Electronic Supplementary Information for Dalton Transactions

Ground and Excited State Properties of Photoactive Platinum(IV) Diazido Complexes: Theoretical Considerations

Alexander Yu. Sokolov* and Henry F. Schaefer III

Center for Computational Quantum Chemistry

University of Georgia

Athens, Georgia 30602

* E-mail for correspondence: alex@ccqc.uga.edu

Supporting Information

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Table S1. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **1t** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -712.8291558461

Pt	0.000000	0.000000	0.000000
O	-0.931001	-0.354022	1.750629
H	-0.260705	-0.434166	2.436601
N	0.128725	-1.991270	-0.435220
H	0.872857	-2.125627	-1.116432
H	-0.754946	-2.274498	-0.851884
H	0.300647	-2.551812	0.393219
N	-1.803361	-0.008832	-0.995214
N	-2.784727	0.255621	-0.321145
N	-3.738664	0.502159	0.235484
O	0.931001	0.354022	-1.750629
H	0.260705	0.434166	-2.436601
N	-0.128725	1.991270	0.435220
H	-0.872857	2.125627	1.116432
H	0.754946	2.274498	0.851884
H	-0.300647	2.551812	-0.393219
N	1.803361	0.008832	0.995214
N	2.784727	-0.255621	0.321145
N	3.738664	-0.502159	-0.235484

Table S2. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **1c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -712.8279662756

Pt	-0.569966	0.053112	-0.040492
N	0.758924	1.036103	-1.205246
N	1.556446	1.740435	-0.603391
N	2.331327	2.412201	-0.129257
N	0.837476	-0.817001	1.121947
N	1.683968	-1.460518	0.518595
N	2.506178	-2.072483	0.043327
N	-1.999055	1.087418	-1.175015
H	-2.684401	0.492855	-1.627708
H	-1.457690	1.561782	-1.894343
H	-2.445877	1.792170	-0.594936
N	-1.907486	-1.091235	1.099185
H	-2.626217	-0.547899	1.564494
H	-1.323830	-1.528633	1.808920
H	-2.311858	-1.823802	0.522754
O	-0.670620	-1.475130	-1.349708
H	0.069568	-1.439963	-1.961935
O	-0.800260	1.568085	1.268699
H	-0.056560	1.603039	1.876626

Table S3. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **2c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -791.4333593550

Pt	0.357584	0.090915	-0.057723
N	-1.043513	1.554000	0.000854
N	-1.827308	1.564524	-0.934895
N	-2.592834	1.645693	-1.763525
N	-1.004913	-1.388607	-0.305045
N	-1.909541	-1.407364	0.514230
N	-2.780789	-1.496602	1.229944
N	1.749940	1.676101	-0.010177
H	1.510189	2.160852	-0.873352
H	2.701140	1.345311	-0.134068
C	1.666611	2.573950	1.158885
H	0.652408	2.966768	1.209540
H	1.856834	1.992460	2.059307
H	2.382893	3.394192	1.068261
N	1.764802	-1.475246	0.086823
H	2.688222	-1.130290	0.327170
C	1.842886	-2.381480	-1.076330
H	1.423916	-1.957912	0.916586
H	2.133455	-1.801325	-1.950585
H	0.849819	-2.793030	-1.249194
H	2.556570	-3.188037	-0.891367
O	0.630729	0.294586	-2.045382
H	-0.108786	-0.090675	-2.523684
O	0.358420	-0.111236	1.948827
H	-0.445748	0.261792	2.320543

Table S4. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **3c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -1307.8545430835

Pt	0.219021	0.001083	0.000330
N	1.571341	1.386728	-0.413628
N	2.327788	1.642999	0.526764
N	3.078863	1.960860	1.301853
N	1.582590	-1.371611	0.417811
N	2.341660	-1.623789	-0.521586
N	3.095804	-1.937253	-1.295489
N	-1.332858	1.592023	-0.420318
F	-2.529451	1.109666	-0.825178
F	-0.984314	2.433983	-1.402097
F	-1.640545	2.394910	0.606239
N	-1.322093	-1.601791	0.418263
F	-2.515256	-1.128334	0.842502
F	-0.959763	-2.454727	1.385567
F	-1.639084	-2.393106	-0.614615
O	0.101499	-0.476330	-1.938017
H	0.768498	-0.001088	-2.442759
O	0.093009	0.476780	1.938651
H	0.763426	0.007545	2.444501

Table S5. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **4c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -1285.9748070420

Pt	0.344032	0.069547	0.022840
N	-1.038988	1.354843	0.875423
N	-1.758948	1.921565	0.069315
N	-2.460548	2.480988	-0.618340
N	-1.120112	-1.089227	-0.872988
N	-1.909963	-1.589557	-0.088672
N	-2.676974	-2.084562	0.578276
P	1.823284	1.547446	0.989223
H	1.520912	1.818468	2.327185
H	1.832671	2.807790	0.379327
H	3.193627	1.241591	1.052465
P	1.719486	-1.537804	-0.885995
H	1.606804	-2.785327	-0.260585
H	1.431852	-1.802478	-2.228690
H	3.111851	-1.348066	-0.915116
O	0.472922	1.144715	-1.694125
H	-0.301759	0.930696	-2.224332
O	0.325830	-1.011611	1.741956
H	-0.443510	-0.731709	2.248673

Table S6. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **5c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -1881.6606779840

Pt	-0.001507	-0.223882	-0.000292
N	-1.459651	-1.625859	0.339919
N	-1.683201	-2.347056	-0.628811
N	-1.945363	-3.055732	-1.463613
N	1.427802	-1.656523	-0.336367
N	1.629300	-2.384191	0.632267
N	1.870117	-3.099814	1.467648
P	-1.769327	1.193873	0.287349
F	-2.550009	1.028059	1.616963
F	-2.912722	1.095123	-0.755542
F	-1.505315	2.735003	0.292249
P	1.795547	1.159697	-0.287224
F	2.933676	1.042022	0.759348
F	2.576769	0.974228	-1.614016
F	1.561362	2.705529	-0.297822
O	-0.342273	-0.198422	-1.997560
H	0.178103	-0.909164	-2.388087
O	0.339927	-0.199868	1.997207
H	-0.193825	-0.899419	2.389877

Table S7. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **6c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -752.5153659447

Pt	0.308172	0.059342	0.072749
N	-0.533077	1.688449	0.840292
N	-1.420926	2.198416	0.164511
N	-2.243482	2.739578	-0.384988
N	-1.350246	-0.466651	-0.884670
N	-1.859193	-1.513526	-0.488822
N	-2.410411	-2.460136	-0.223873
O	-0.210951	-0.961373	1.695622
H	-0.789306	-0.423862	2.245101
O	1.209598	0.907028	-1.534621
H	0.609376	1.263466	-2.192523
O	1.335628	-1.648600	-0.717866
H	1.923199	-2.097793	-0.102940
H	1.835179	-1.268922	-1.456082
O	2.175015	0.838264	0.867468
H	1.999545	1.389627	1.637878
H	2.388719	1.414941	0.113293

Table S8. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **7c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -826.2974915561

Pt	0.265286	0.003714	-0.008307
N	-1.181194	1.226438	0.719095
N	-1.894366	1.733389	-0.142211
N	-2.599721	2.241994	-0.857787
N	-1.168964	-1.238907	-0.726597
N	-1.867386	-1.752666	0.142856
N	-2.557941	-2.267883	0.868163
O	0.249958	0.901534	-1.824342
H	-0.455664	0.488211	-2.334405
O	0.276269	-0.894667	1.809331
H	-0.431712	-0.492739	2.325076
C	1.566085	1.381144	0.650605
O	2.240728	2.173909	1.061095
C	1.585921	-1.367146	-0.648174
O	2.270822	-2.161447	-1.038073

Table S9. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **8c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -751.3582875787

Pt	-0.124399	-0.141026	0.111938
N	-1.753551	1.126345	-0.231599
N	-2.252585	1.196407	-1.309574
N	-2.800809	1.333802	-2.314636
N	0.820183	1.377687	1.202743
N	2.004813	1.418626	1.311005
N	3.138527	1.546066	1.476036
O	-1.030480	-0.919405	1.763473
H	-0.298227	-1.381473	2.183502
O	0.819133	0.426788	-1.595217
H	0.353397	-0.081992	-2.266772
O	1.420378	-1.355717	0.514596
H	1.967425	-1.248434	-0.270425
O	-1.036288	-1.569844	-0.959411
H	-1.486456	-2.058078	-0.261745

Table S10. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **9c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -785.4604140882

Pt	0.295728	-0.057045	-0.045567
N	-1.292057	1.148629	0.648425
N	-1.683176	2.089096	0.021660
N	-2.120209	3.002990	-0.513038
N	-1.115598	-1.533340	-0.577020
N	-1.749778	-2.074194	0.278624
N	-2.410565	-2.639328	1.028658
O	0.351495	-0.814094	1.842056
H	-0.296672	-0.281126	2.313348
O	0.090381	0.689947	-1.931591
H	0.902583	1.153947	-2.149299
C	1.770904	-1.253260	-0.599060
N	2.641982	-1.931665	-0.947234
C	1.604255	1.358181	0.405921
N	2.362403	2.201959	0.639564

Table S11. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **10c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -1096.2634778196

Pt	0.325430	0.029323	-0.059127
N	1.763284	1.365892	-0.539430
N	2.597632	1.575339	0.324527
N	3.411993	1.836310	1.065931
N	1.693242	-1.423140	0.259254
N	2.385097	-1.715531	-0.701157
N	3.068889	-2.056262	-1.536188
O	0.143878	-0.390381	-2.026615
H	0.906417	-0.019671	-2.481132
O	0.404780	0.454048	1.913956
H	1.185744	0.027340	2.279339
C	-1.793201	1.704021	-1.392771
C	-1.262716	2.449360	0.742649
C	-2.706208	2.730242	-1.563925
H	-1.565285	0.965554	-2.155905
C	-2.158004	3.500577	0.634998
H	-0.653383	2.265058	1.623000
C	-2.892231	3.643706	-0.534592
H	-3.252952	2.809260	-2.496736
H	-2.266329	4.195227	1.460198
H	-3.598299	4.461195	-0.644877
C	-1.551952	-2.230896	-0.672243
C	-1.744693	-1.488488	1.520661
C	-2.511526	-3.207102	-0.462539
H	-1.043445	-2.080871	-1.620549
C	-2.710700	-2.441182	1.796214
H	-1.362332	-0.785327	2.255079
C	-3.101191	-3.314653	0.789736
H	-2.781044	-3.872891	-1.274516
H	-3.139518	-2.495115	2.790462
H	-3.853323	-4.074087	0.980848
N	-1.097215	1.572942	-0.256606
N	-1.189068	-1.391438	0.306344

Table S12. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **11c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -1052.1558160444

Pt	0.210393	0.205846	0.006584
N	1.486819	1.731703	-0.371466
N	2.359748	1.891294	0.462143
N	3.199319	2.115251	1.188720
N	1.784242	-0.987288	0.469120
N	1.813000	-2.058573	-0.098241
N	1.898939	-3.082824	-0.580933
O	0.234569	-0.310656	-1.947050
H	1.003777	0.103865	-2.347217
O	-0.006679	0.693883	1.959862
H	0.789460	0.426440	2.427893
N	-1.105825	-1.380213	0.257860
C	-1.780700	-1.734750	1.402181
C	-1.363109	-2.277471	-0.669431
C	-2.468024	-2.879373	1.148859
H	-1.686349	-1.134012	2.293938
H	-0.948201	-2.250619	-1.667639
H	-3.108579	-3.485510	1.769047
H	-2.522765	-4.016764	-0.658410
N	-2.193851	-3.204615	-0.164248
N	-1.335166	1.527613	-0.355468
C	-1.788110	2.378662	0.537053
C	-1.993398	1.748602	-1.540880
H	-1.431179	2.428003	1.556560
C	-2.877932	2.762626	-1.348797
H	-1.746699	1.165463	-2.414964
H	-3.234395	3.886959	0.431581
H	-3.576596	3.243165	-2.014593
N	-2.734503	3.146569	-0.030559

Table S13. The energy E (in a.u.) and theoretical Cartesian coordinates (in Å) for the optimized structure of the complex **12c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

E_{GS} = -1095.0515378293

Pt	0.535202	0.053088	0.003412
N	1.907443	1.520860	-0.176297
N	2.746534	1.568576	0.710665
N	3.559886	1.687946	1.485948
N	1.945479	-1.377318	0.186823
N	2.789719	-1.400720	-0.696216
N	3.609723	-1.496502	-1.467753
N	-1.081746	1.352804	-0.068919
C	-0.966951	2.676133	-0.136069
H	0.051940	3.050405	-0.163165
C	-2.086375	3.493484	-0.170939
H	-1.965723	4.569021	-0.224533
C	-3.340223	2.904451	-0.133712
H	-4.237109	3.515072	-0.157018
C	-3.445156	1.520910	-0.065741
H	-4.420002	1.049379	-0.035876
C	-2.287624	0.758453	-0.035299
N	-1.046848	-1.288878	0.072103
C	-0.897401	-2.608753	0.139274
H	0.130919	-2.956188	0.166911
C	-1.995012	-3.455221	0.173733
H	-1.846087	-4.527208	0.227527
C	-3.263868	-2.899343	0.135930
H	-4.144410	-3.533307	0.159006
C	-3.405048	-1.519034	0.067601
H	-4.392053	-1.073649	0.037135
C	-2.267993	-0.726396	0.037764
O	0.471848	-0.136535	-2.004177
H	1.162728	0.419870	-2.376351
O	0.460936	0.241115	2.010785
H	1.165492	-0.296262	2.385258

Figure S1. Structure of complex **2c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

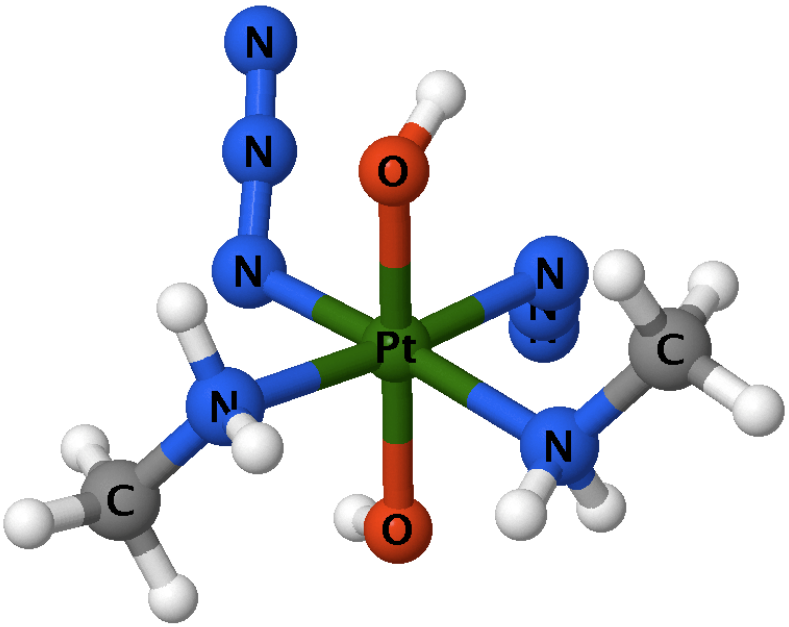

Figure S2. Structure of complex **3c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

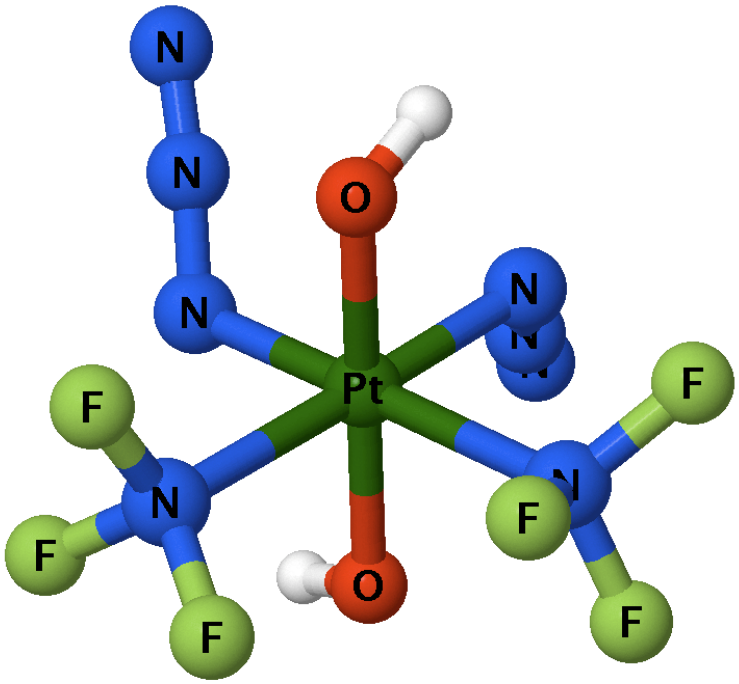

Figure S3. Structure of complex **4c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

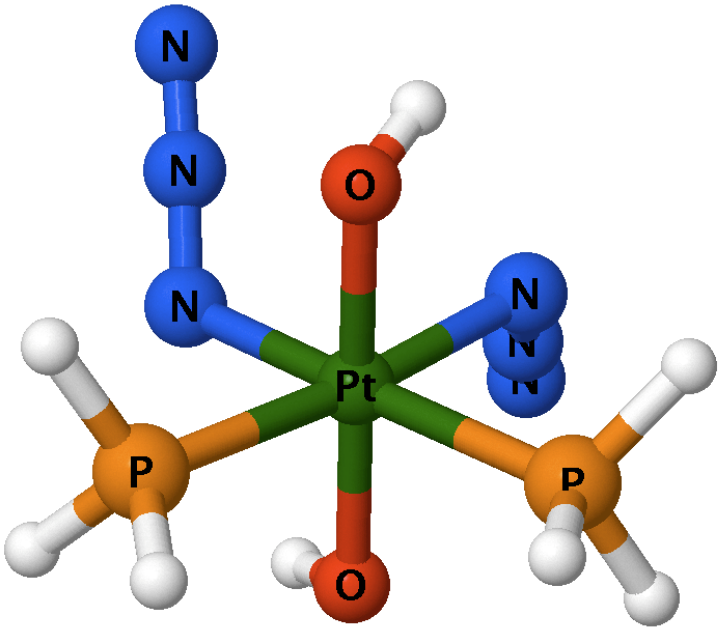

Figure S4. Structure of complex **5c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

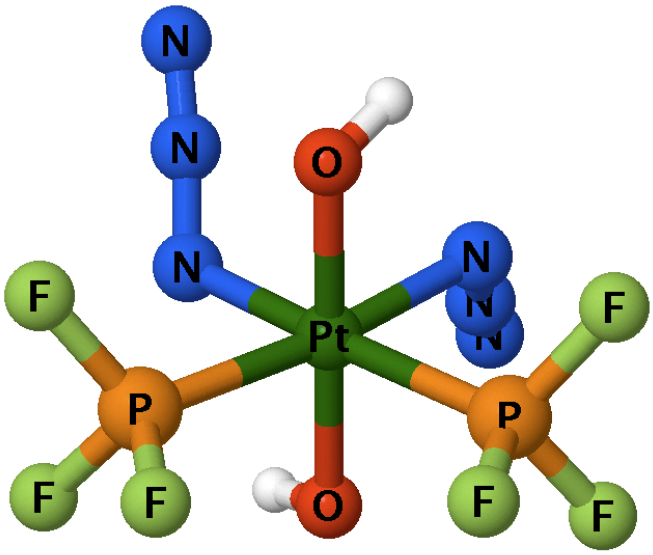

Figure S5. Structure of complex **6c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

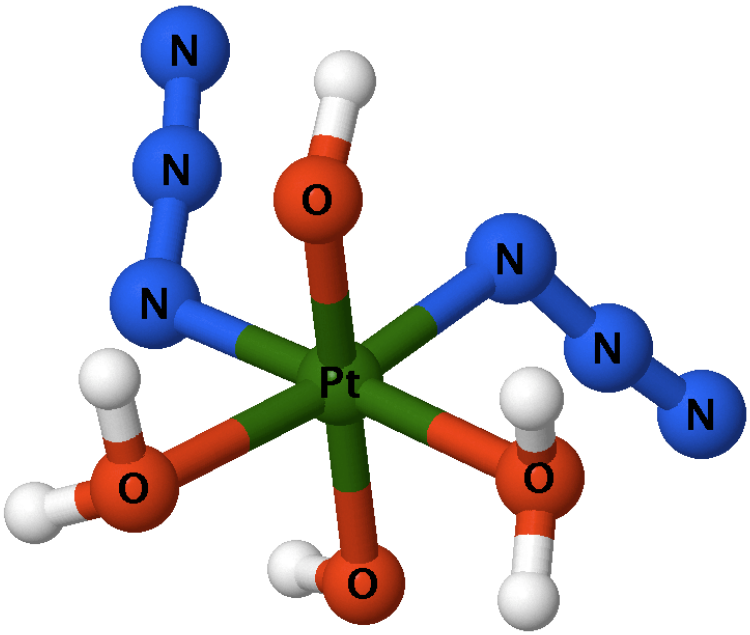

Figure S6. Structure of complex **7c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

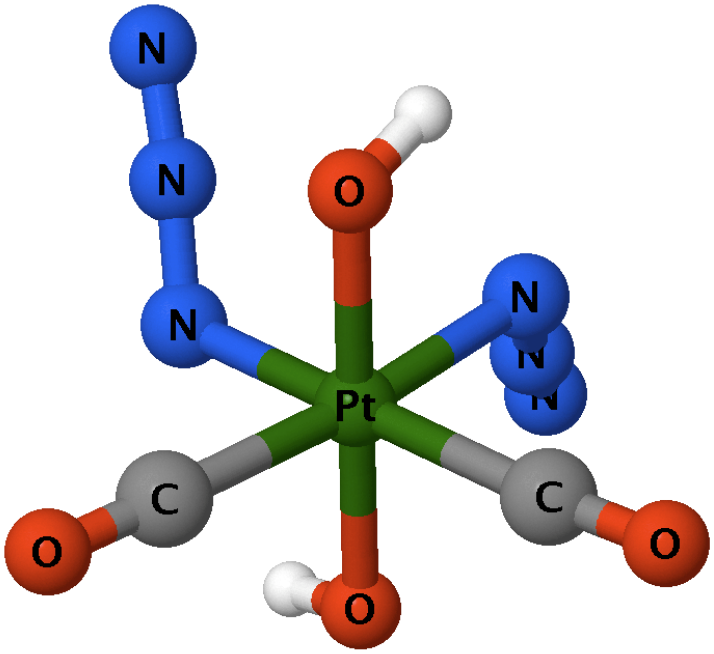

Figure S7. Structure of complex **8c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

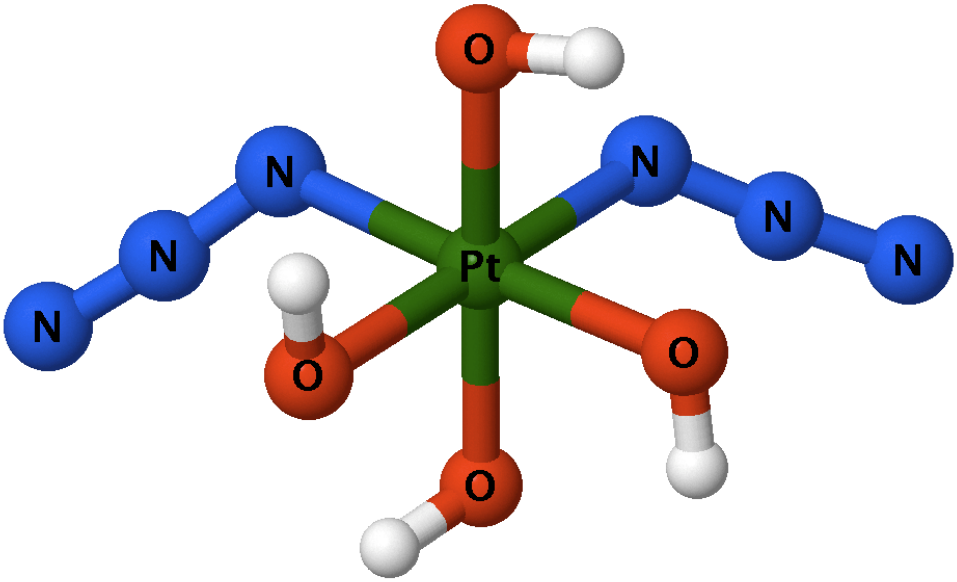

Figure S8. Structure of complex **9c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

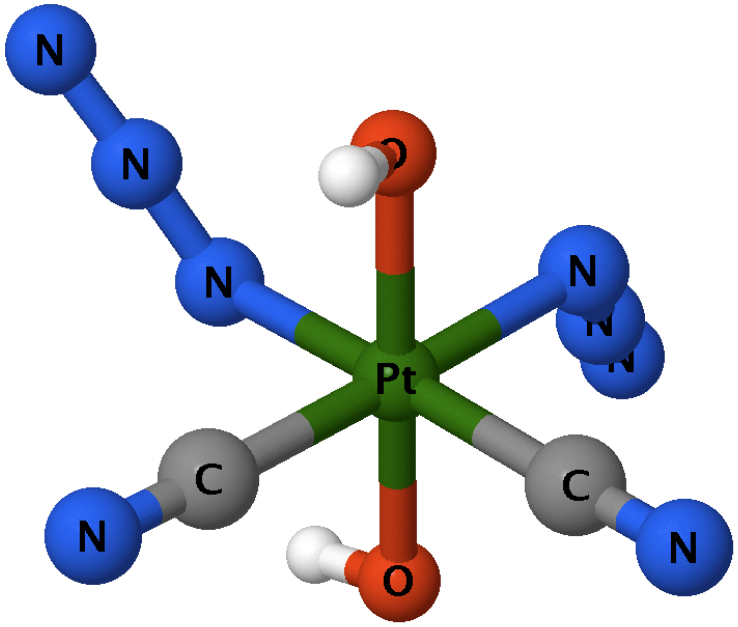

Figure S9. Structure of complex **10c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

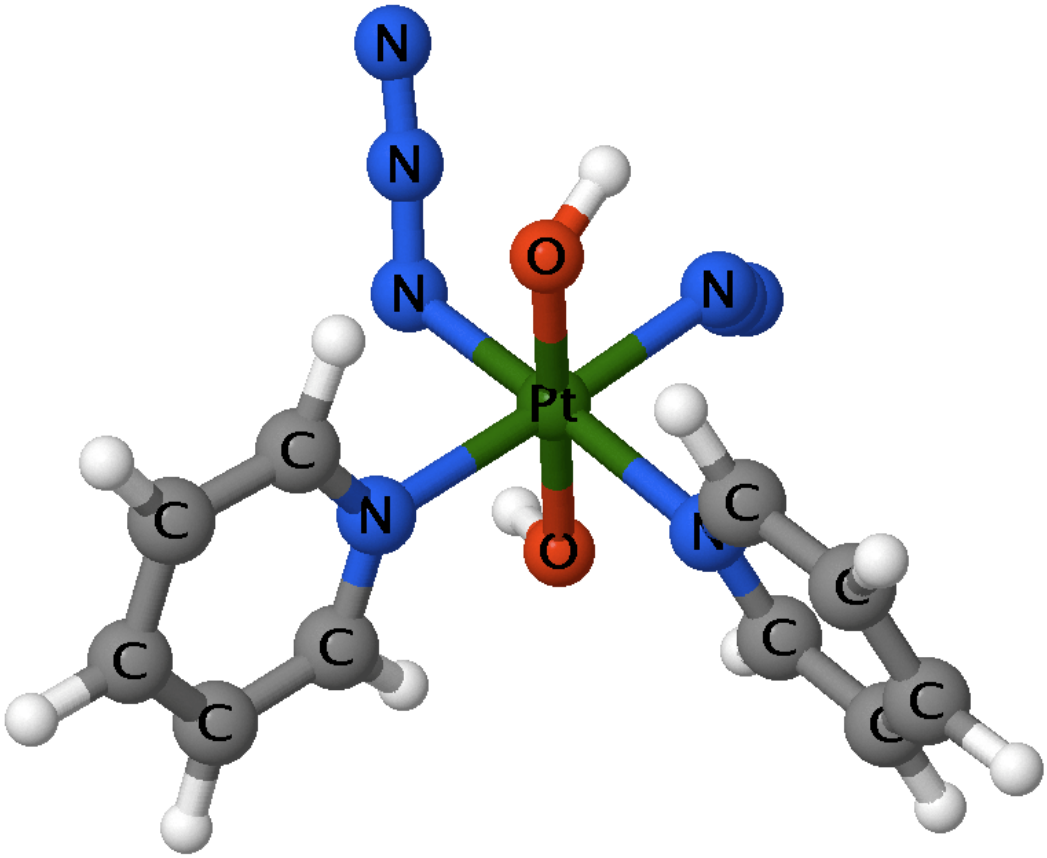

Figure S10. Structure of complex **11c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

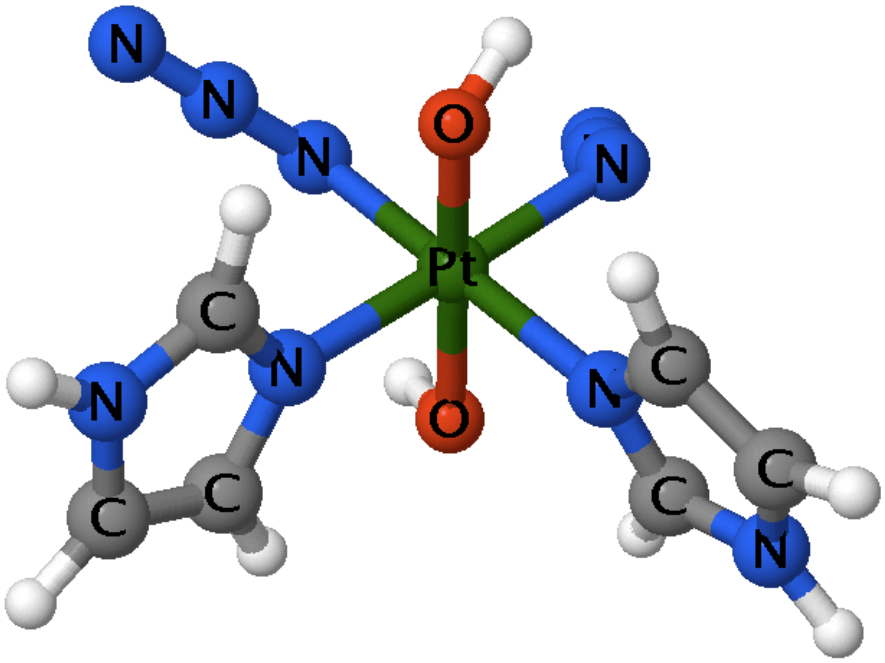

Figure S11. Structure of complex **12c** optimized using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

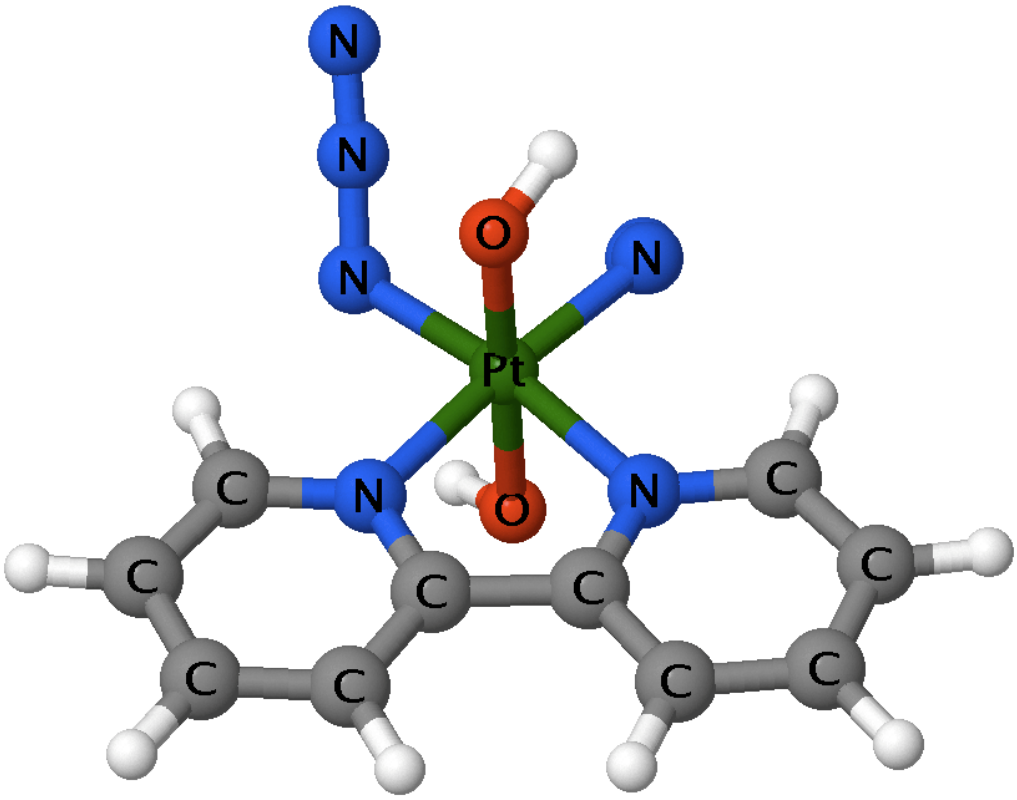

Figure S12. Electronic spectrum of complex **2c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

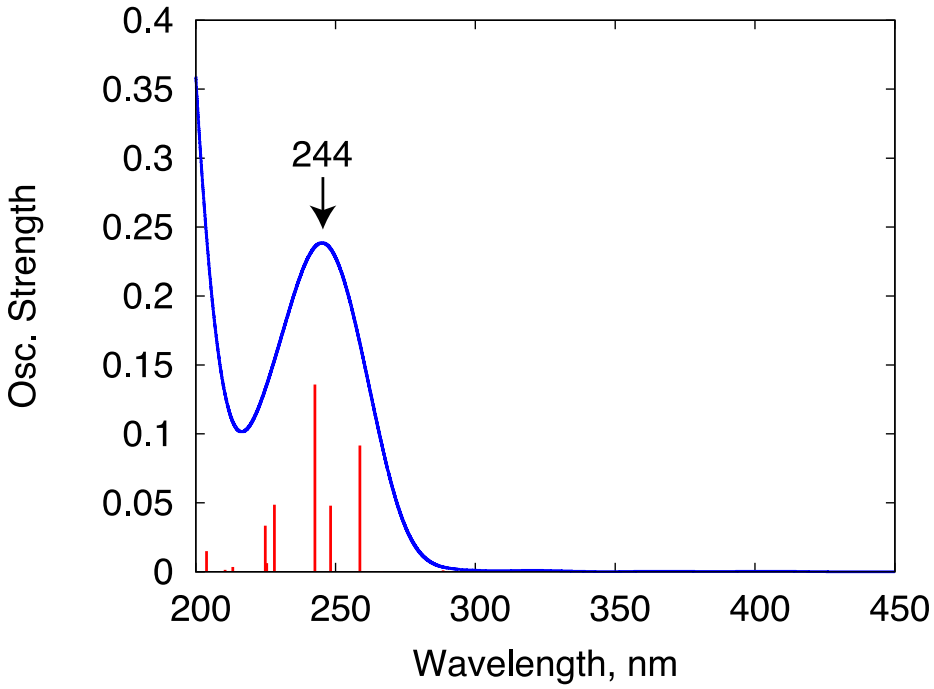

Figure S13. Electronic spectrum of complex **3c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

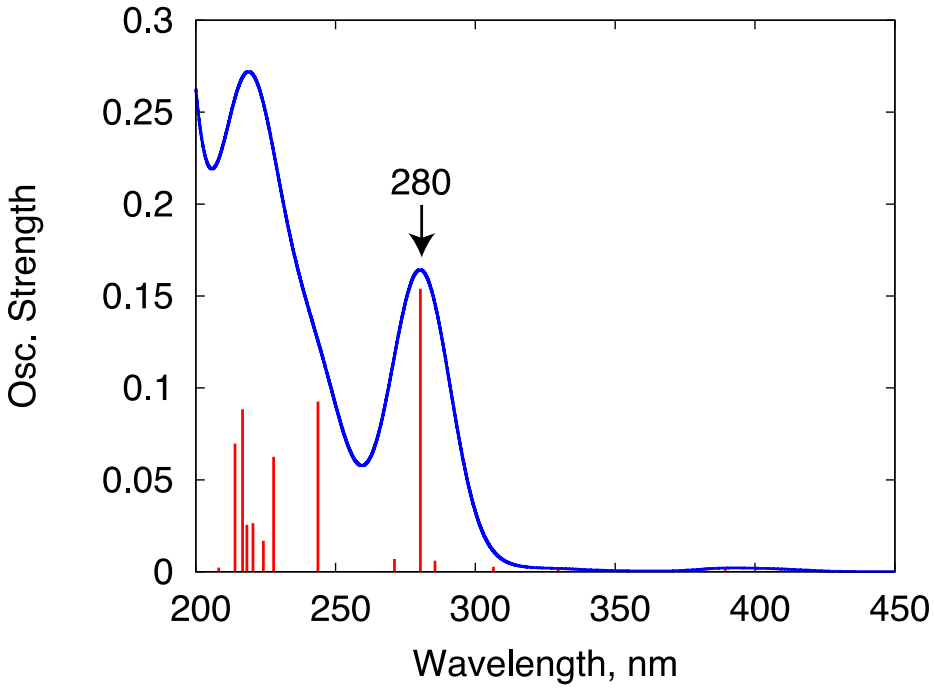

Figure S14. Electronic spectrum of complex **4c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

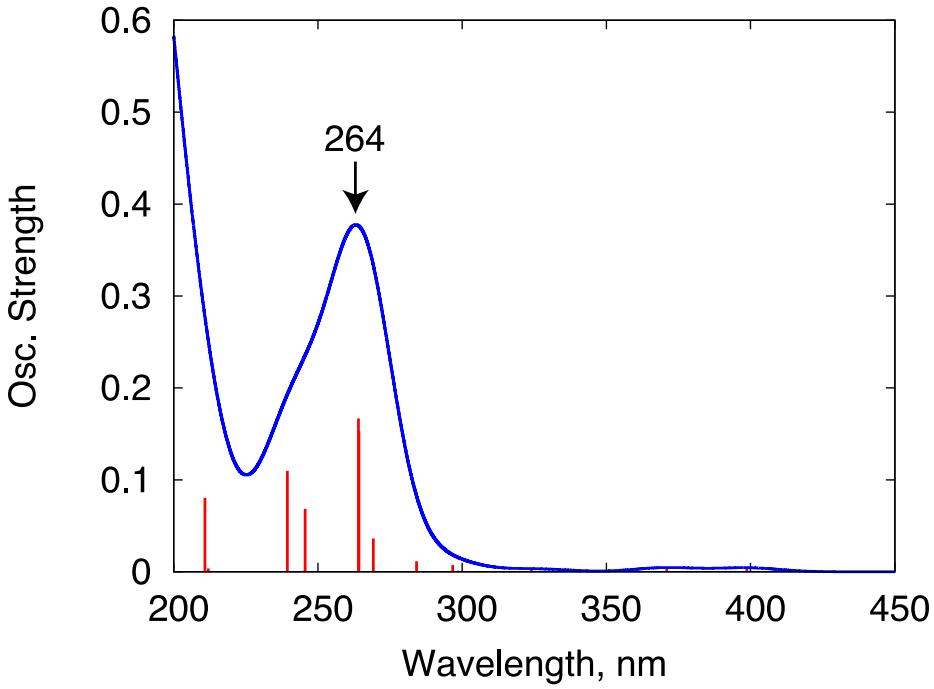

Figure S15. Electronic spectrum of complex **5c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

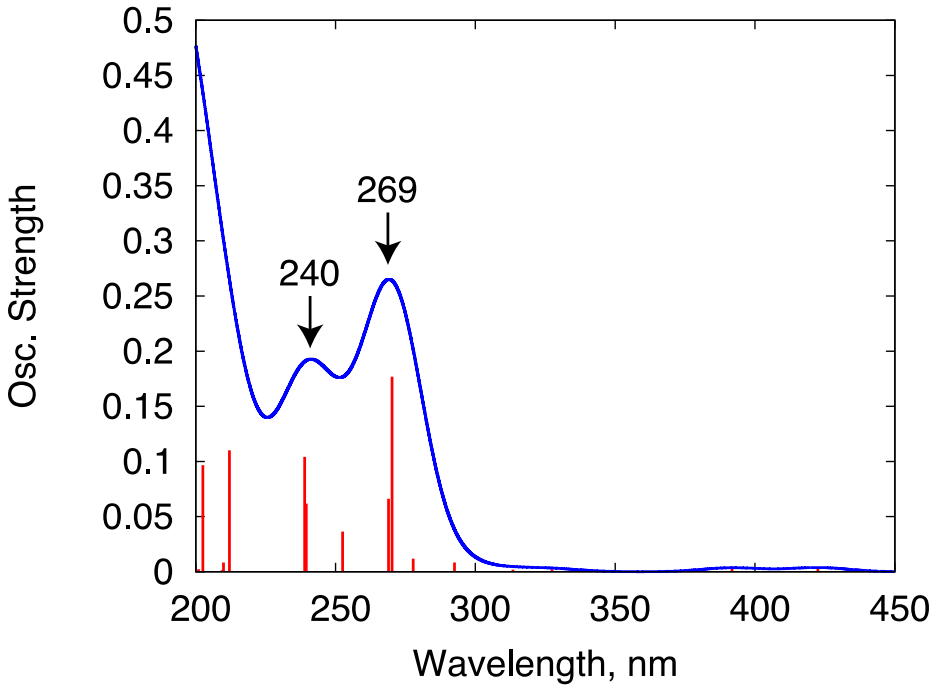

Figure S16. Electronic spectrum of complex **6c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

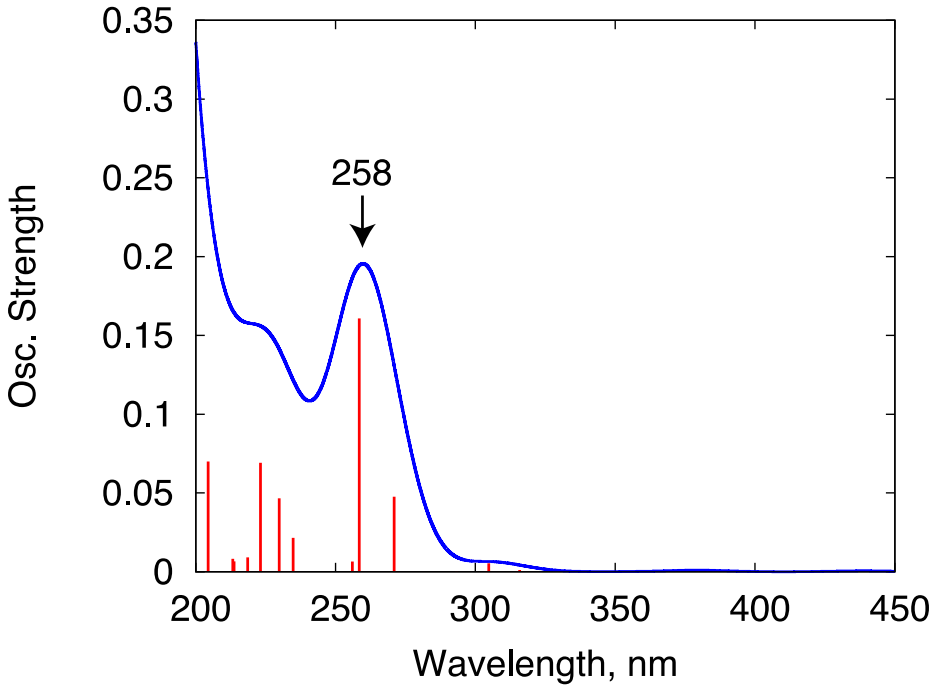

Figure S17. Electronic spectrum of complex **7c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

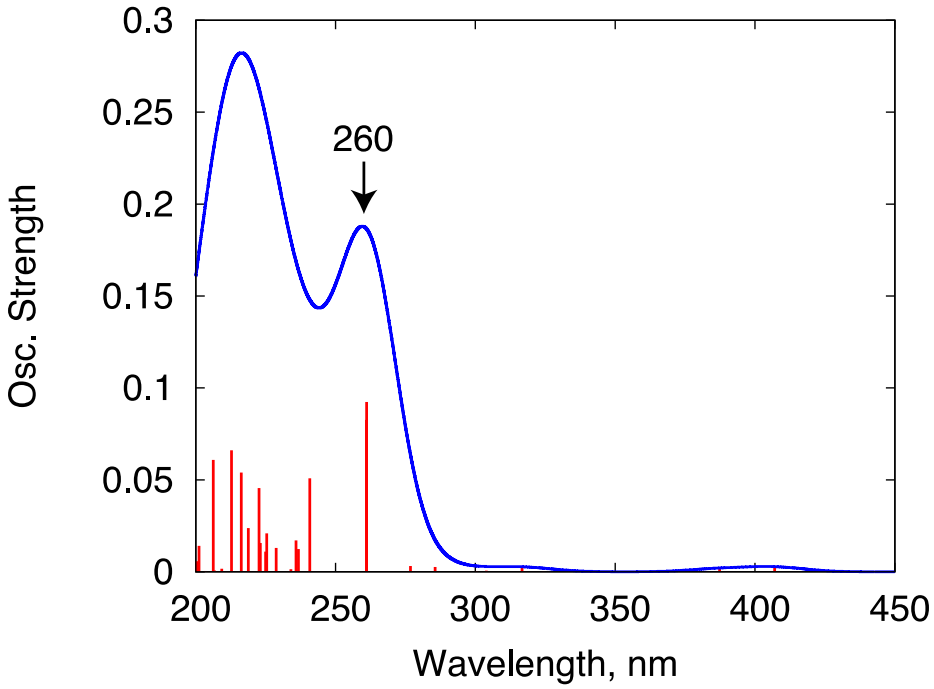

Figure S18. Electronic spectrum of complex **8c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

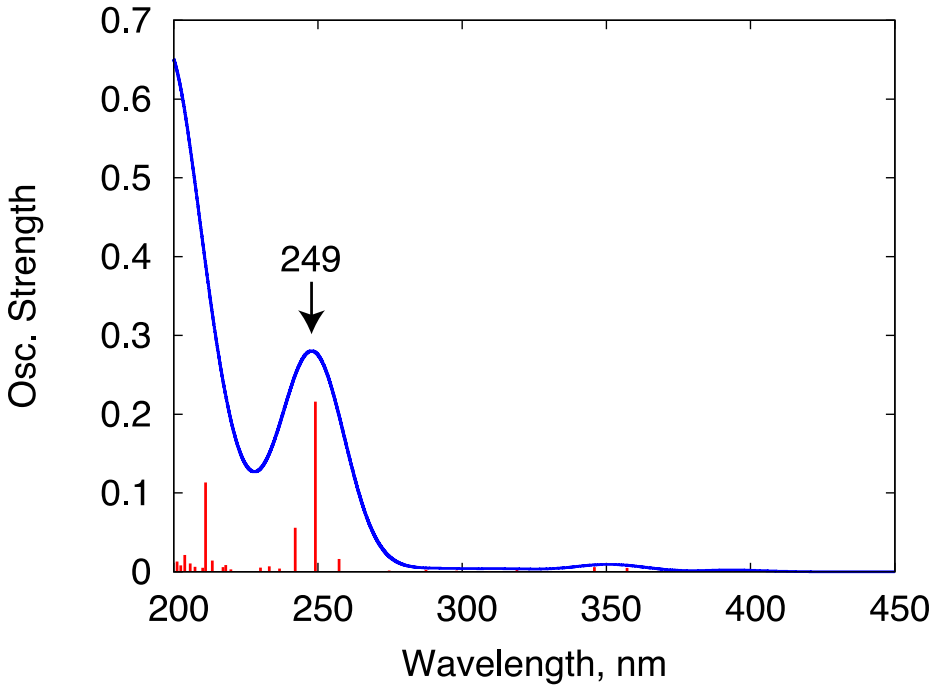

Figure S19. Electronic spectrum of complex **9c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

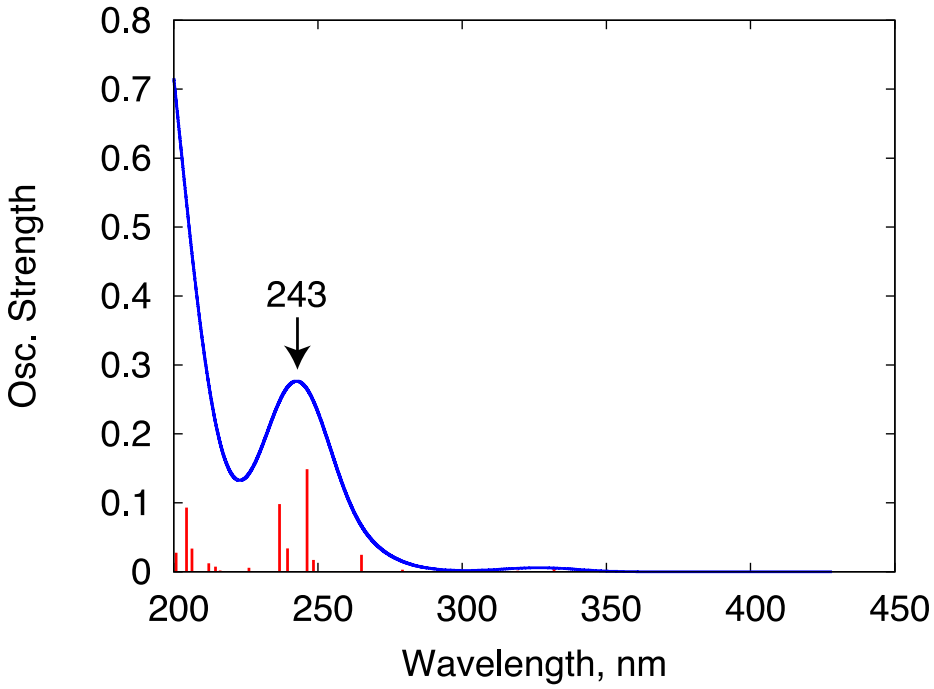

Figure S20. Electronic spectrum of complex **10c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

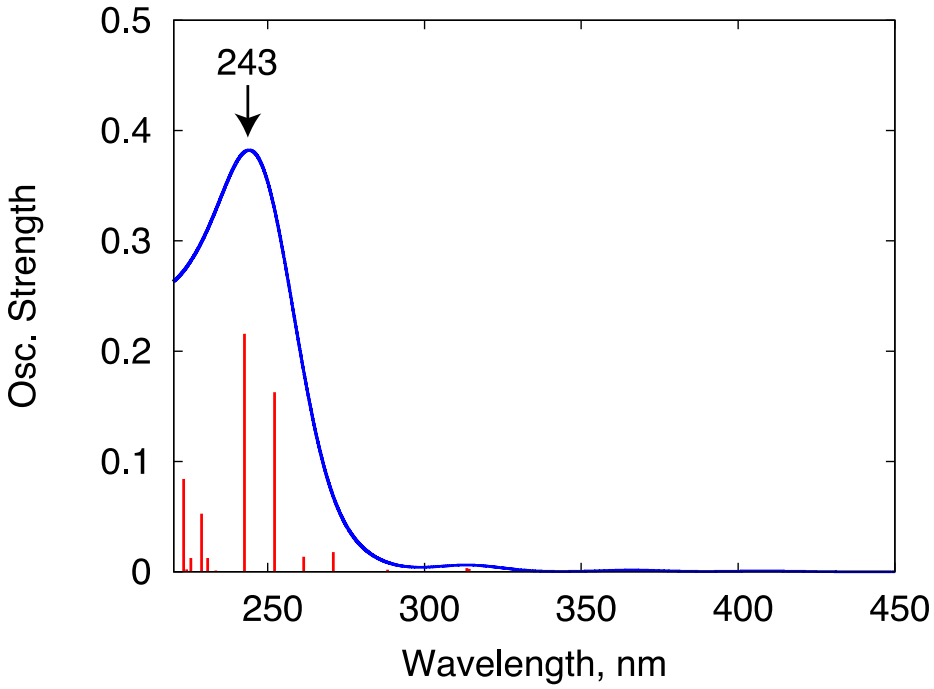

Figure S21. Electronic spectrum of complex **11c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.

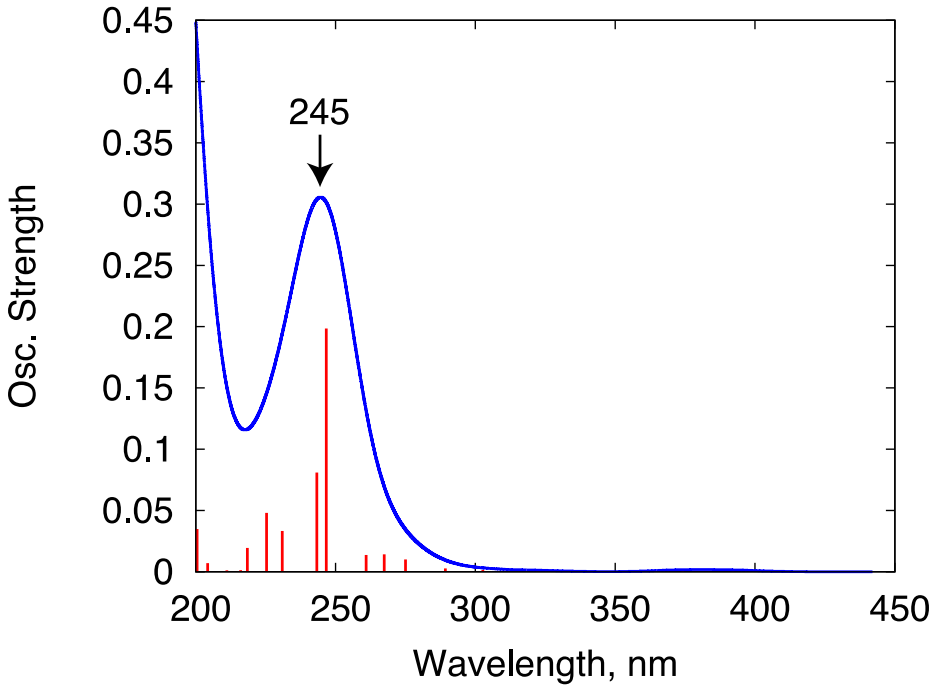

Figure S22. Electronic spectrum of complex **12c** computed using the ωB97X density functional with CRENBL(Pt)/6-311+G* basis set.