Synthesis of Ru(II) and Os(II) Photosensitizers Bearing one 9,10-diamino-1,4,5,8-tetraazaphenanthrene Scaffold

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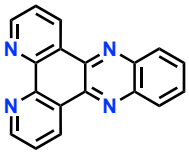
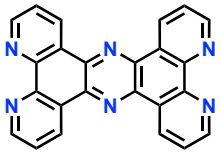
Structure of the extended ligands

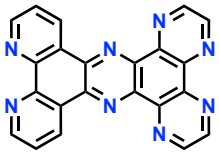
1,4,5,8,9,12-hexaazatriphenylene
HAT



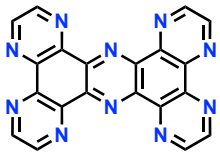
dipyrido[3,2-a:2',3'-c]phenazine
dppz



tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine
TPPHZ



1,10-phenanthrolino[5,6-b]-1,4,5,8,9,12-hexaazatriphenylene
PHEHAT



1,4,5,8-tetraazaphenanthrene[9,10-b]-1,4,5,8,9,12-hexaazatriphenylene
TAPHAT

Chart S1. Structure of 1,4,5,8,9,12-hexaazatriphenylene (HAT), dipyrido[3,2-a:2',3'-c]phenazine (dppz), tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine (TPPHZ), 1,10-phenanthrolino[5,6-b]-1,4,5,8,9,12-hexaazatriphenylene (PHEHAT) and 1,4,5,8-tetraazaphenanthrene[9,10-b]-1,4,5,8,9,12-hexaazatriphenylene (TAPHAT)

^{1}H NMR and HR-MS characterization

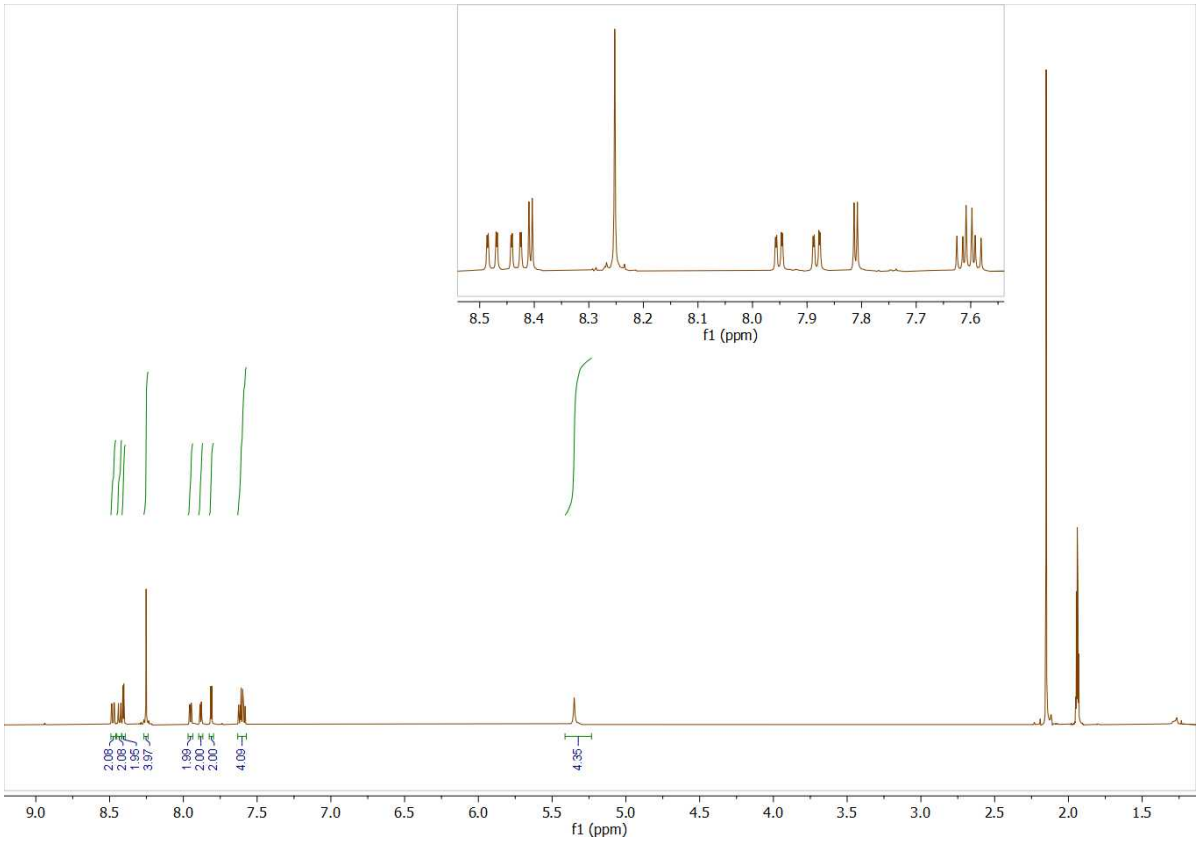


Figure S1. ^{1}H NMR spectrum of $[Os(phen)_2(diNH_2TAP)]^{2+}$ recorded in CD_3CN at 500 MHz and 298 K.

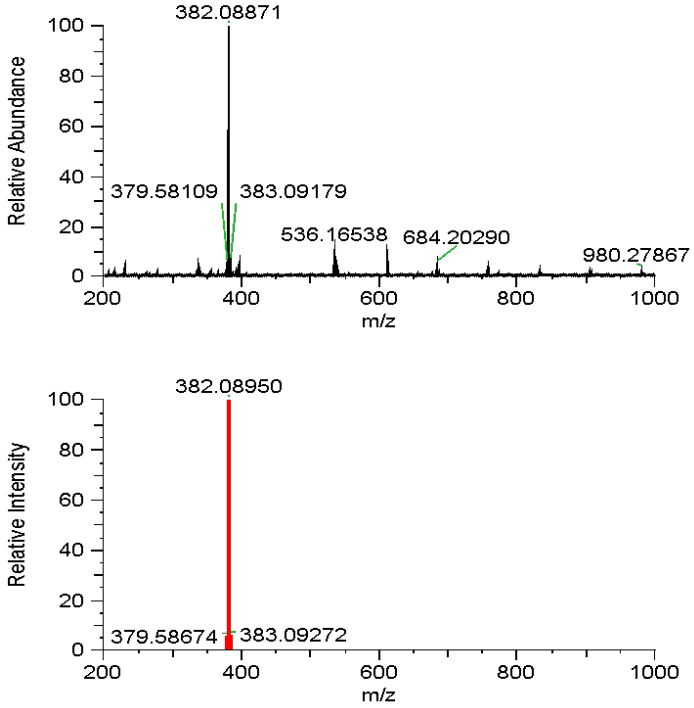


Figure S2. HR-MS spectrum of $[Os(phen)_2(diNH_2TAP)]^{2+}$.

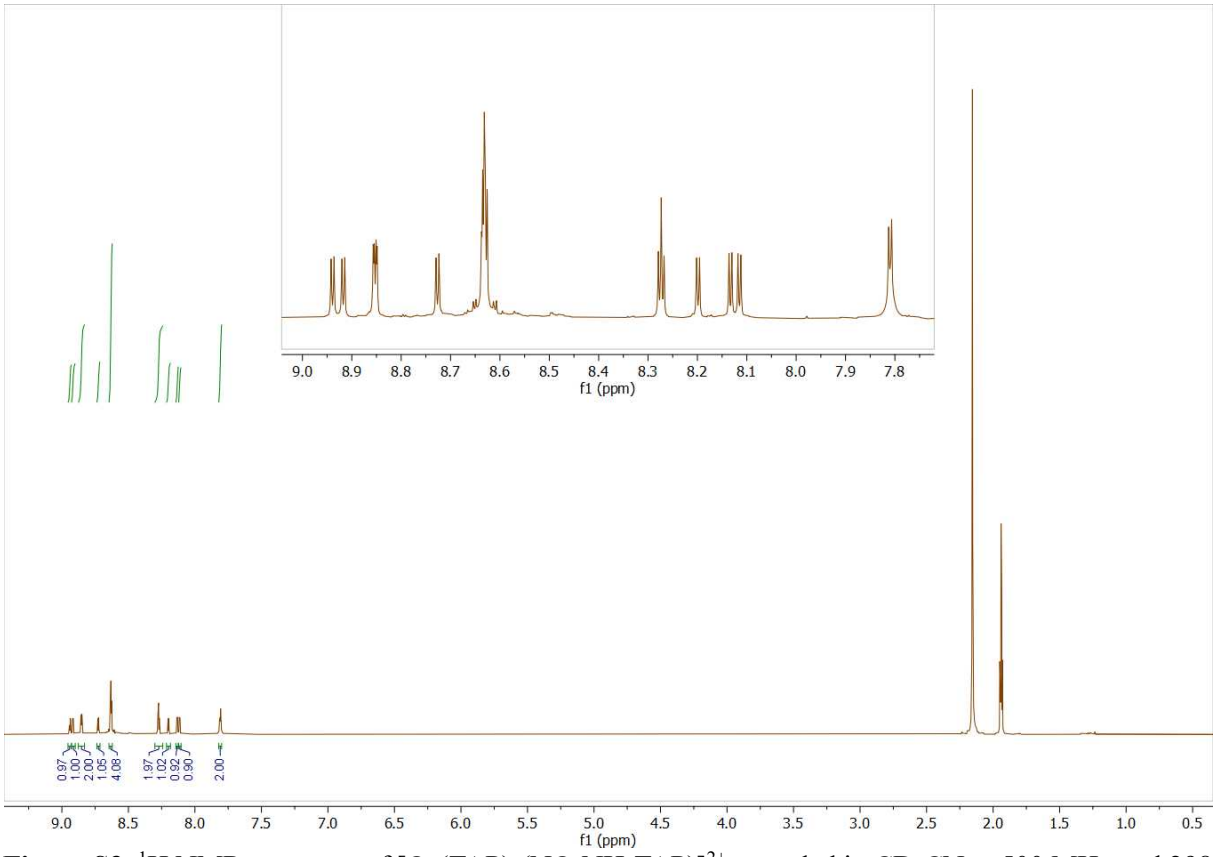


Figure S3. ^{1}H NMR spectrum of $[Os(TAP)_2(NO_2NH_2TAP)]^{2+}$ recorded in CD_3CN at 500 MHz and 298 K.

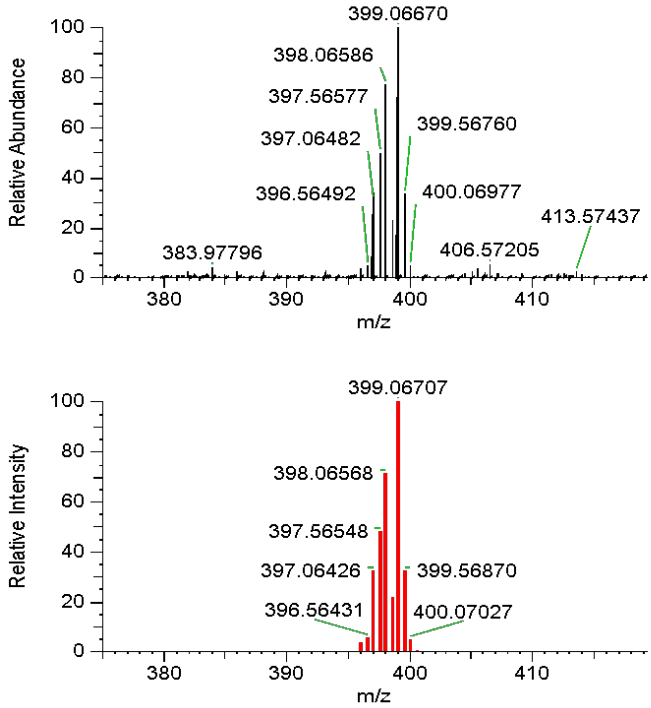


Figure S4. HR-MS spectrum of $[Os(TAP)_2(NO_2NH_2TAP)]^{2+}$.

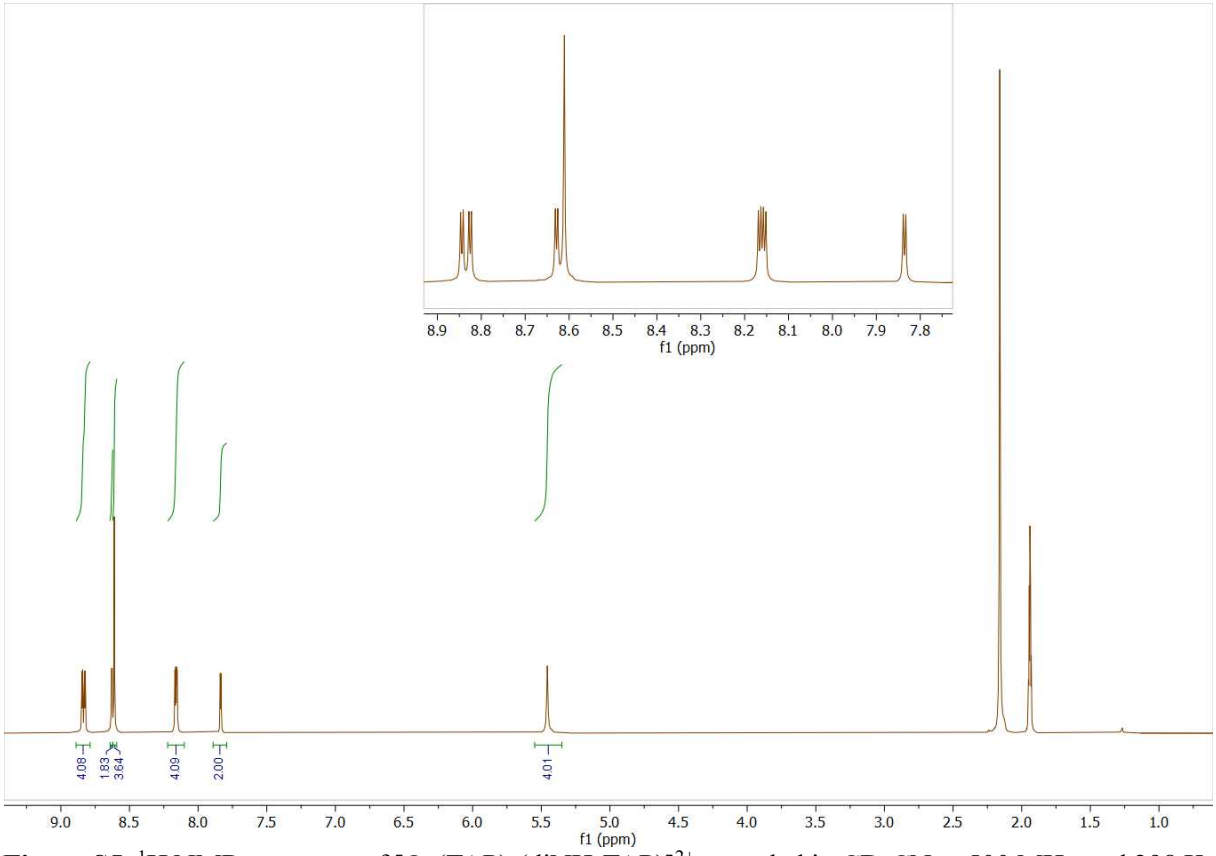


Figure S5. ^{1}H NMR spectrum of $[Os(TAP)_2(diNH_2TAP)]^{2+}$ recorded in CD_3CN at 500 MHz and 298 K.

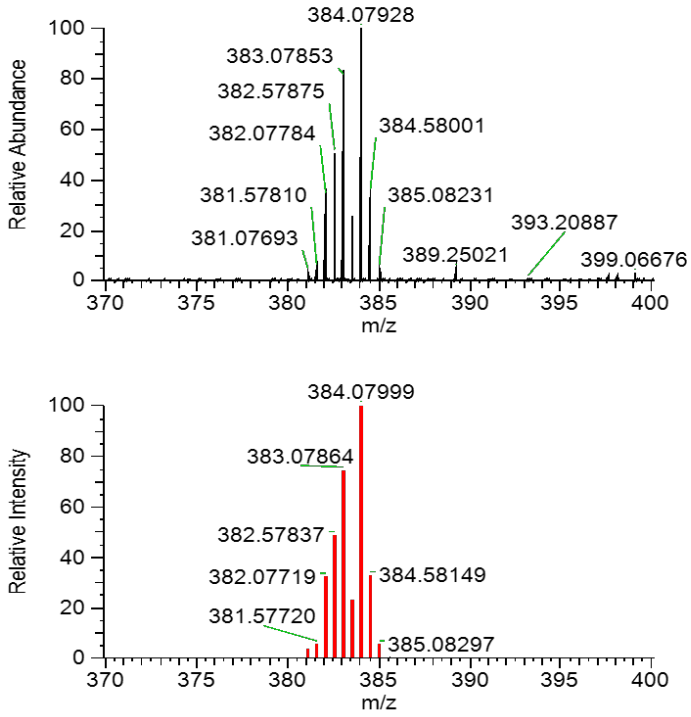


Figure S6. HR-MS spectrum of $[Os(TAP)_2(diNH_2TAP)]^{2+}$.

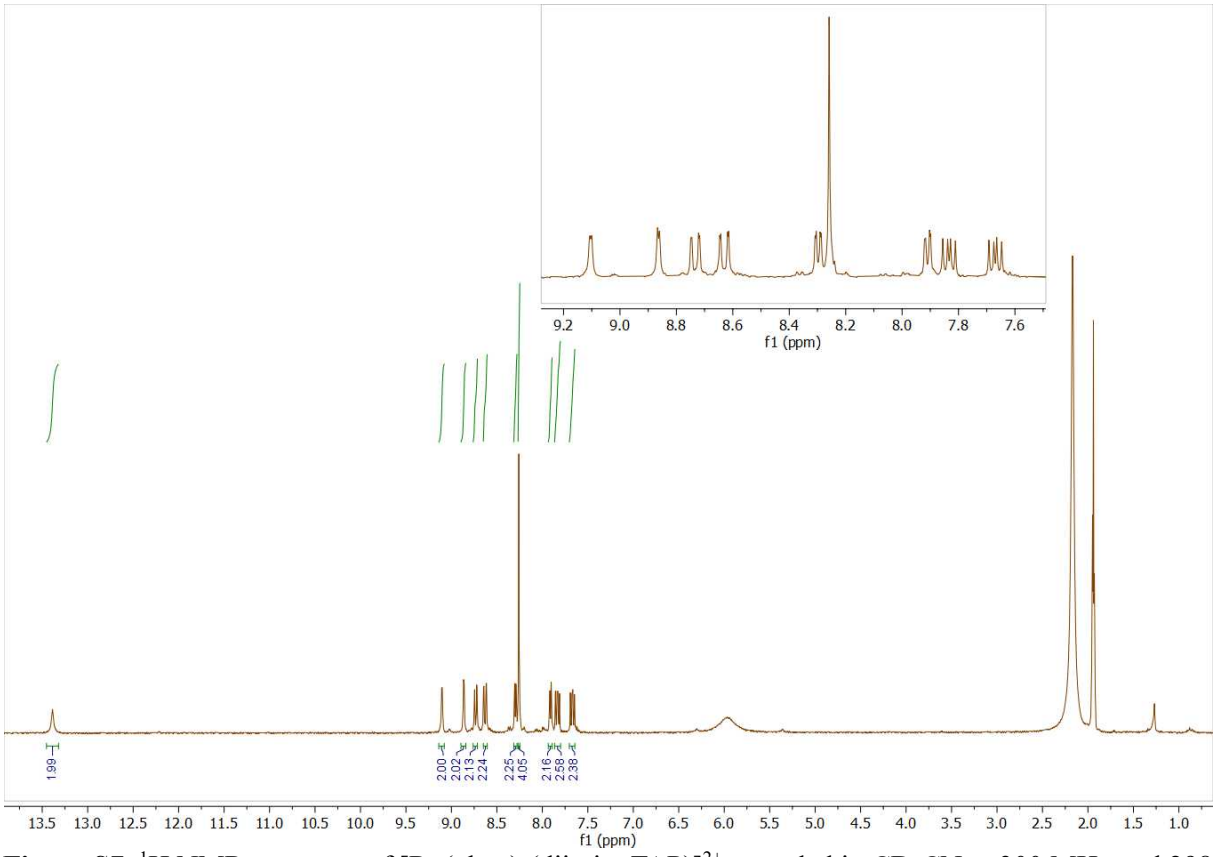


Figure S7. ^{1}H NMR spectrum of $[Ru(phen)_2(diiminoTAP)]^{2+}$ recorded in CD_3CN at 300 MHz and 298 K.

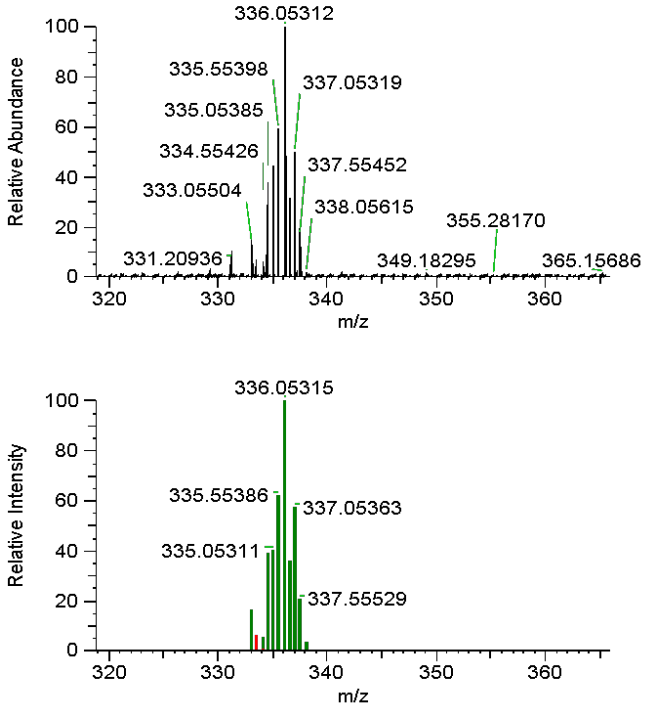


Figure S8. HR-MS spectrum of $[Ru(phen)_2(diiminoTAP)]^{2+}$.

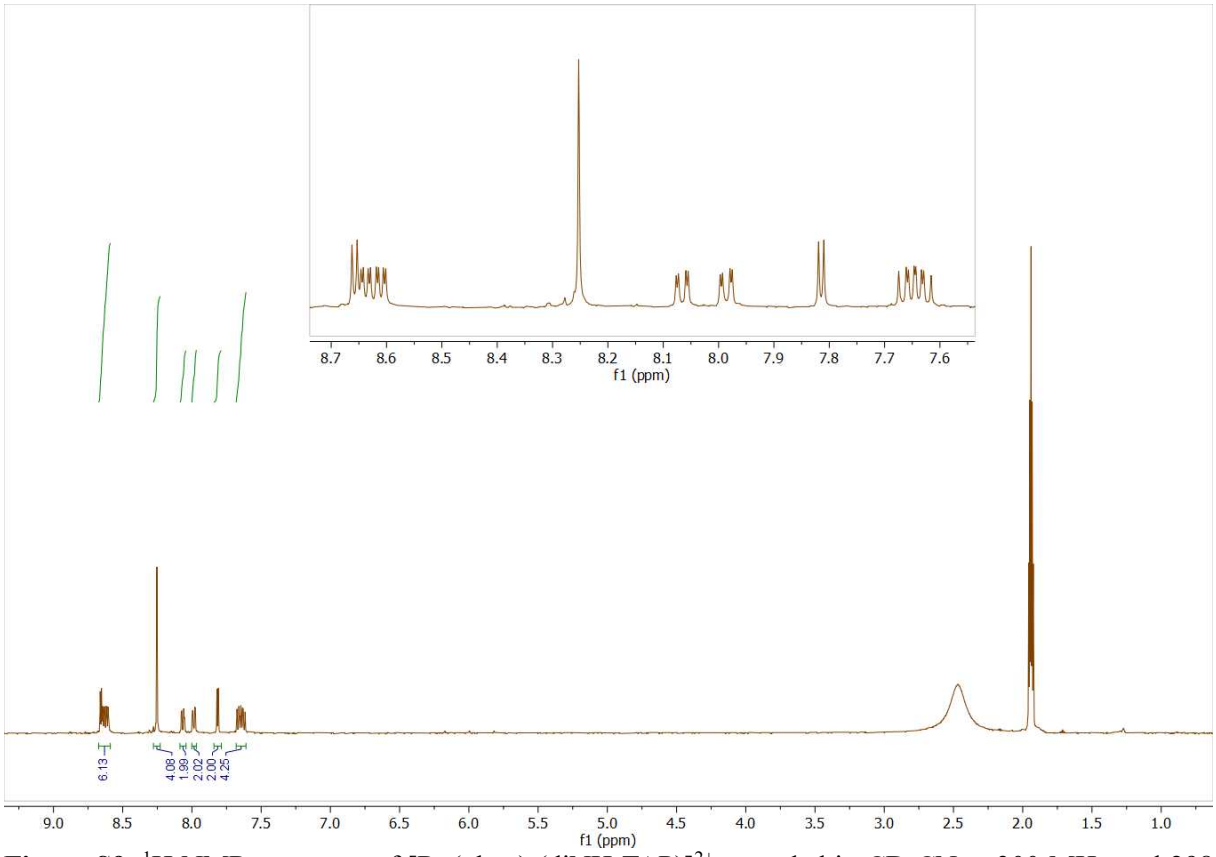


Figure S9. ^{1}H NMR spectrum of $[Ru(phen)_2(diNH_2TAP)]^{2+}$ recorded in CD_3CN at 300 MHz and 298 K.

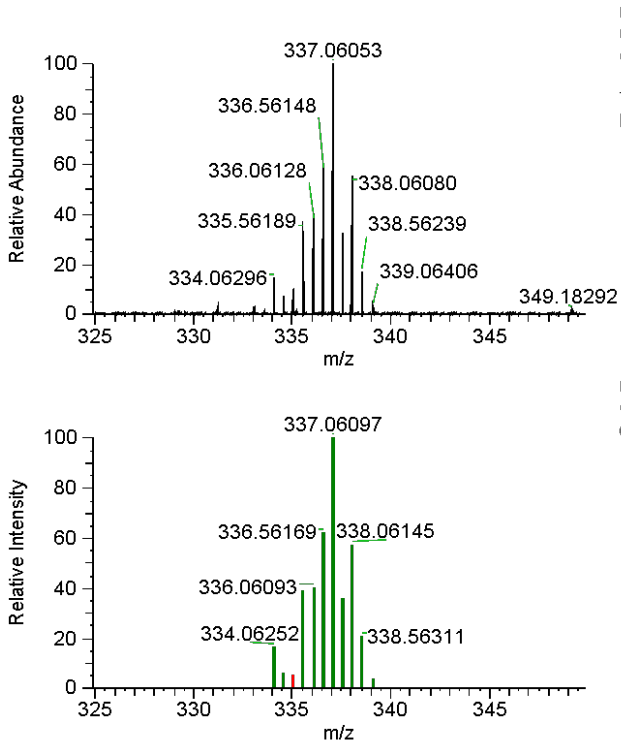


Figure S10. HR-MS spectrum of $[Ru(phen)_2(diNH_2TAP)]^{2+}$.

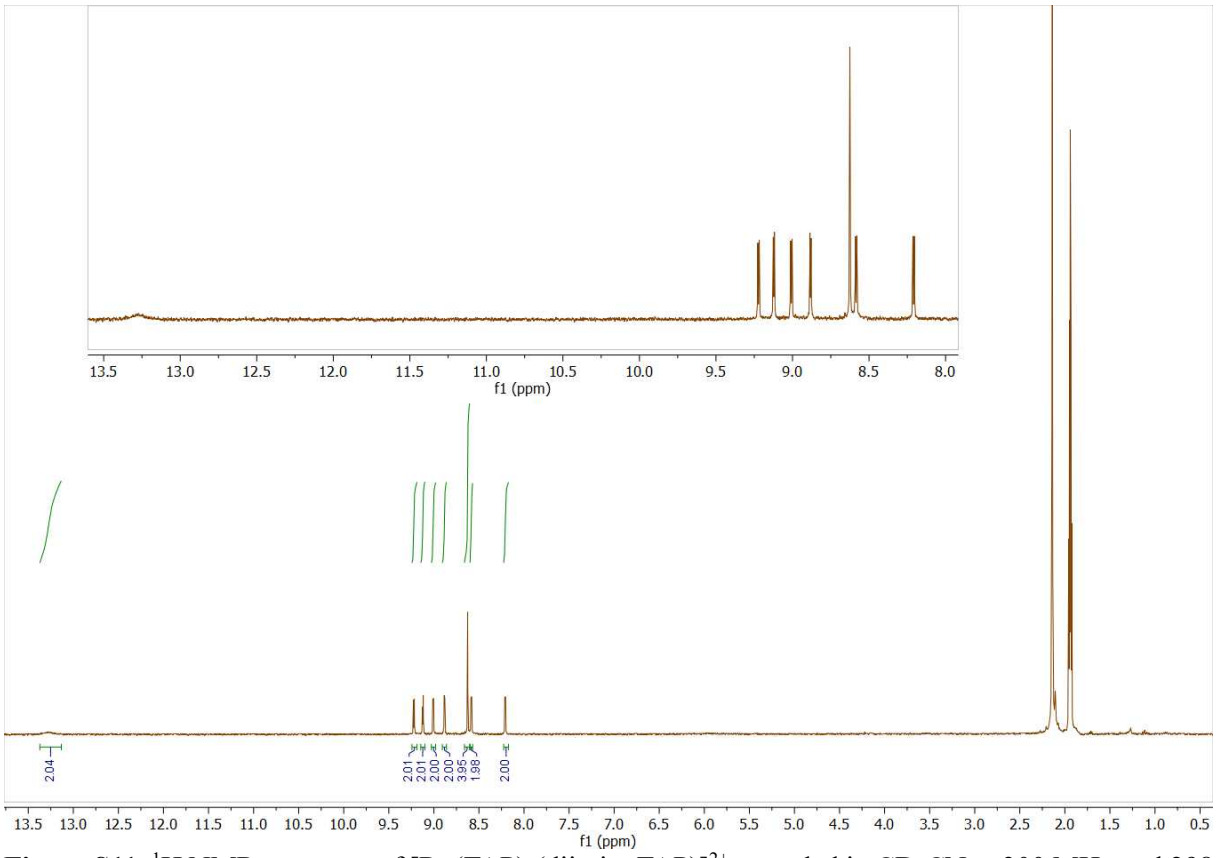


Figure S11. ^{1}H NMR spectrum of $[Ru(TAP)_2(diiminoTAP)]^{2+}$ recorded in CD_3CN at 300 MHz and 298 K.

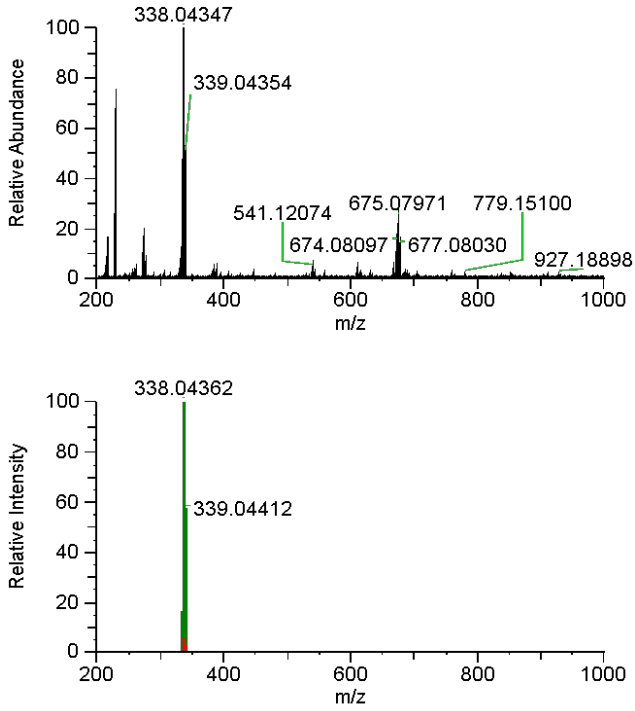


Figure S12. HR-MS spectrum of $[Ru(TAP)_2(diiminoTAP)]^{2+}$.

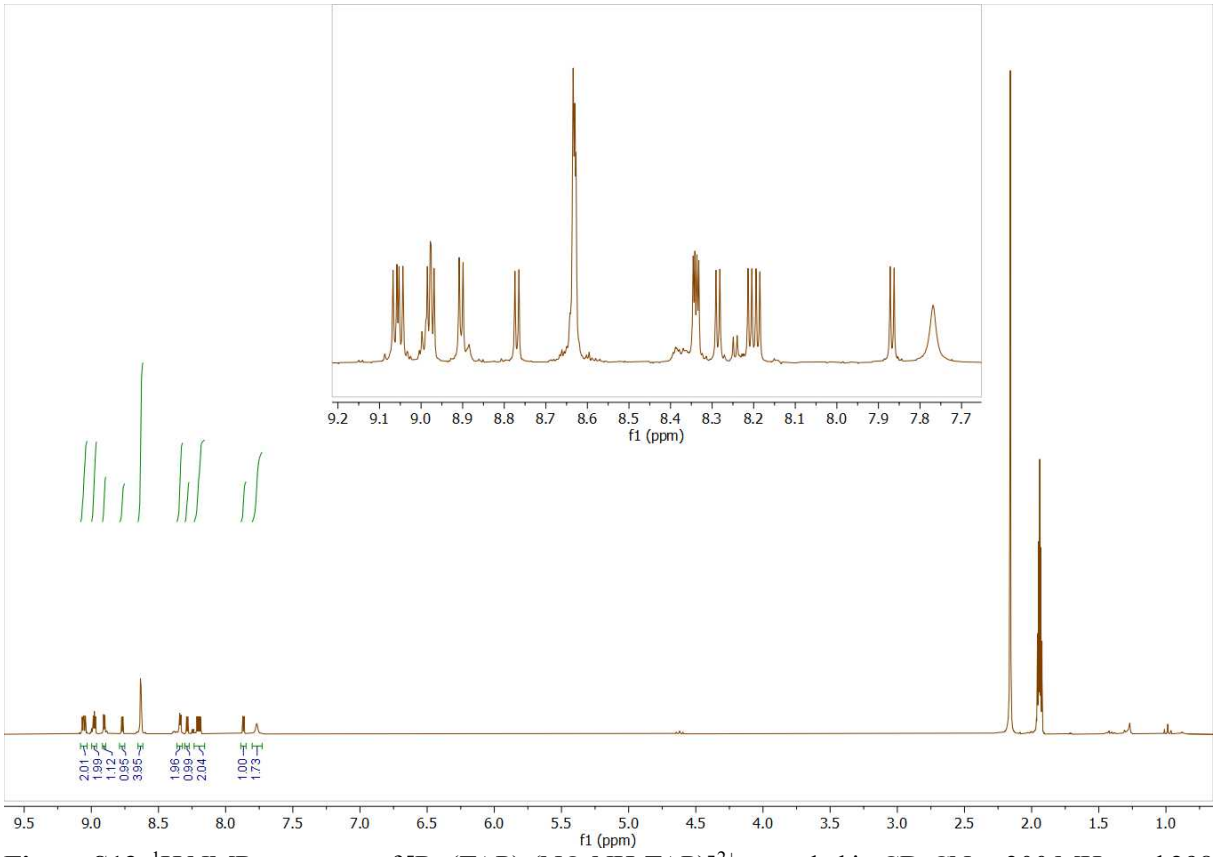


Figure S13. ^{1}H NMR spectrum of $[Ru(TAP)_2(NO_2NH_2TAP)]^{2+}$ recorded in CD_3CN at 300 MHz and 298 K.

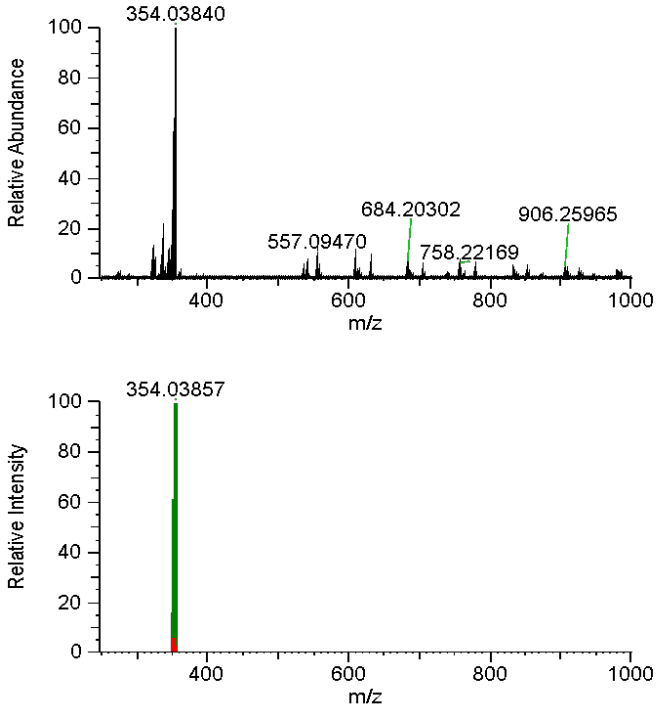


Figure S14. HR-MS spectrum of $[Ru(TAP)_2(NO_2NH_2TAP)]^{2+}$.

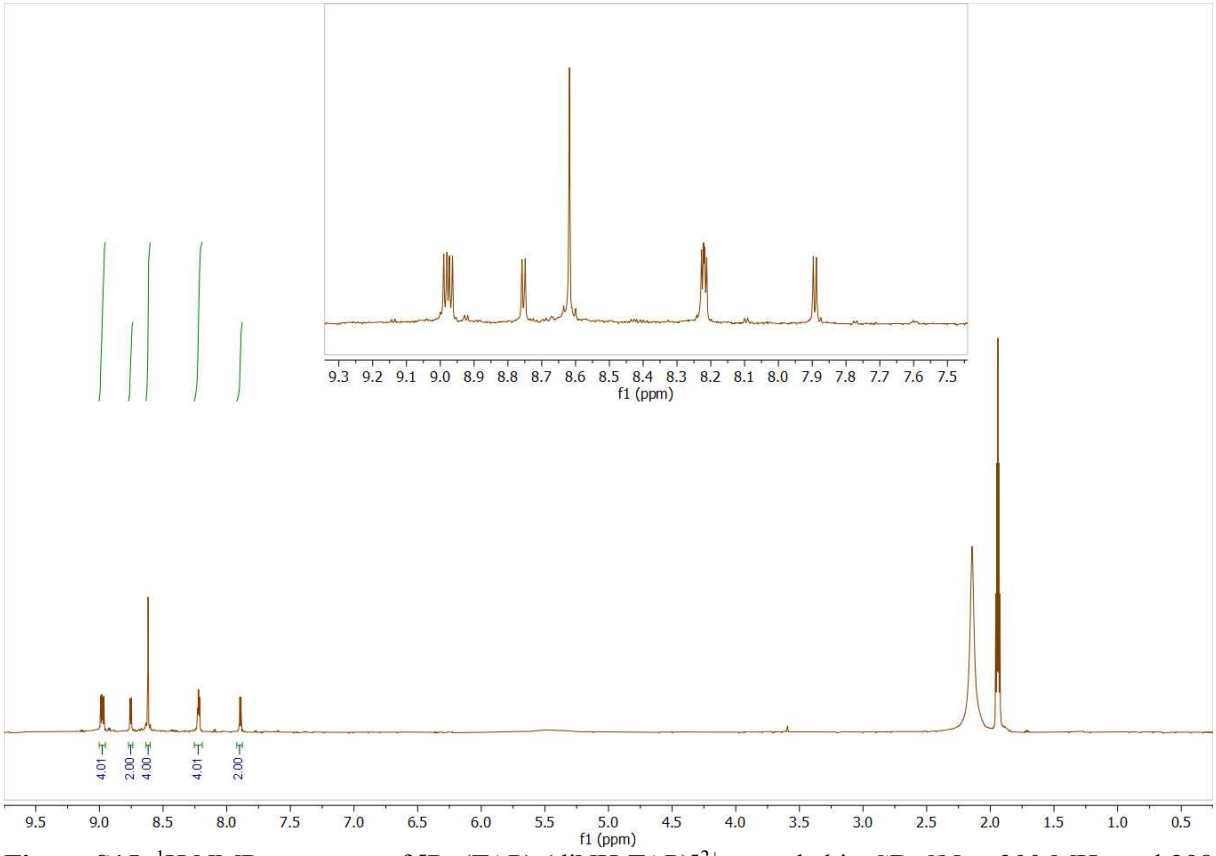


Figure S15. ^{1}H NMR spectrum of $[Ru(TAP)_2(diNH_2TAP)]^{2+}$ recorded in CD_3CN at 300 MHz and 298 K.

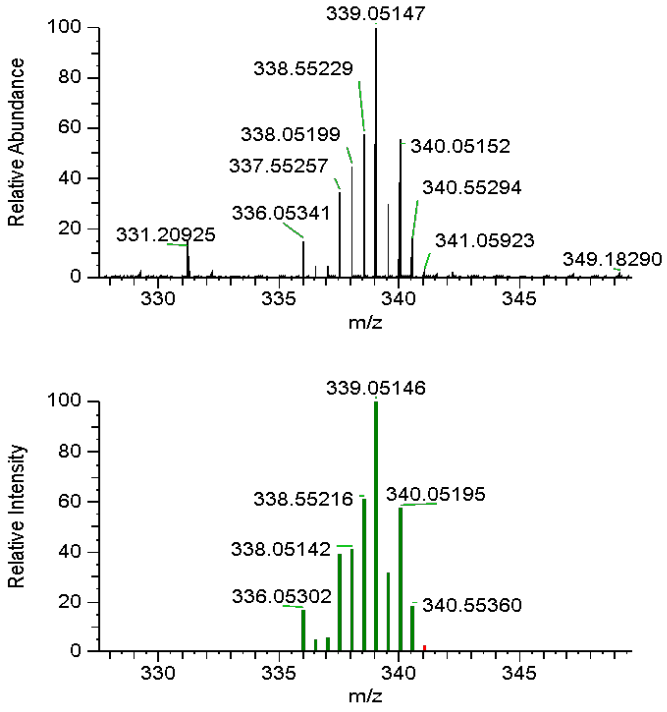


Figure S16. HR-MS spectrum of $[Ru(TAP)_2(diNH_2TAP)]^{2+}$.

Electrochemistry

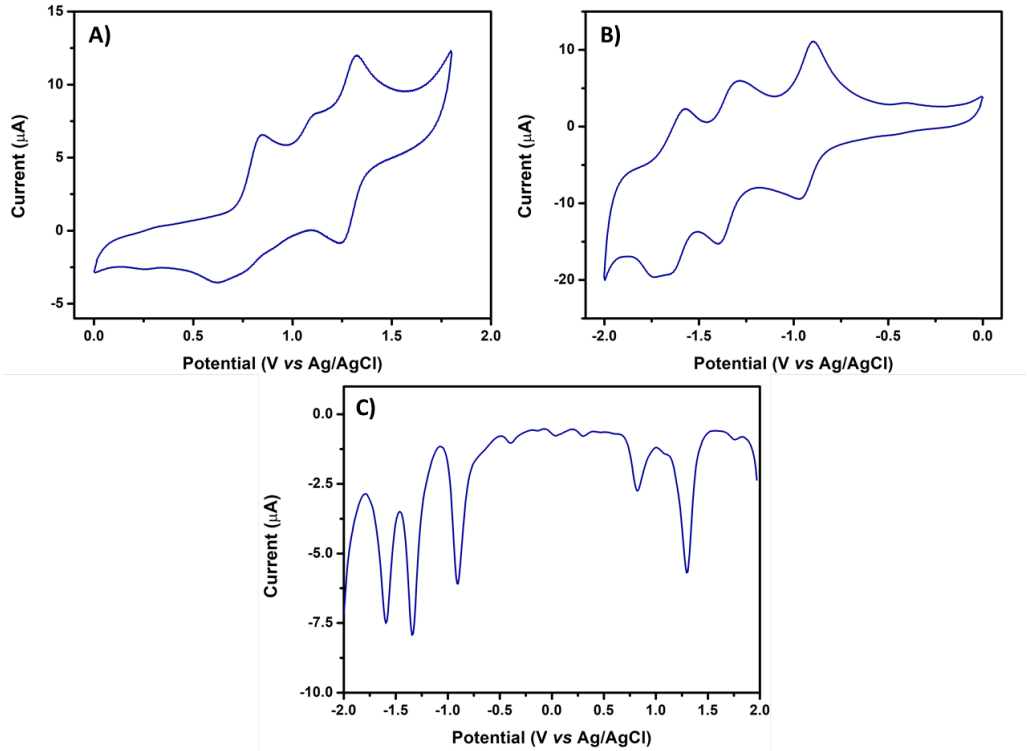


Figure S17. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Os(phen)_2(diNH_2TAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1M) as supporting electrolyte.

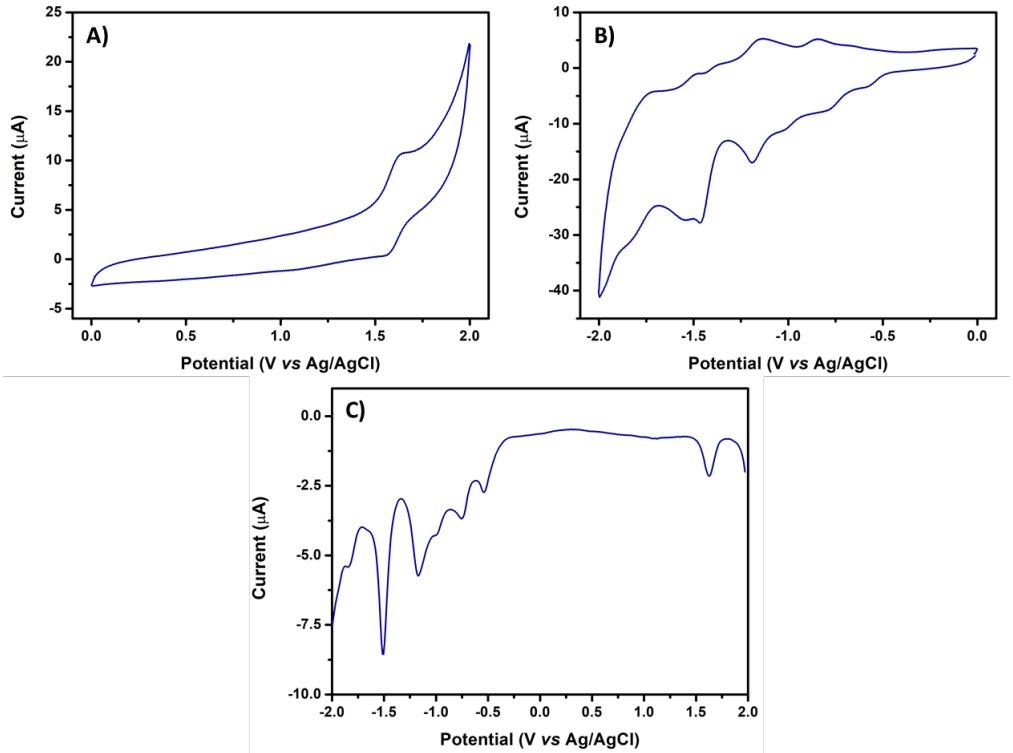


Figure S18. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Os(TAP)_2(NO_2NH_2TAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

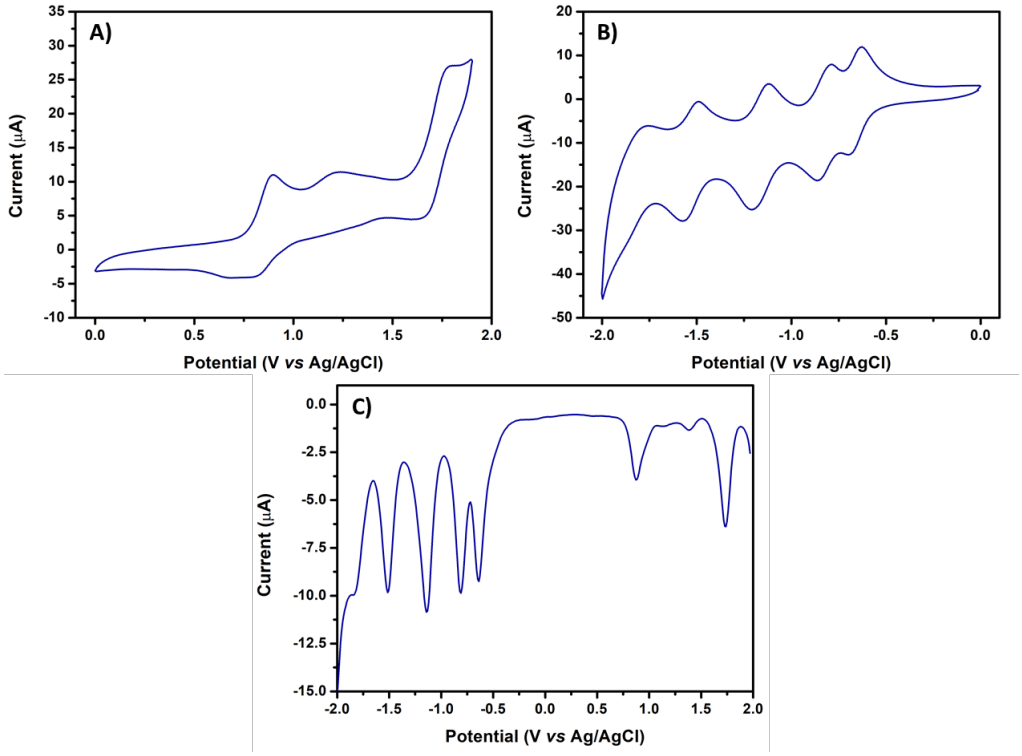


Figure S19. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Os(TAP)_2(diNH_2TAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

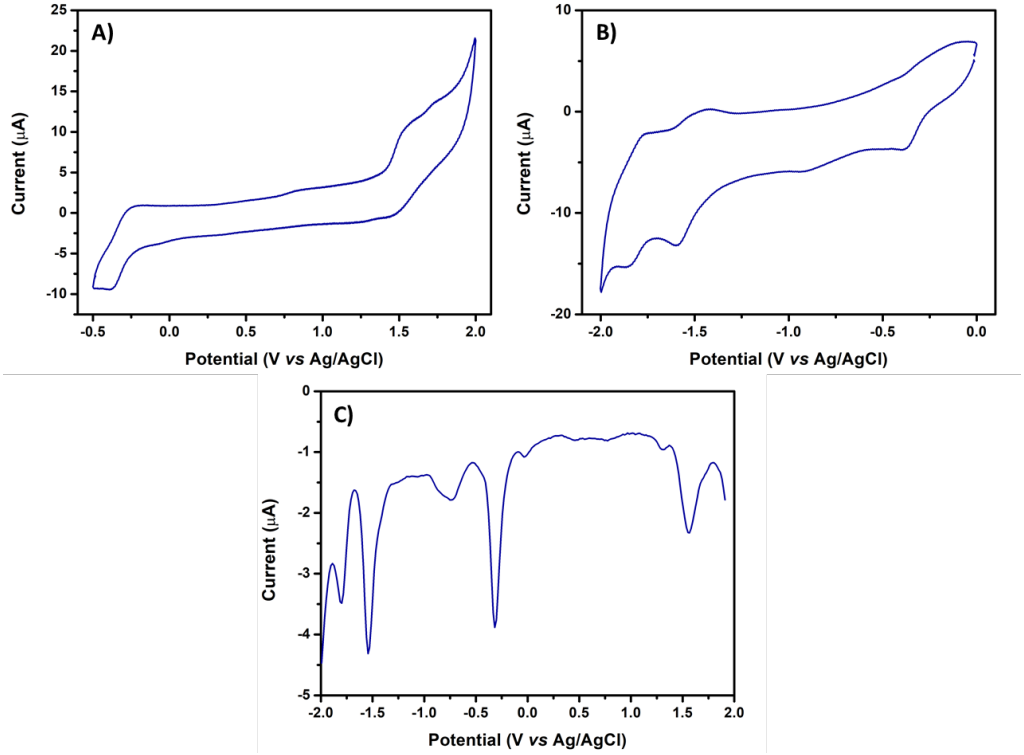


Figure S20. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Ru(phen)_2(diiminoTAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

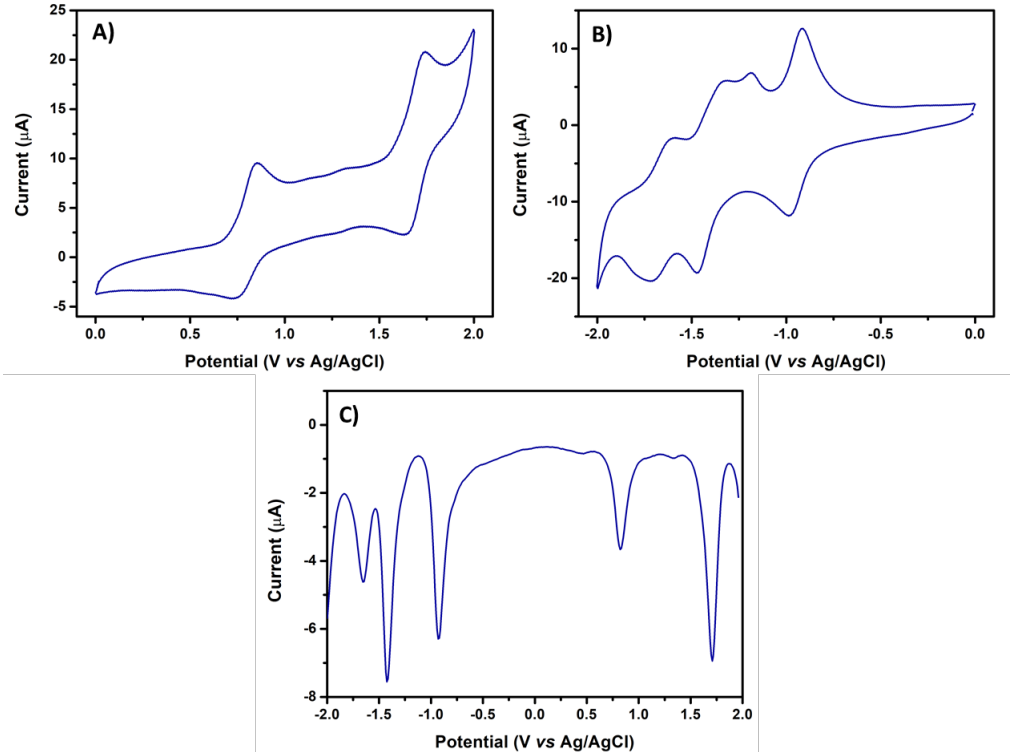


Figure S21. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Ru(phen)_2(diNH_2TAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

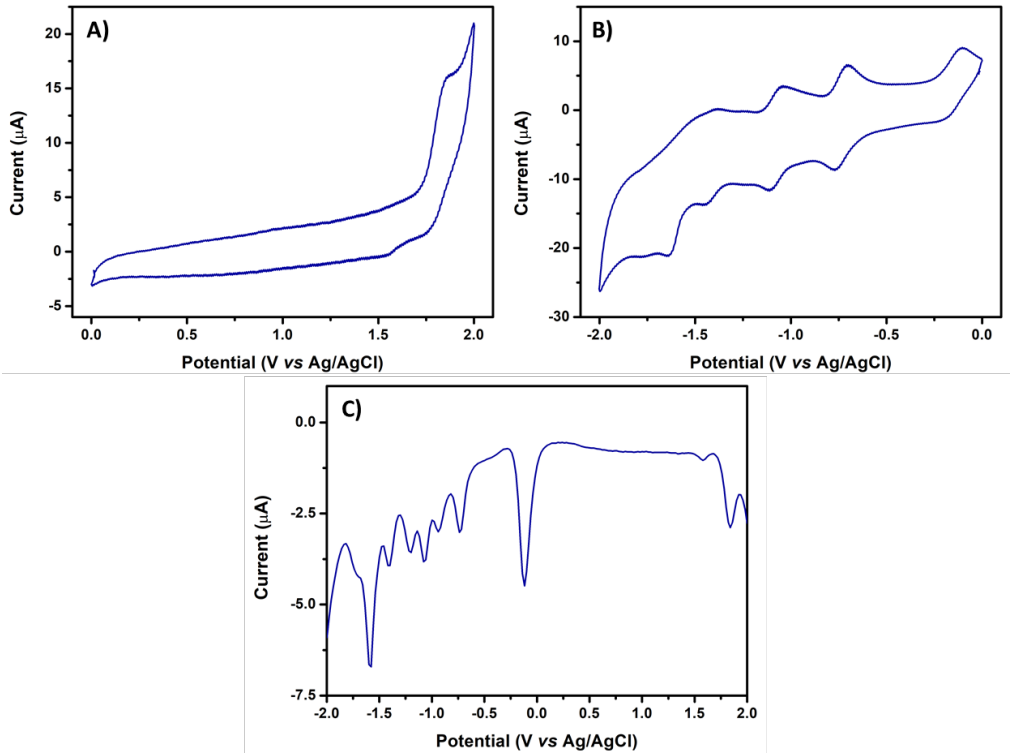


Figure S22. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Ru(TAP)_2(diiminoTAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

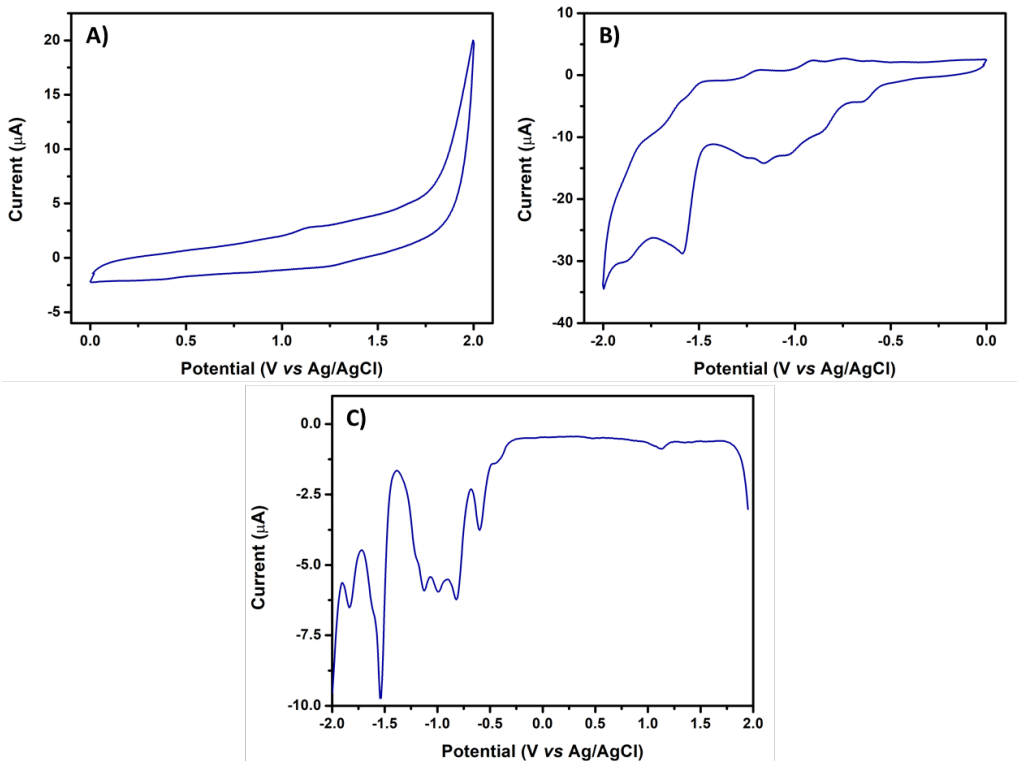


Figure S23. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Ru(TAP)_2(NO_2NH_2TAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

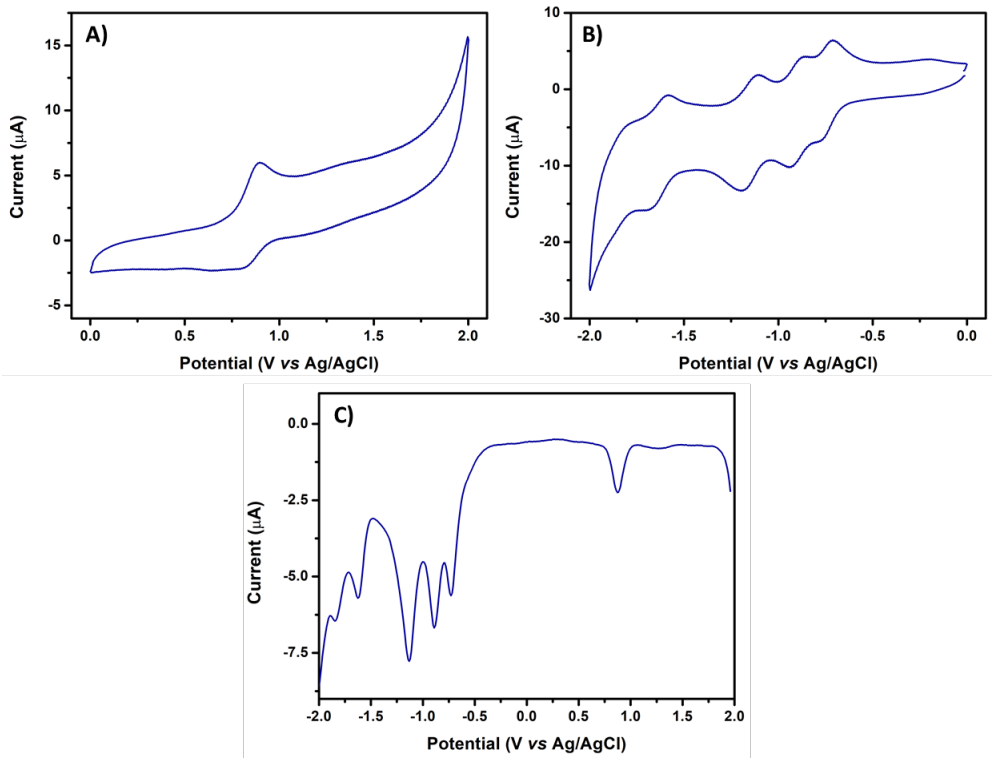


Figure S24. Cyclic voltammograms (A, B) and differential pulse voltammogram (C) of $[Ru(TAP)_2(diNH_2TAP)]^{2+}$ in acetonitrile (0.1 V/s) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

DFT Calculations

Table S1. Cartesian Coordinates (in Å) of the equilibrium geometry of the singlet state of the the $Ru(phen)_2(diNH_2TAP)]^{2+}$ complex.

Ru	-0.30625	0.00001	-0.00003
C	-2.45636	-0.60559	-2.16445
C	1.30569	1.6717	2.10848
C	-2.45627	0.60519	2.16457
C	-2.08952	-2.25419	-0.54335
C	2.50489	0.43593	0.55223
C	-2.08991	2.25387	0.54343
C	-1.36398	-2.65822	0.6154
C	-1.36457	2.65801	-0.6154
C	2.50495	-0.43552	-0.55231
C	0.26651	-2.12112	2.2078
C	0.26586	2.12118	-2.20795
C	1.30594	-1.67142	-2.10859
C	-3.4444	-1.39815	-2.77726
C	2.53314	2.128	2.64142
C	-3.44434	1.39761	2.77753
C	0.07992	-3.36037	2.84764
C	0.07894	3.36036	-2.84782
C	2.53346	-2.12757	-2.64151
H	-2.19793	-0.36729	2.55835
H	0.35984	1.98498	2.52416
H	-2.19819	0.36692	-2.55829
H	0.9842	1.40501	-2.58059
H	0.36013	-1.9848	-2.5243
H	0.98473	-1.40482	2.58041
H	2.52803	2.81292	3.48042
H	-3.95129	1.01686	3.65486
H	-3.95154	-1.01748	-3.65452
H	0.67125	3.59276	-3.72346
H	2.52845	-2.8125	-3.4805
H	0.67238	-3.5927	3.72319
N	-1.78614	-1.01802	-1.07164
N	-1.78626	1.01775	1.07167
N	1.29004	0.82467	1.06154
N	-0.43826	-1.76813	1.11566
N	1.29017	-0.8244	-1.06166
N	-0.43873	1.76808	-1.11572
C	-3.75354	-2.64625	-2.2579
C	-0.85299	-4.26114	2.35637
C	-0.85409	4.26096	-2.35649
C	-3.75374	2.64566	2.25822
C	-3.06769	3.10767	1.1091
C	-1.60987	3.91993	-1.20889
C	3.72997	0.88856	1.09747
C	3.73011	-0.88801	-1.09752
C	-1.60897	-3.92021	1.20888
C	-3.06724	-3.10815	-1.10889
H	-1.01086	5.21836	-2.83982
H	-4.51104	3.2685	2.72035
H	-4.51083	-3.26919	-2.7199
H	-1.0095	-5.21859	2.83968
N	3.72365	1.75498	2.15957
N	3.72391	-1.75442	-2.15962

C	4.9785	-0.4522	-0.53863
C	4.97843	0.45292	0.53858
N	6.14479	-0.92864	-1.0882
N	6.14464	0.92952	1.08813
H	7.00167	-0.94036	-0.55855
H	6.06435	-1.58063	-1.85455
H	7.00158	0.94112	0.55859
H	6.06416	1.5815	1.85448
C	-3.30409	-4.3857	-0.49077
C	-2.60397	-4.7757	0.61866
C	-2.60495	4.77525	-0.61856
C	-3.30485	4.38516	0.49098
H	-2.78898	-5.74147	1.07523
H	-4.05338	5.03715	0.92672
H	-4.05257	-5.03781	-0.92643
H	-2.79021	5.74097	-1.07514

Table S2. Cartesian Coordinates (in Å) of the equilibrium geometry of the singlet state of the the $Ru(TAP)_2(diNH_2TAP)]^{2+}$ complex.

Ru	-0.31824	0.00000	0.0000
C	-2.49309	0.67312	2.16127
C	1.30081	-1.63585	-2.13984
C	-2.49309	-0.67312	-2.16127
C	-2.0796	2.25769	0.51998
C	2.49745	-0.42614	-0.55962
C	-2.0796	-2.25769	-0.51998
C	-1.35327	2.64482	-0.63082
C	-1.35327	-2.64482	0.63082
C	2.49745	0.42614	0.55962
C	0.25699	2.13504	-2.21953
C	0.25699	-2.13504	2.21953
C	1.30081	1.63585	2.13984
C	-3.46758	1.54156	2.70642
C	2.5311	-2.07902	-2.68279
C	-3.46758	-1.54156	-2.70642
C	0.02248	3.39752	-2.81301
C	0.02248	-3.39752	2.81301
C	2.5311	2.07902	2.68279
H	-2.28618	0.28604	-2.61207
H	0.35708	-1.94351	-2.56369
H	-2.28618	-0.28604	2.61207
H	0.98528	-1.45116	2.62907
H	0.35708	1.94351	2.56369
H	0.98528	1.45116	-2.62907
H	2.52732	-2.74654	-3.53534
H	-4.01947	-1.23638	-3.5862
H	-4.01947	1.23638	3.5862
H	0.58776	-3.6859	3.68995
H	2.52732	2.74654	3.53534
H	0.58776	3.6859	-3.68995
N	-1.79554	1.02726	1.0683
N	-1.79554	-1.02726	-1.0683
N	1.28688	-0.81174	-1.07763
N	-0.4308	1.75345	-1.12983
N	1.28688	0.81174	1.07763
N	-0.4308	-1.75344	1.12983
C	-3.04952	-3.12112	-1.0739
C	-1.58572	-3.90035	1.23272
C	3.72436	-0.86626	-1.11307
C	3.72436	0.86625	1.11307
C	-1.58572	3.90035	-1.23272
C	-3.04952	3.12112	1.07389
N	3.71742	-1.71232	-2.19183
N	3.71742	1.71232	2.19183
C	4.97315	0.44229	0.54833
C	4.97315	-0.44229	-0.54833
N	6.13598	0.90823	1.10783
N	6.13598	-0.90824	-1.10783
H	7.00127	0.91175	0.59255
H	6.05844	1.54025	1.89091
H	7.00127	-0.91174	-0.59255
H	6.05844	-1.54025	-1.89091
C	-3.28097	4.39464	0.45178
C	-2.57332	4.77153	-0.65999
C	-2.57332	-4.77153	0.65999

C	-3.28097	-4.39464	-0.45178
H	-2.73473	5.72914	-1.13874
H	-4.02925	-5.0398	-0.89457
H	-4.02925	5.0398	0.89456
H	-2.73473	-5.72914	1.13874
N	-0.87565	-4.27081	2.3436
N	-3.75058	-2.74144	-2.18722
N	-3.75058	2.74144	2.18722
N	-0.87565	4.27081	-2.3436

Table S3. Cartesian Coordinates (in Å) of the equilibrium geometry of the singlet state of the the $Ru(phen)_2(diiminoTAP)]^{2+}$ complex.

Ru	0.51642	-0.00011	0.00002
C	2.58119	-0.69173	2.24967
C	2.58175	0.69272	-2.24889
C	2.31563	-2.26297	0.53792
C	-2.25753	0.44628	-0.56775
C	2.31429	2.26393	-0.53741
C	1.64276	-2.62463	-0.66461
C	1.6407	2.62527	0.66483
C	-2.25742	-0.44769	0.56718
C	0.04968	-2.04583	-2.28448
C	0.04728	2.04575	2.2841
C	3.53724	-1.5096	2.88058
C	3.53714	1.51142	-2.87971
C	0.27699	-3.25364	-2.96873
C	0.27333	3.25391	2.96814
H	2.29965	-0.25923	-2.67412
H	2.29798	0.25986	2.67498
H	-0.67561	1.32622	2.64087
H	-0.67349	-1.32674	-2.6415
H	3.98971	1.17204	-3.80247
H	3.98929	-1.16992	3.80349
H	-0.28991	3.45907	3.86919
H	-0.28568	-3.45901	-3.87009
N	1.98169	-1.05157	1.10047
N	1.98158	1.05215	-1.0999
N	-1.0525	0.77572	-0.99723
N	0.72004	-1.73064	-1.15919
N	-1.05233	-0.77652	0.99694
N	0.71844	1.73072	1.15926
C	3.8877	-2.72732	2.31843
C	1.2099	-4.15923	-2.48586
C	1.20575	4.16007	2.48543
C	3.88638	2.72951	-2.31761
C	3.26742	3.13898	-1.11178
C	1.9202	3.8588	1.30073
C	-3.51683	0.89459	-1.13493
C	-3.51658	-0.89631	1.13444
C	1.92359	-3.85773	-1.30075
C	3.2694	-3.13721	1.11239
H	1.3906	5.09453	3.00261
H	4.62183	3.37007	-2.79056
H	4.62366	-3.36722	2.79146
H	1.39583	-5.09331	-3.00331
C	-4.7401	0.45422	-0.57702
C	3.54971	-4.38207	0.4476
C	2.9048	-4.72762	-0.70905
C	2.90083	4.72944	0.70918
C	3.54642	4.38423	-0.44718
H	3.12104	-5.6694	-1.20029
H	4.28154	5.04891	-0.88636
H	4.28533	-5.04616	0.88685
H	3.11603	5.67155	1.20024
C	-4.73999	-0.45614	0.57663
C	-4.65119	2.13537	-2.71152
C	-5.8714	1.70149	-2.16005
C	-4.65063	-2.13754	2.71102

C	-5.87093	-1.70385	2.15965
H	-1.02866	1.41249	-1.79784
H	-1.02842	-1.41315	1.79766
N	-5.91763	-0.87243	1.10488
N	-3.4774	-1.73454	2.19946
N	-3.47786	1.73262	-2.20006
N	-5.91788	0.87013	-1.10529
H	-6.81659	2.02862	-2.57561
H	-4.6247	2.80447	-3.56238
H	-6.81603	-2.03107	2.57534
H	-4.62391	-2.8066	3.56191

Table S4. Cartesian Coordinates (in Å) of the equilibrium geometry of the singlet state of the the $Ru(TAP)_2(diiminoTAP)]^{2+}$ complex.

Ru	-0.54025	0.00000	0.00000
C	-2.63732	-0.76429	-2.22808
C	-2.63731	0.76432	2.22808
C	-2.30234	-2.27644	-0.50568
C	2.23956	0.44861	0.57132
C	-2.30231	2.27646	0.50568
C	-1.61972	-2.62064	0.68423
C	-1.61969	2.62065	-0.68423
C	2.23955	-0.44864	-0.57131
C	-0.04619	-2.06251	2.2966
C	-0.04617	2.0625	-2.29661
C	-3.58011	-1.66042	-2.786
C	-3.58008	1.66046	2.786
C	-0.30462	-3.30186	2.92897
C	-0.30459	3.30184	-2.92898
H	-2.41241	-0.17607	2.70828
H	-2.41241	0.17609	-2.70828
H	0.67986	1.36885	-2.69364
H	0.67985	-1.36888	2.69364
H	-4.08565	1.39584	3.70578
H	-4.08567	-1.39579	-3.70577
H	0.23492	3.56127	-3.83069
H	0.23488	-3.56129	3.83068
N	-2.00059	-1.06631	-1.08564
N	-2.00058	1.06633	1.08564
N	1.04161	0.77739	1.00152
N	-0.70671	-1.71937	1.17838
N	1.0416	-0.77741	-1.00152
N	-0.70669	1.71937	-1.17838
C	-3.24292	3.16624	1.06771
C	-1.87218	3.85435	-1.32261
C	3.5017	0.89576	1.13747
C	3.5017	-0.89579	-1.13747
C	-1.87222	-3.85435	1.32261
C	-3.24296	-3.16621	-1.06771
C	4.72194	0.45536	0.57803
C	-3.50127	-4.4141	-0.40518
C	-2.83951	-4.74666	0.74819
C	-2.83945	4.74669	-0.7482
C	-3.50121	4.41413	0.40518
H	-3.01945	-5.68534	1.25677
H	-4.23006	5.07747	0.85342
H	-4.23012	-5.07743	-0.85342
H	-3.01938	5.68536	-1.25678
C	4.72194	-0.45539	-0.57803
C	4.63322	2.13536	2.71427
C	5.85313	1.70104	2.16123
C	4.63321	-2.13538	-2.71427
C	5.85312	-1.70107	-2.16123
H	1.01746	1.41328	1.80346
H	1.01745	-1.41329	-1.80345
N	5.89962	-0.87035	-1.10553
N	3.4604	-1.73215	-2.20199
N	3.46041	1.73213	2.202
N	5.89962	0.87032	1.10553
H	6.79854	2.0277	2.57628

H	4.60673	2.80378	3.56532
H	6.79853	-2.02773	-2.57628
H	4.60672	-2.8038	-3.56532
N	-1.1948	4.18592	-2.46567
N	-3.8888	2.83634	2.22923
N	-1.19485	-4.18592	2.46566
N	-3.88884	-2.8363	-2.22923