99%)
456.7	0	B	HOMO->L+2 (99%)
447.7	0	B	H-11->LUMO (25%), H-8->LUMO (73%)
447.4	0.0053	E	HOMO->L+3 (98%)

Table S21. Singlet electronic transition obtained from TD-DFT for **5** from singlet ground state; G03, optimized and TD with rb3lyp/LanL2DZ(f)[Rh] 6-31G**[C,H,N]) with CPCM (DCM).

Wavelength (nm)	Osc. Strength	Symm.	Major contributions
1273.58332	0	B	HOMO->LUMO (83%)
731.249405	0.011	E	H-6->LUMO (10%), H-4->LUMO (70%), H-2->LUMO (10%)
731.249405	0.011	E	H-7->LUMO (10%), H-5->LUMO (70%), H-1->LUMO (10%)
645.074592	0.0016	E	H-5->LUMO (10%), H-1->LUMO (85%)
644.94037	0.0017	E	H-4->LUMO (10%), H-2->LUMO (85%)
536.980106	0.0364	A	HOMO->L+1 (85%)
522.276998	0.0045	A	H-3->LUMO (98%)
475.523862	0	B	H-11->LUMO (21%), H-8->LUMO (69%)
460.08363	0	B	HOMO->L+2 (97%)
446.641942	0.0067	E	HOMO->L+3 (96%)