Electronic Supplementary Information

for

Controlling the redox properties of a pyrroloquinolinequinone (PQQ) derivative in a ruthenium(II) coordination sphere

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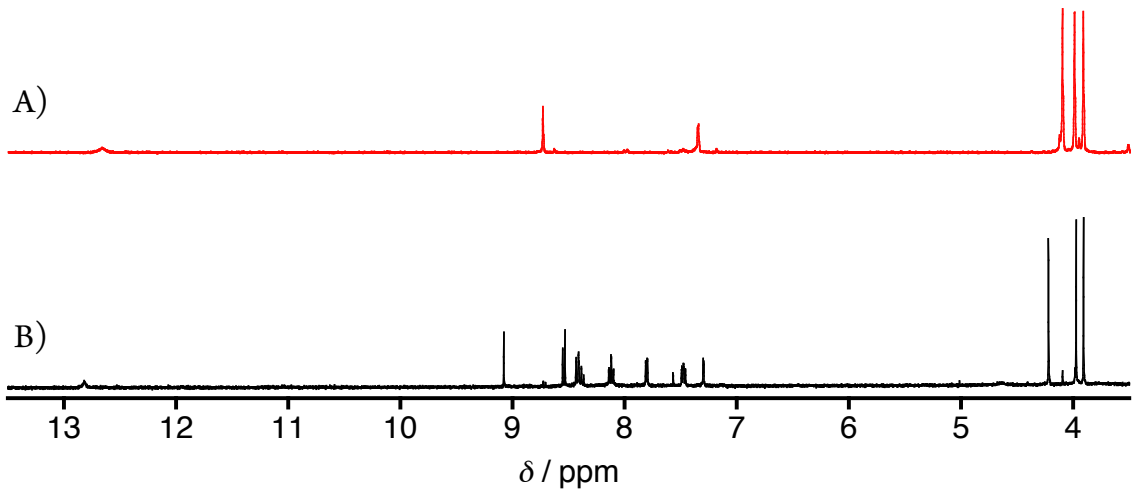

Fig. S1. ^{1}H NMR spectra of PQQTME (A) and **2** (B) in CD_3CN.

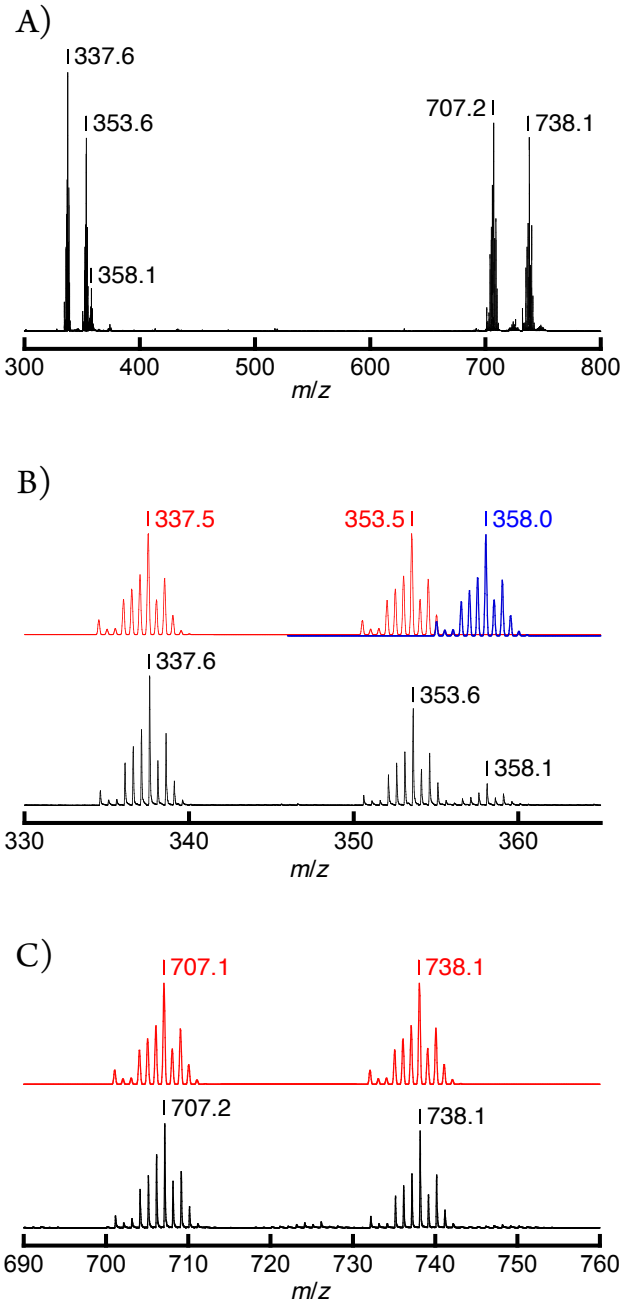

Fig. S2. ESI-TOF-MS spectrum of **2** in MeCN and the simulation (upper coloured spectra in (B) and (C)). The *m*/*z* range: A) 300 — 800, B) 330 — 370, and C) 690 — 760.

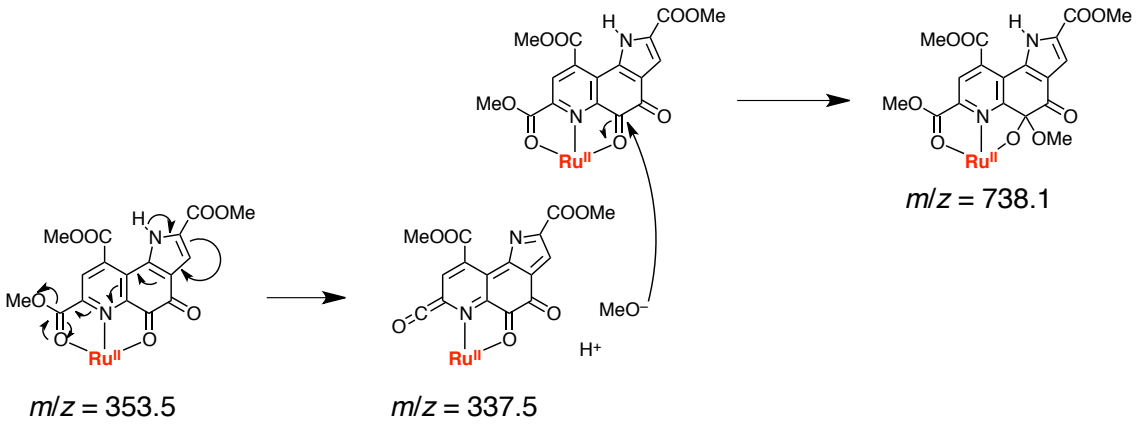

Fig. S3. A proposed reaction mechanism for the formation of fragments observed in ESI-TOF-MS spectra. The cleavage between the oxygen atom of the methoxy group and the carbon atom of the carbonyl group at 7'-position of the PQQTME can form a putative ketene (m/z = 337.5) and the subsequent nucleophilic attack of a methoxide ion toward the carbonyl group of 5-position of the PQQTME ligand of another molecule to afford the methoxide adduct (m/z = 738.1), occurring upon ionization for ESI-TOF-MS measurements.

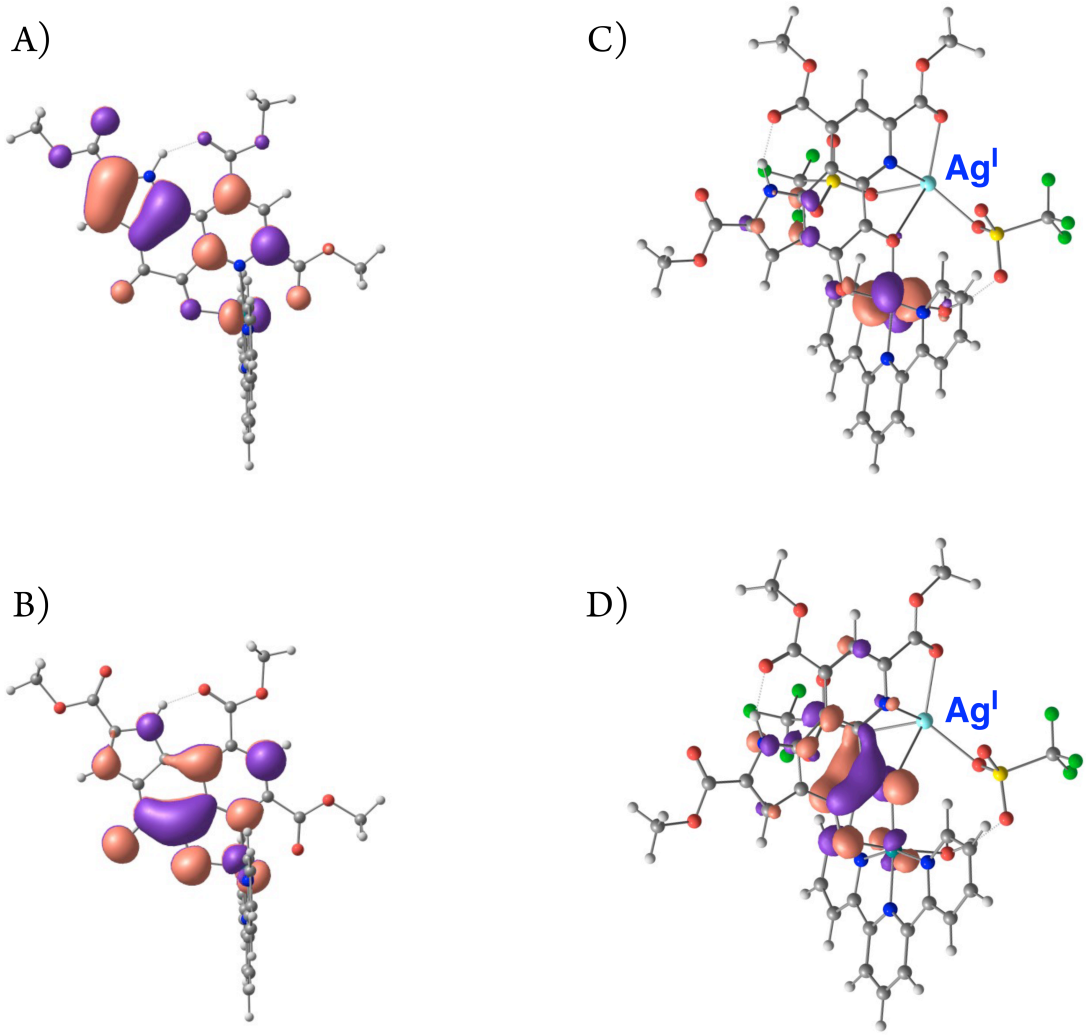

Fig. S4. The frontier orbitals of **2** and **5** calculated at the B3LYP level. HOMO (A) and LUMO (B) of **2**, and HOMO (C) and LUMO (D) of **5**.

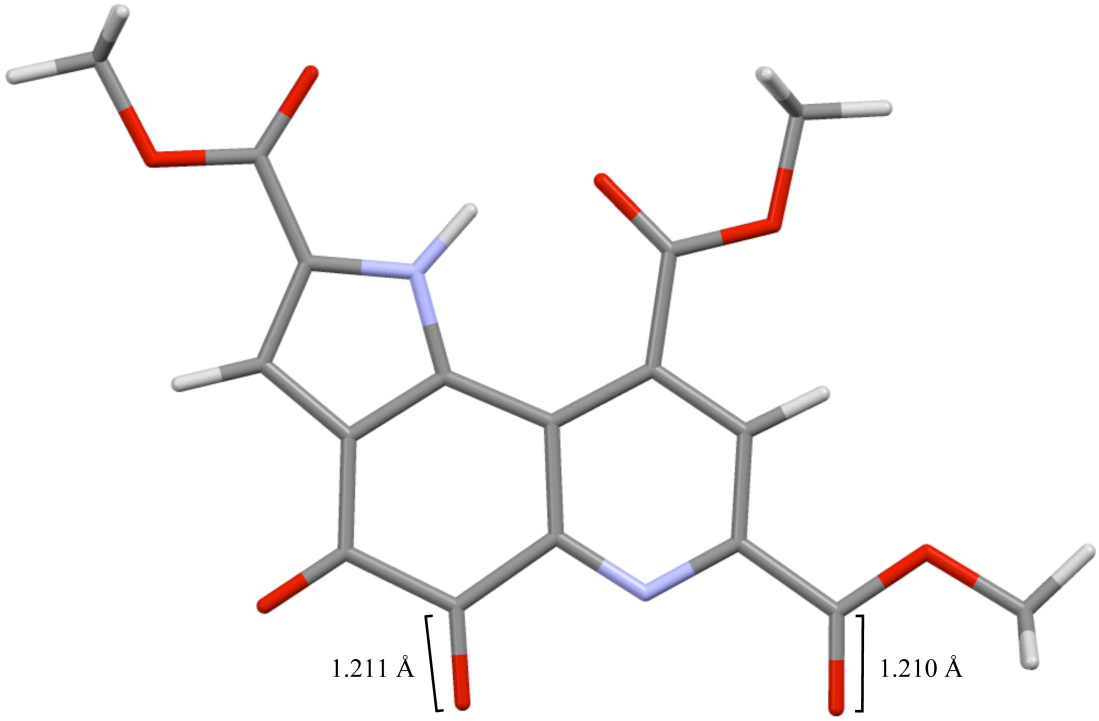

Fig. S5. The optimized structure of PQQTME molecule at the B3LYP level.

Table S1. Selected bond lengths (Å) and angles (°) of **3**

Ru1–O1	1.984(6)	Ru2–O9	1.996(6)
Ru1–N2	2.099(8)	Ru2–N8	2.096(8)
Ru1–N3	2.089(8)	Ru2–N9	2.074(7)
Ru1–N4	1.978(8)	Ru2–N10	1.970(7)
Ru1–N5	2.067(9)	Ru2–N11	2.082(8)
Ru1–N6	2.034(9)	Ru2–N12	2.020(9)
O1–Ru1–N2	78.3(3)	O9–Ru2–N8	77.4(3)
O1–Ru1–N3	92.9(3)	O9–Ru2–N9	94.1(3)
O1–Ru1–N4	90.3(3)	O9–Ru2–N10	91.6(3)
O1–Ru1–N5	87.6(3)	O9–Ru2–N11	91.8(3)
O1–Ru1–N6	176.9(3)	O9–Ru2–N12	176.5(3)
N2–Ru1–N3	103.4(3)	N8–Ru2–N9	104.1(3)
N2–Ru1–N4	168.4(3)	N8–Ru2–N10	168.4(3)
N2–Ru1–N5	97.7(3)	N8–Ru2–N11	98.0(3)
N2–Ru1–N6	104.2(3)	N8–Ru2–N12	101.6(3)
N3–Ru1–N4	78.6(3)	N9–Ru2–N10	80.0(3)
N3–Ru1–N5	158.6(3)	N9–Ru2–N11	157.9(3)
N3–Ru1–N6	88.3(3)	N9–Ru2–N12	89.4(3)
N4–Ru1–N5	80.0(3)	N10–Ru2–N11	78.6(3)
N4–Ru1–N6	87.3(3)	N10–Ru2–N12	89.1(3)
N5–Ru1–N6	90.2(3)	N11–Ru2–N12	85.0(3)

Table S2. Cartesian coordinates of [{(terpy)(OH_2)Ru^{II}}(PQQTME){Ag($OTf)_2$}]$^+$ (**1**).

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.295482	-3.026136	-3.748582
C	3.097602	-2.627968	-2.432776
N	2.230668	-1.625905	-2.113935
C	1.567561	-1.001846	-3.094625
C	1.726938	-1.346582	-4.437175
C	2.598889	-2.376815	-4.769300
C	3.818815	-3.227704	-1.286335
N	3.525760	-2.651584	-0.106950
C	4.093202	-3.040961	1.050093
C	5.013255	-4.086986	1.055536
C	5.328376	-4.708488	-0.153382
C	4.731872	-4.279366	-1.338886
C	3.650484	-2.253488	2.225495
N	2.737573	-1.278253	1.960444
C	2.322295	-0.485023	2.955172
C	2.770957	-0.637326	4.265593
C	3.688741	-1.643291	4.549330
C	4.138264	-2.459221	3.510334
Ru	2.184942	-1.213650	-0.057664
O	3.727273	0.191839	-0.422217
O	0.560037	-2.450479	0.290662
C	-0.537206	-1.875346	0.486126
C	-1.771175	-2.483841	0.813044
C	-2.917296	-1.698316	1.089925
C	-2.962422	-0.230568	1.052516
C	-1.740967	0.410938	0.696849
C	-0.521278	-0.383858	0.409029
C	-4.056831	0.639605	1.300158
C	-3.860385	2.015658	1.163180

C	-2.623188	2.513492	0.774560
N	-1.585903	1.719624	0.556110
C	-2.126171	-3.851052	0.948095
C	-3.457988	-3.857781	1.296370
N	-3.907897	-2.563315	1.377990
Ag	0.181718	2.781305	-0.884657
O	-0.505986	1.555859	-2.757981
S	-1.780894	0.766412	-2.650625
C	-2.204547	0.438964	-4.431862
F	-2.403451	1.582189	-5.078081
C	-5.453788	0.215756	1.688342
O	-5.831402	-0.927522	1.878783
C	-2.400543	3.977347	0.506369
O	-1.418371	4.407794	-0.068580
O	0.575600	0.131049	0.149534
C	-4.408960	-4.955246	1.576498
O	-5.565024	-4.753666	1.884968
O	-3.394703	4.730212	0.948461
C	-3.277145	6.145769	0.694450
O	-3.839450	-6.153830	1.448255
C	-4.704055	-7.275891	1.696714
O	-6.268999	1.252300	1.813439
C	-7.633501	0.947901	2.168880
O	-1.551717	-0.582233	-2.071205
O	-2.928419	1.509723	-2.114218
F	-3.302566	-0.306847	-4.508602
F	-1.198685	-0.220647	-5.027313
O	3.786606	1.875348	1.524136
S	2.657115	2.825236	1.285685
O	2.354797	2.953152	-0.177410
C	3.366890	4.481386	1.743907
F	2.454641	5.427674	1.531459
O	1.487086	2.632559	2.153245

F	4.442542	4.735601	1.006314
F	3.704879	4.480508	3.030405
H	3.867650	0.803126	0.368388
H	-4.859621	-2.261453	1.630182
H	-1.492433	-4.713647	0.801493
H	-4.680563	2.698360	1.335269
H	-5.088166	-7.239293	2.719240
H	-4.085795	-8.161326	1.548258
H	-5.543259	-7.269038	0.996681
H	-8.084594	0.310613	1.405140
H	-8.139411	1.911523	2.219737
H	-7.664532	0.438611	3.134641
H	0.892336	-0.203884	-2.801885
H	1.164607	-0.805617	-5.190141
H	2.742930	-2.671997	-5.804962
H	3.990280	-3.825496	-3.982088
H	4.977605	-4.757422	-2.280372
H	6.042765	-5.526360	-0.171616
H	5.480382	-4.413926	1.977596
H	4.866937	-3.238948	3.703182
H	4.062768	-1.786781	5.559266
H	2.410028	0.040089	5.032662
H	1.636631	0.315640	2.693396
H	3.493336	0.802800	-1.138873
H	-4.173441	6.593845	1.122183
H	-2.377813	6.537205	1.175393
H	-3.225708	6.326857	-0.381715

Table S3. Cartesian coordinates of $[Ru^{II}(terpy)(PQQTME)]^{2+}$ (**2**).

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.297768	-0.495262	-0.000266
C	2.302381	0.548528	-0.000117
C	0.954705	0.043570	-0.000170
C	0.569959	-1.364757	-0.000501
C	1.644978	-2.449085	-0.000684
C	2.999274	-1.894915	-0.000480
C	2.415956	1.985282	0.000200
C	1.245237	2.772272	0.000408
C	-0.021659	2.188003	0.000377
N	-0.135614	0.837423	0.000097
Ru	-1.920121	-0.008810	0.000051
N	-2.315264	-0.175062	2.062538
C	-3.484691	-0.829759	2.355205
C	-3.880928	-1.042068	3.679739
C	-3.076226	-0.581328	4.726801
C	-1.886552	0.088333	4.418613
C	-1.547308	0.267968	3.076140
C	-4.271407	-1.277003	1.184623
N	-3.704181	-0.952477	-0.000033
C	-4.271588	-1.276413	-1.184757
C	-5.488399	-1.969411	-1.214048
C	-6.095502	-2.315866	-0.000187
C	-5.488203	-1.970022	1.213758
C	-3.485070	-0.828589	-2.355252
N	-2.315609	-0.173996	-2.062457
C	-1.547820	0.269519	-3.075968
C	-1.887253	0.090486	-4.418476
C	-3.076948	-0.579070	-4.726796
C	-3.881486	-1.040309	-3.679823

C	-1.356648	2.833668	0.000553
O	-1.363600	4.142655	0.000541
O	-0.657188	-1.659612	-0.000505
O	1.339514	-3.630031	-0.000811
O	-2.396768	2.127767	0.000560
C	-2.655219	4.829648	0.000600
H	-0.630316	0.781865	-2.801493
H	-1.228386	0.467516	-5.195253
H	-3.373977	-0.739845	-5.760059
H	-4.808471	-1.561776	-3.895387
H	-5.957510	-2.238862	-2.154458
H	-7.038739	-2.855580	-0.000244
H	-5.957156	-2.239966	2.154106
H	-4.807902	-1.563598	3.895200
H	-3.373103	-0.742546	5.760039
H	-1.227563	0.464986	5.195469
H	-0.629824	0.780395	2.801750
H	1.335543	3.852581	0.000652
C	3.729044	2.732169	0.000401
N	4.662458	-0.393784	-0.000042
C	4.218266	-2.598181	-0.000677
H	-2.406683	5.890308	0.000605
H	-3.215549	4.556228	-0.896747
H	-3.215475	4.556200	0.897985
C	5.231642	-1.628459	-0.000394
O	4.833519	2.208022	0.000616
O	3.551195	4.051941	0.000521
C	4.761484	4.866269	0.000902
H	4.408727	5.897690	0.000945
H	5.351580	4.652066	0.895238
H	5.351995	4.652281	-0.893211
C	6.720183	-1.726526	-0.000363
O	7.424403	-0.733191	-0.000079

O	7.124079	-2.996421	-0.000625
C	8.562867	-3.205399	-0.000579
H	8.695298	-4.287557	-0.000825
H	9.004810	-2.756784	-0.894290
H	9.004695	-2.757204	0.893400
H	5.159503	0.506760	0.000274
H	4.355041	-3.671039	-0.001126

Table S4. Cartesian coordinates of $[Ru^{II}(terpy)(PQQTME)(H_2O)]^{2+}$ (**5**).

Atom	Coordinates (Angstroms)		
	X	Y	Z
N	3.103431	2.569284	-0.021324
C	2.422561	1.405125	-0.006217
C	1.032157	1.757516	-0.007123
C	0.939044	3.183731	-0.023803
C	2.240596	3.648685	-0.032244
C	2.942217	0.033682	0.007787
C	1.948477	-1.004119	0.022855
C	0.516304	-0.660020	0.022248
C	0.044924	0.751131	0.005552
N	2.192488	-2.317486	0.036027
C	3.458994	-2.723963	0.036410
C	4.527052	-1.811333	0.022682
C	4.296605	-0.426387	0.008025
O	-1.222764	0.917694	0.008786
Ru	-2.330853	-0.810124	0.017218
O	-0.396515	-1.530049	0.039994
C	5.528089	0.459389	-0.006545
O	6.648386	-0.252248	-0.005984
C	7.897025	0.498577	-0.019383
C	3.675237	-4.227645	0.051788
O	4.983579	-4.521749	0.053135
C	5.314196	-5.935284	0.067279
C	2.826058	5.016718	-0.050600
O	1.878424	5.958912	-0.060311
C	2.357414	7.330574	-0.079643
N	-2.675942	-0.717216	-2.048148
C	-3.860543	-0.106781	-2.371630
C	-4.262798	0.028798	-3.703664
C	-3.446543	-0.469450	-4.725834

C	-2.242952	-1.096660	-4.385211
C	-1.897139	-1.198586	-3.034679
C	-4.659219	0.369946	-1.219355
N	-4.100317	0.083268	-0.017671
C	-4.675427	0.443742	1.156655
C	-5.893542	1.134228	1.153972
C	-6.493719	1.439926	-0.074793
C	-5.877742	1.058154	-1.273747
C	-3.897506	0.027036	2.346688
N	-2.725950	-0.634775	2.074718
C	-1.967160	-1.070674	3.099209
C	-2.320657	-0.870653	4.436584
C	-3.509002	-0.188893	4.723803
C	-4.304899	0.261285	3.663877
O	-3.221396	-2.797450	-0.029600
O	2.766671	-5.029500	0.061281
O	5.523930	1.684829	-0.017552
O	4.029783	5.198760	-0.055645
H	-3.776613	-3.078303	0.715176
H	4.138157	2.604410	-0.023961
H	0.041553	3.786131	-0.029692
H	5.542516	-2.185063	0.023049
H	2.963130	7.528646	0.808720
H	1.459316	7.949128	-0.084185
H	2.956231	7.505753	-0.977454
H	7.948755	1.115673	-0.919762
H	8.681217	-0.258507	-0.016570
H	7.958109	1.132066	0.868940
H	-0.973013	-1.681679	-2.728715
H	-1.579438	-1.504573	-5.142224
H	-3.748678	-0.372795	-5.765586
H	-5.203927	0.512147	-3.945863
H	-6.341061	1.297509	-2.225219

H	-7.438761	1.975938	-0.097826
H	-6.369377	1.431346	2.082753
H	-5.232748	0.787345	3.865063
H	-3.814618	-0.013329	5.752190
H	-1.673452	-1.243449	5.225220
H	-1.053009	-1.594699	2.832937
H	-2.566416	-3.501653	-0.170122
H	6.403897	-5.978004	0.065760
H	4.906834	-6.405914	0.966172
H	4.903564	-6.424571	-0.820078

Table S5. Cartesian coordinates of $[Ru^{II}(PQQTME^{\bullet-})(terpy)]^{1+}$ (**2**$^{\bullet-}$).

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.271581	-0.464590	-0.000037
C	2.285730	0.583052	0.000068
C	0.926645	0.060814	0.000020
C	0.535412	-1.322790	-0.000106
C	1.562958	-2.384738	-0.000210
C	2.934856	-1.852691	-0.000176
C	2.411457	2.012167	0.000185
C	1.252788	2.825481	0.000259
C	-0.011180	2.237521	0.000226
N	-0.143620	0.894330	0.000103
Ru	-1.944089	0.032274	0.000024
N	-2.291319	-0.169501	2.055129
C	-3.447736	-0.845909	2.353387
C	-3.822349	-1.088967	3.680136
C	-3.006385	-0.643222	4.723397
C	-1.825285	0.040577	4.409622
C	-1.509424	0.252485	3.066603
C	-4.237390	-1.292725	1.186447
N	-3.682454	-0.939807	-0.000071
C	-4.237423	-1.292436	-1.186659
C	-5.433638	-2.019500	-1.213757
C	-6.034517	-2.379287	-0.000214
C	-5.433606	-2.019795	1.213400
C	-3.447804	-0.845329	-2.353512
N	-2.291382	-0.168989	-2.055120
C	-1.509521	0.253256	-3.066512
C	-1.825423	0.041682	-4.409575
C	-3.006529	-0.642046	-4.723484
C	-3.822457	-1.088056	-3.680310

C	-1.333004	2.896816	0.000298
O	-1.326737	4.218291	0.000351
O	-0.738399	-1.630121	-0.000202
O	1.293254	-3.590278	-0.000372
O	-2.387817	2.219445	0.000275
C	-2.613437	4.891209	0.000400
H	-0.598345	0.771652	-2.782672
H	-1.153215	0.401880	-5.182879
H	-3.284742	-0.828213	-5.757644
H	-4.740034	-1.625846	-3.896644
H	-5.888400	-2.309634	-2.155238
H	-6.961489	-2.946080	-0.000270
H	-5.888340	-2.310160	2.154823
H	-4.739920	-1.626808	3.896365
H	-3.284566	-0.829647	5.757519
H	-1.153052	0.400579	5.182996
H	-0.598254	0.770947	2.782864
H	1.348397	3.902970	0.000348
C	3.726991	2.737882	0.000241
N	4.641897	-0.391588	-0.000041
C	4.136951	-2.586572	-0.000261
H	-2.377341	5.955545	0.000443
H	-3.179507	4.617497	-0.894185
H	-3.179480	4.617418	0.894977
C	5.174231	-1.649186	-0.000174
O	4.837231	2.222435	0.000266
O	3.570185	4.072142	0.000225
C	4.791149	4.850288	0.000265
H	4.467359	5.892232	0.000235
H	5.382925	4.626792	0.892194
H	5.383003	4.626765	-0.891604
C	6.646882	-1.801415	-0.000200
O	7.412729	-0.850838	-0.000069

O	7.013300	-3.093743	-0.000292
C	8.437038	-3.337153	-0.000273
H	8.545536	-4.422970	-0.000357
H	8.897928	-2.902087	-0.892137
H	8.897882	-2.902230	0.891684
H	5.158210	0.491048	0.000063
H	4.238185	-3.662405	-0.000371

Table S6. Cartesian coordinates of [{Ru^{II}(terpy)(OH_2)}(PQQTME$^{\bullet-}$){Ag($OTf)_2$}] (**5**$^{\bullet-}$).

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.025150	-4.297495	-3.573251
C	0.850680	-3.859035	-2.256747
N	0.628501	-2.536251	-1.974739
C	0.587935	-1.648755	-2.983537
C	0.771607	-2.019972	-4.317738
C	0.986361	-3.368767	-4.618223
C	0.902072	-4.747004	-1.078678
N	0.730652	-4.087798	0.098611
C	0.755980	-4.733773	1.294912
C	0.957365	-6.117928	1.338943
C	1.132845	-6.818999	0.138444
C	1.105888	-6.131558	-1.082224
C	0.555658	-3.832514	2.447061
N	0.375124	-2.512256	2.125101
C	0.195081	-1.615881	3.110231
C	0.180359	-1.979950	4.459696
C	0.358534	-3.324543	4.800373
C	0.550174	-4.260642	3.778457
Ru	0.424736	-2.154456	0.066067
O	2.505457	-1.763644	0.204953
O	-1.634802	-2.268904	-0.032456
C	-2.191695	-1.097156	-0.068772
C	-3.608288	-0.900225	-0.114742
C	-4.168862	0.410366	-0.148859
C	-3.372570	1.614878	-0.144764
C	-1.927995	1.402388	-0.137429
C	-1.360317	0.063052	-0.069447
C	-3.797822	2.983126	-0.134260
C	-2.831251	3.996048	-0.164899

C	-1.470549	3.671018	-0.216659
N	-1.037721	2.411402	-0.193981
C	-4.671925	-1.835403	-0.137334
C	-5.844949	-1.087023	-0.188583
N	-5.529407	0.248101	-0.194340
Ag	1.381171	2.021345	-0.355567
O	3.625150	-0.604050	-1.914609
S	3.286784	0.481967	-2.890143
C	4.746513	1.665896	-2.741321
F	4.849407	2.132415	-1.487751
C	-5.229689	3.448720	-0.096222
O	-6.231438	2.763390	-0.263083
C	-0.409529	4.736113	-0.304111
O	0.781301	4.509044	-0.433594
O	-0.070183	-0.137478	-0.011325
C	-7.262435	-1.488632	-0.239382
O	-8.190433	-0.695250	-0.285615
O	-0.924568	5.975365	-0.228287
C	0.037362	7.051631	-0.301237
O	-7.405611	-2.831433	-0.228779
C	-8.765090	-3.304333	-0.277989
O	-5.323720	4.768169	0.142080
C	-6.662407	5.307441	0.176439
O	3.261929	0.079487	-4.309544
O	2.106685	1.321077	-2.471331
F	4.582121	2.707476	-3.573209
F	5.887505	1.038364	-3.062266
O	2.954712	-0.300890	2.396354
S	2.586891	1.134046	2.633541
O	2.850016	2.030523	1.460179
C	3.875195	1.698736	3.883919
F	3.686497	2.990503	4.193627
O	1.284708	1.338907	3.313562

F	5.112521	1.549345	3.394203
F	3.769265	0.971542	5.010310
H	2.721594	-1.197858	0.995030
H	-6.185004	1.030635	-0.254724
H	-4.594962	-2.912860	-0.121177
H	-3.130768	5.033759	-0.156348
H	-9.330119	-2.942881	0.587027
H	-8.695797	-4.393939	-0.263157
H	-9.258654	-2.962537	-1.193234
H	-7.160063	5.155932	-0.785942
H	-6.537723	6.371488	0.384941
H	-7.247941	4.824026	0.963773
H	0.439208	-0.610858	-2.702821
H	0.778280	-1.252342	-5.084441
H	1.141098	-3.690962	-5.644936
H	1.203536	-5.348513	-3.778505
H	1.246663	-6.665579	-2.016353
H	1.293437	-7.893620	0.154331
H	0.982557	-6.642164	2.288791
H	0.699943	-5.309583	4.014535
H	0.359668	-3.640969	5.840752
H	0.051341	-1.206801	5.210947
H	0.093563	-0.576499	2.817457
H	2.898539	-1.313072	-0.591676
H	-0.546440	7.969540	-0.212299
H	0.760180	6.969324	0.515667
H	0.569824	7.020336	-1.256486

Table S7. Cartesian coordinates of PQQTME.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-1.066050	-2.998417	0.000156
C	0.479541	-2.865525	-0.000105
C	1.104029	-1.467512	-0.000060
C	0.313031	-0.264537	-0.000068
C	-1.137588	-0.467799	-0.000090
C	-1.781042	-1.731872	0.000052
C	1.054980	0.960513	-0.000017
C	2.457706	0.890411	0.000012
C	3.106515	-0.344690	-0.000014
H	3.042137	1.798939	0.000052
N	2.431337	-1.496112	-0.000046
O	-1.591185	-4.101143	0.000408
O	1.170785	-3.859378	-0.000338
C	-3.177681	-1.514624	0.000048
H	-3.948661	-2.272275	0.000143
N	-2.125454	0.468959	-0.000227
H	-1.938843	1.477711	-0.000412
C	-3.358599	-0.136207	-0.000155
C	-4.569577	0.703875	-0.000300
O	-4.543967	1.924871	-0.000219
O	-5.695344	-0.036622	0.000114
C	4.613784	-0.452354	0.000017
C	0.473533	2.352253	-0.000003
O	-0.712708	2.656267	-0.000442
O	5.232826	-1.492526	0.000060
O	1.425997	3.297740	0.000325
O	5.191134	0.774342	0.000030
C	-6.928895	0.710760	0.000349
H	-7.722324	-0.038661	0.000675

H	-6.992797	1.342092	0.892288
H	-6.993287	1.341836	-0.891735
C	0.959236	4.665982	0.000195
H	0.357074	4.860928	0.892291
H	1.863917	5.275794	0.000528
H	0.357702	4.860972	-0.892316
C	6.633415	0.773206	0.000083
H	7.014087	0.264486	-0.891143
H	6.927460	1.824571	0.000095
H	7.014022	0.264484	0.891335
