Supplementary Information

Cobalt Porphyrins as Homogeneous Catalysts for Water Oxidation

Takashi Nakazono,[a] Alexander Rene Parent,[a,b] and Ken Sakai* [a,b,c]

[a] *Department of Chemistry, Faculty of Sciences, Kyushu University,*
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
[b] *International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University,*
Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan
[c] *International Research Center for Molecular Systems (IRCMS), Kyushu University,*
Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

Experimental Details

Materials

All solvents and reagents were of the highest quality available and were used as received. **TCPP** (*meso*-tetrakis(4-carboxyphenyl)porphyrin) and **TPPS** (*meso*-tetrakis(4-sulfophenyl)porphyrin) were purchased from Tokyo Chemical Industry Co., Ltd. and were used as received. **TPyP** (*meso*-Tetrakis(4-pyridyl)porphyrin) was preapared as previously described.[1] $[Ru^{II}(bpy)_3](NO_3)_2 \cdot 3H_2O$ was prepared as previously described.[2]

CoTMPyP [[*meso*-tetra(4-N-methylpyridyl)porphyrinato]cobalt(II)]$(PF_6)_4 \cdot 4H_2O$ [3]

TPyP (0.20 g, 0.178 mmol) and $Co(CH_3CO_2)_2 \cdot 4H_2O$ (0.20 g, 0.7 mmol) were dissolved in DMF (dimethylformamide) (20 mL). The reaction mixture was refluxed for 3.5 h, followed by cooling to room temperature. CH_3I (5 mL) was added dropwise to the solution and the reaction mixture was further refluxed for 6.5 h. After cooling to room temperature, the volatiles were removed by evaporation, and the residue was re-dissolved in water (30 mL). Addition of a saturated $NaPF_6$ solution (ca. 5 mL) caused deposition of a purple solid, which was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield 0.20 mg (0.14 mmol, 85 %). Elemental analysis of **CoTMPyP** calcd. (%) for $C_{44}H_{36}N_8P_4F_{24}Co \cdot 4H_2O$ (1387.7): C 38.08, H 3.20, N 8.08; found: C 38.12, H 2.99, N 8.01.

CoTCPP [[*meso*-tetra(4-carboxyphenyl)porphyrinato]cobalt(III)]$Cl \cdot 7H_2O$ [4]

$CoCl_2 \cdot 6H_2O$ (0.090 g, 6 mmol), and **TCPP** (0.090 g, 1 mmol) were dissolved in DMSO (25 mL), followed by refluxing for 24 h. After the solution was cooled to room temperature, 1 M HCl (ca. 75 mL) was added to the solution to cause deposition of the crude product as a purple solid, which was collected by filtration, washed with water, and dried in vacuo. This was redissolved in 0.1 M NaOH (ca. 20 mL) followed by addition of 1 M HCl (ca. 40), which caused deposition of the product as a purple solid. This was collected by filtration and dried in vacuo. Yield 0.090 mg (0.089 mmol, 89 %). Elemental analysis of **CoTCPP** calcd. (%) for $C_{48}H_{28}N_4O_8ClCo \cdot 7H_2O$ (1009.3): C 57.12, H 4.19 N 5.55. Found: C 56.71, H 3.89, N 5.54.

CoTPPS [[*meso*-tetra(4-sulfonatophenyl)porphyrinato]cobalt(III)]$\cdot 9H_2O$ [3,5]

$CoCl_2 \cdot 6H_2O$ (0.090 g, 6 mmol), and **TPPS** (0.090 g, 1 mmol) were dissolved in water (25 mL). After adjusting the pH at 7.5 by adding 1 M NaOH, the solution was refluxed for 24 h and allowed to cool to room temperature. The solution was then filtered for the removal of insoluble materials. The filtrate was then passed through a column containing a Dowex 50W-X8 cation-exchange resin in the H^+ form (50-100-mesh) in order to remove residual Co^{3+} in the reaction mixture. To the resultant solution was added four volume equivalents of acetone to ppt. the **CoTPPS** as a purple solid, which was collected by filtration, washed with acetone and diethyl ether, and dried in vacuo. Yield 0.060 g (0.05 mmol, 50 %). Elemental analysis of **CoTPPS** calcd. (%) for $C_{44}H_{27}N_4O_{12}S_4Co \cdot 9H_2O$ (1153.0): C 45.83, H 3.93, N 4.86. Found: C 45.62, H 3.92, N 4.82.

UV-Visible Measurements

UV-Visible absorption spectra were recorded on a Shimadzu UV2450SIM spectrophotometer. All the sample solutions were maintained at 20 °C during the spectrophotometric measurements.

Oxygen Production

Photochemical oxygen production from water was analyzed by using an automatic H_2/O_2 monitoring system developed in our group. In this system, continuous flow of Ar (10.0 mL/min, controlled by a STEC SEC-E40/PAC-D2 digital mass flow controller) was bubbled through a photolysis solution (10 mL) contained in a Pyrex vial (*ca.* 20 mL). The vent gas from the vial was introduced into a valve which allowed the automatic injection of the sample gas onto a gas chromatograph (Shimadzu GC-8A equipped with a molecular sieve 5 Å column of 2 m × 3 mm *i.d.*, at 30 ºC). The injection of the sample gas was controlled by a control software operating on a Windows system and the output signal from the thermal conductivity detector of the gas chromatograph was analyzed in a Shimadzu C-R8A integrator which was also controlled within the same control program. Photolysis solutions were degassed with Ar for at least 30 min prior to the photolysis. Photoirradiation was performed using an ILC Technology CERMAX LX-300 300 W Xe lamp equipped with a CM-1 cold mirror ($400 < \lambda < 800$ nm). The photolysis vial was immersed in a 20 ºC water bath to remove IR radiation and to eliminate temperature effects.

General Procedure for Dynamic Light Scattering Analysis

Dynamic light scattering (DLS) experiments were carried out using a ELSZ-2 (Otsuka Electronics Co. Ltd. Japan). A He laser operating at 660 nm was used. The DLS measurements were carried out for a 0.1 M phosphate buffer solution at pH = 11 containing 10 μM catalyst, 1 mM $[Ru^{II}(bpy)_3](NO_3)_2$, and 5.0 mM $Na_2S_2O_8$.

Stopped-Flow Measurements

A UNISOKU USP-SFM-S20 stopped-flow system was employed, for which dead time spent for mixing was ca. 3 ms and minimum spectral recording interval was 1 ms. Spectra were recorded on a UNISOKU Polychromator PK120 equipped with a 512 element photodiode array detector, which allowed rapid scanning with a 150 W Xe lamp equipped with a HOYA L-37 interference filter eliminating the lights below 370 nm. The reaction was initiated by mixing equal volumes of a 5 μM **CoTPPS** solution and a 50 μM $Ru^{III}(bpy)_3^{3+}$ solution. Both contained acetate buffer (0.1 M, pH 5) to maintain pH. The $Ru^{III}(bpy)_3^{3+}$ solution contained an additional electrolyte (0.1 M $NaNO_3$) remaining from the bulk electrolysis of $Ru^{II}(bpy)_3(NO_3)_2$ at 1.2 V vs. SCE. All these experiments were carried out at 5 ˚C under Ar atmosphere.

General Procedure for ESI-MS Measurements

ESI-TOF mass spectra were recorded on a JEOL JMS-T100LC mass spectrometer in positive ion mode.

DFT Calculations

Geometries were optimized at the B3LYP level of DFT using the LanL2DZ basis set for Co and the 6-31G** basis set for H, C, N, and O with the contribution of water solvation taken into account using the polarizable continuum model (PCM) method implemented in Gaussian 09.[6] Figures were made using GaussView 5.09 and Mercury 3.1.

Table S1. DFT calculated energies for various oxidation and spin states of Co oxyl (or oxo) porphyrins.

	Total Energy not Corrected for Zero Point Energy (hartrees)	Sum of Electronic and Zero Point Energy (hartrees)	Zero Point Energy (hartrees)	Relative Energies (kcal/mol)	Table Number
Co(III) Oxyl Doublet	-1208.671884	-1208.393624	0.27826	-	S2
Co(III) Oxyl Hextet	-1208.666565	-1208.393224	0.273341	+0.25[a]	S3
Co(IV) Oxyl Triplet	-1208.472596	-1208.197099	0.275497	-	S4
Co(V) Oxo Singlet	-1208.433897	-1208.155748	0.278149	+24.95[b]	S5

[a] Relative to the calculated energy of the Co(III) oxyl doublet.

[b] Relative to the calculated energy of the Co(IV) oxyl triplet.

As shown, the Co(III) oxyl species may exist as either a doublet or hextet in solution, however upon oxidation to a Co(IV) oxyl only the triplet state is energetically accessible.

Table S2. DFT calculated cartesian coordinates, charge densities, and spin densities for the Co(III) oxyl doublet ($\mathrm{Co^{III}}$-O•) (formally [Co(IV)(O)(porphyrin)]). Atoms with localized spin density are highlighted.

Atom	x	y	z	Charge Densities	Spin Densities
Co1	-0.000022	0.000003	0.049496	0.657439	-0.655453
N2	1.995229	0.006469	-0.118847	-0.576181	0.044116
N3	-1.995252	-0.006504	-0.118838	-0.576178	0.044119
N4	0.006598	-1.984436	-0.106116	-0.588939	0.055822
N5	-0.006562	1.984479	-0.106064	-0.586462	0.054332
C6	4.214448	-0.666318	-0.103036	-0.13194	-0.000727
C7	1.087551	2.825387	-0.091482	0.286963	-0.009875
C8	2.835568	-1.085375	-0.10285	0.286611	-0.009893
C9	2.828224	1.103937	-0.103718	0.286118	-0.01002
C10	-0.694208	4.197822	-0.088176	-0.131006	0.000438
C11	-2.828229	-1.103967	-0.103724	0.286599	-0.009892
C12	-2.835572	1.085354	-0.102846	0.286137	-0.010022
C13	2.412377	2.424159	-0.08956	-0.193722	0.027492
C14	-0.666404	-4.202298	-0.08869	-0.130845	0.000498
C15	-1.106201	2.81816	-0.090703	0.286947	-0.009877
C16	-1.087513	-2.825375	-0.091498	0.287729	-0.01007
C17	-4.214455	0.666296	-0.103047	-0.131796	-0.000632
C18	2.428396	-2.408288	-0.088151	-0.193767	0.027386
C19	0.694237	-4.197799	-0.088148	-0.130827	0.000496
C20	1.106227	-2.818141	-0.090715	0.287714	-0.010071
C21	4.209872	0.694148	-0.10364	-0.131777	-0.000633
C22	0.666447	4.202316	-0.088714	-0.131019	0.000439
C23	-4.209878	-0.694176	-0.103659	-0.131922	-0.000729
C24	-2.42838	2.408284	-0.08815	-0.193722	0.027496
C25	-2.412354	-2.424174	-0.089567	-0.193771	0.027384
O26	-0.000068	0.000025	1.78892	-0.279585	1.431294
H27	3.174188	3.195975	-0.078464	0.12732	-0.001239
H28	3.195217	-3.175116	-0.076422	0.127405	-0.001237
H29	-3.195202	3.17511	-0.076437	0.127322	-0.001239
H30	-3.174148	-3.196007	-0.078468	0.127405	-0.001237
H31	5.059857	-1.341347	-0.105002	0.121013	0.000204
H32	-1.374625	5.038837	-0.091026	0.121899	0.000186
H33	-1.341206	-5.047807	-0.092029	0.121934	0.000174
H34	-5.059864	1.341326	-0.10502	0.121028	0.000204
H35	1.374653	-5.038815	-0.09097	0.121934	0.000174
H36	5.050705	1.374885	-0.106164	0.121029	0.000204
H37	1.341255	5.047822	-0.092078	0.121898	0.000186
H38	-5.05071	-1.374914	-0.106198	0.121014	0.000204

Table S3. DFT calculated cartesian coordinates, charge densities, and spin densities for the Co(III) oxyl hextet (Co^{III}-O•) (formally [Co(IV)(O)(porphyrin)]). Atoms with localized spin density are highlighted.

Atom	x	y	z	Charge Densities	Spin Densities
Co1	0.000079	0.000063	0.487992	0.7481	1.565774
N2	-0.202483	-2.04795	-0.097246	-0.585629	0.178795
N3	0.202393	2.047994	-0.097226	-0.585627	0.178792
N4	-2.048255	0.202443	-0.09708	-0.588138	0.078962
N5	2.04827	-0.202521	-0.097002	-0.584741	0.078915
C6	-1.091655	-4.170398	-0.260571	-0.127716	-0.001794
C7	2.750566	-1.361616	-0.16336	0.269165	0.012055
C8	-1.361667	-2.750335	-0.163472	0.28362	-0.079783
C9	0.814711	-2.969847	-0.160084	0.283065	-0.07908
C10	4.307362	0.266391	-0.257418	-0.143643	0.090744
C11	-0.814769	2.969866	-0.160099	0.283602	-0.079796
C12	1.361611	2.750323	-0.163482	0.283091	-0.079063
C13	2.171683	-2.652289	-0.170401	-0.165426	0.360992
C14	-4.170649	1.091569	-0.260902	-0.143418	0.092795
C15	2.970081	0.814742	-0.160445	0.269153	0.011999
C16	-2.750601	1.361555	-0.16335	0.270416	0.011772
C17	1.091601	4.170391	-0.26062	-0.127544	-0.002557
C18	-2.652406	-2.17165	-0.170827	-0.165719	0.362312
C19	-4.307376	-0.266469	-0.25739	-0.143396	0.092859
C20	-2.97009	-0.814812	-0.160481	0.270405	0.011706
C21	0.26637	-4.307165	-0.256656	-0.127518	-0.002531
C22	4.170619	-1.091653	-0.26096	-0.143661	0.090691
C23	-0.266435	4.307183	-0.256699	-0.12769	-0.001765
C24	2.652378	2.171611	-0.170875	-0.165436	0.361014
C25	-2.171727	2.652269	-0.170371	-0.165711	0.362297
O26	0.000125	0.000101	2.173471	-0.35871	1.464859
H27	2.864189	-3.487292	-0.226117	0.136091	-0.015639
H28	-3.487288	-2.864305	-0.226551	0.136115	-0.015698
H29	3.487277	2.864241	-0.226684	0.13609	-0.01564
H30	-2.864258	3.487253	-0.226062	0.136119	-0.015697
H31	-1.843343	-4.945031	-0.333509	0.124743	0.000043
H32	5.21616	0.849055	-0.328511	0.111351	-0.004585
H33	-4.94525	1.84325	-0.334259	0.11148	-0.004677
H34	1.843298	4.945011	-0.3336	0.12477	0.000075
H35	-5.216177	-0.849135	-0.328422	0.111482	-0.004679
H36	0.849026	-5.215998	-0.327344	0.124771	0.000075
H37	4.945201	-1.843345	-0.334385	0.111349	-0.004583
H38	-0.849078	5.216021	-0.327433	0.124746	0.000042

Table S4. DFT calculated cartesian coordinates, charge densities, and spin densities for the Co(IV) oxyl triplet (Co^{IV}-O•) (formally [Co(V)(O)(porphyrin)]$^{+}$). Atoms with localized spin density are highlighted.

Atom	x	y	z	Charge Densities	Spin Densities
Co1	0.000007	-0.000002	0.154738	0.795892	1.483593
N2	0.005519	1.979537	-0.014845	-0.580615	-0.121328
N3	-0.005525	-1.979486	-0.015252	-0.580621	-0.121289
N4	2.014548	-0.006688	-0.224944	-0.57984	-0.144492
N5	-2.014562	0.006748	-0.224837	-0.577292	-0.1433
C6	0.686333	4.186888	0.008447	-0.10999	-0.000993
C7	-2.84483	1.089559	-0.204503	0.292213	0.070493
C8	1.093436	2.808626	-0.023737	0.293787	0.068736
C9	-1.095887	2.817767	-0.00274	0.293408	0.068846
C10	-4.2309	-0.676318	-0.2792	-0.110301	-0.003127
C11	1.095878	-2.817697	-0.002942	0.293778	0.068767
C12	-1.093438	-2.808556	-0.02393	0.29343	0.06881
C13	-2.414795	2.415207	-0.093845	-0.129438	-0.277991
C14	4.225977	-0.685462	-0.259754	-0.110158	-0.003091
C15	-2.853375	-1.091828	-0.229298	0.292195	0.070521
C16	2.844825	-1.089482	-0.204579	0.292828	0.070379
C17	-0.686332	-4.186822	0.008492	-0.109925	-0.001142
C18	2.428796	2.400713	-0.123976	-0.12934	-0.278228
C19	4.230882	0.676405	-0.279154	-0.110133	-0.003129
C20	2.85335	1.091902	-0.229303	0.292814	0.070409
C21	-0.675905	4.192624	0.024502	-0.109899	-0.001178
C22	-4.22598	0.685548	-0.259782	-0.110323	-0.003091
C23	0.675894	-4.192558	0.024545	-0.109963	-0.001039
C24	-2.428814	-2.40065	-0.12404	-0.129438	-0.277991
C25	2.414794	-2.415138	-0.093966	-0.129342	-0.278237
O26	0.000065	-0.000691	1.86388	-0.255479	1.575767
H27	-3.174753	3.188771	-0.084772	0.168384	0.011237
H28	3.184439	3.178527	-0.123925	0.168518	0.011249
H29	-3.184452	-3.178469	-0.123911	0.168387	0.011238
H30	3.174755	-3.188698	-0.084801	0.168518	0.011249
H31	1.367	5.026724	-0.001641	0.144799	-0.000168
H32	-5.076133	-1.350059	-0.304888	0.144654	-0.000239
H33	5.066342	-1.365651	-0.271934	0.144716	-0.000252
H34	-1.367007	-5.026654	-0.001406	0.144804	-0.000166
H35	5.076111	1.350156	-0.30478	0.144715	-0.000251
H36	-1.349533	5.038228	0.0283	0.144803	-0.000165
H37	-5.06634	1.365743	-0.272004	0.144653	-0.000241
H38	1.349527	-5.038158	0.028533	0.144802	-0.000166

Table S5. Cartesian coordinates and charge densities for the Co(V) oxo singlet (Co^{V}=O) (formally [Co(V)(O)(porphyrin)]$^{+}$).

Atom	x	y	z	Charge Densities
Co1	0.000457	-0.030095	0.030195	0.769015
N2	1.994745	0.007666	-0.109294	-0.56171
N3	-1.991899	-0.030405	-0.107558	-0.558294
N4	0.017753	-1.983642	-0.065797	-0.576016
N5	-0.018402	1.98768	-0.15347	-0.55162
C6	4.23085	-0.649607	-0.19181	-0.090174
C7	1.083963	2.833998	0.016376	0.311739
C8	2.847727	-1.088541	-0.177032	0.310904
C9	2.808416	1.085982	-0.051528	0.321022
C10	-0.702748	4.197627	-0.077486	-0.108936
C11	-2.815302	-1.093934	-0.000717	0.315138
C12	-2.834317	1.074471	-0.219974	0.311311
C13	2.385811	2.429609	0.054554	-0.159932
C14	-0.650808	-4.21603	-0.00577	-0.089432
C15	-1.090131	2.802508	-0.198422	0.318178
C16	-1.086077	-2.834402	0.020417	0.315592
C17	-4.221441	0.646299	-0.196338	-0.090716
C18	2.443024	-2.391997	-0.186419	-0.158529
C19	0.698865	-4.196544	-0.120697	-0.108223
C20	1.09474	-2.803839	-0.13332	0.319417
C21	4.205764	0.702144	-0.10833	-0.110687
C22	0.643711	4.215339	0.061662	-0.091027
C23	-4.209567	-0.699801	-0.045387	-0.1089
C24	-2.432634	2.376919	-0.301178	-0.158489
C25	-2.389619	-2.438121	0.088624	-0.156781
O26	-0.009739	0.157028	1.729772	-0.471785
H27	3.154982	3.187775	0.146346	0.162198
H28	3.199125	-3.167226	-0.230052	0.162651
H29	-3.194985	3.143521	-0.378729	0.162507
H30	-3.154079	-3.202043	0.170405	0.163807
H31	5.083219	-1.311977	-0.251678	0.152531
H32	-1.393886	5.028523	-0.107255	0.149467
H33	-1.317849	-5.066051	0.03001	0.153489
H34	-5.068114	1.313439	-0.280284	0.152401
H35	1.387841	-5.027485	-0.179312	0.150089
H36	5.033065	1.397674	-0.085136	0.148921
H37	1.303079	5.06331	0.183973	0.151886
H38	-5.04357	-1.384676	0.01776	0.148986

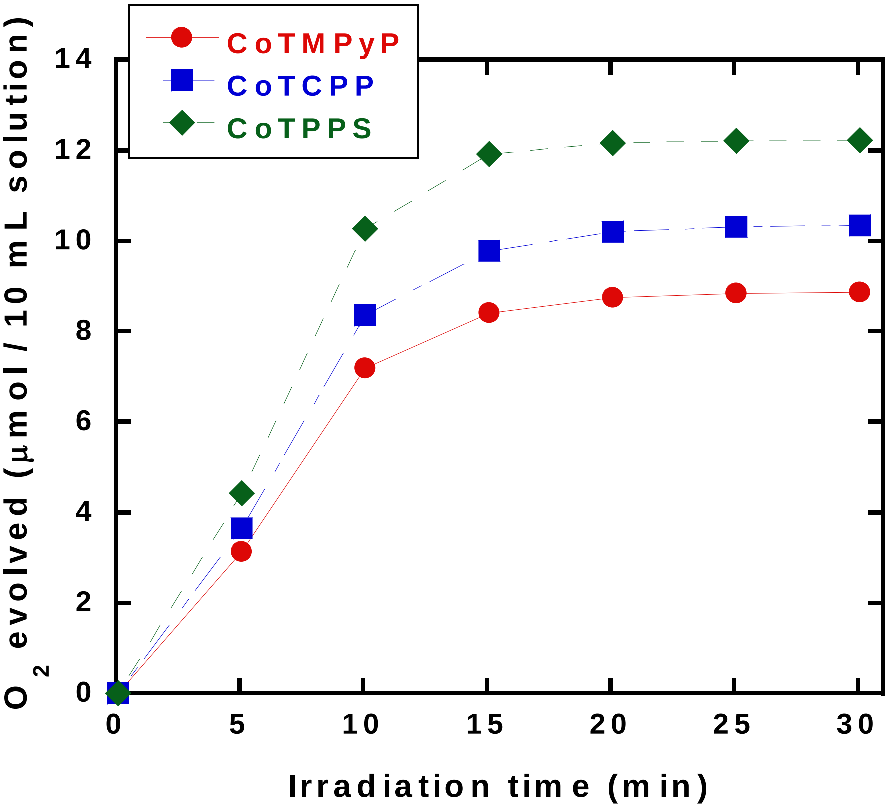

Figure S1. Photo-initiated O_2 production from an aqueous 0.1 M phosphate buffer solution (pH = 11; 10 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru^{II}(bpy)_3](NO_3)_2$ (1 mM) catalyzed by: ●, CoTMPyP (10 μM); ■, CoTcPP (10 μM) ; ◆, CoTPPS (10 μM) under Ar at 20 °C.

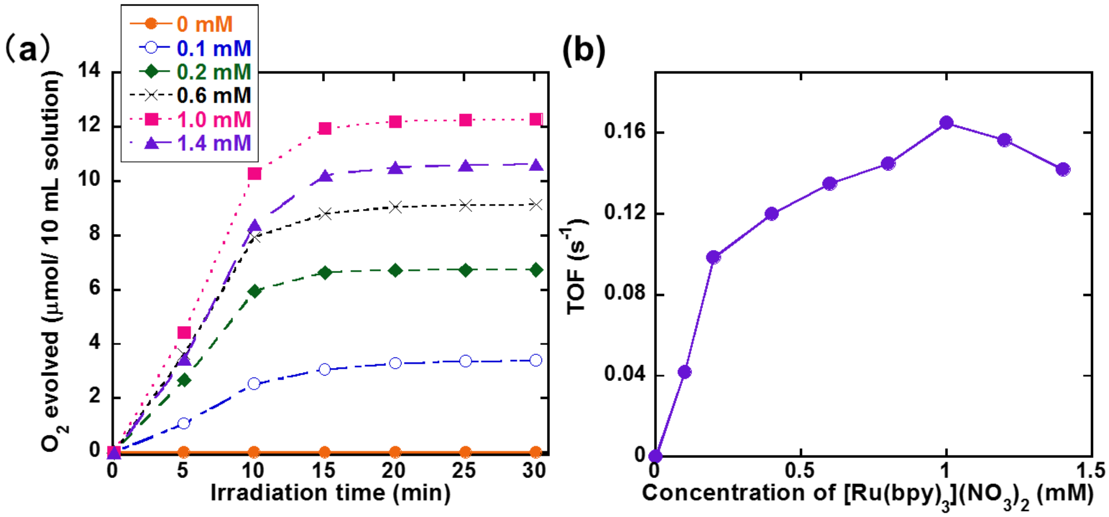

Figure S2. (a) Photo-initiated O_2 production from an aqueous $[Ru^{II}(bpy)_3](NO_3)_2$ solution in 0.1 M pH 11 phosphate buffer containing **CoTPPS** (10 μM) and $Na_2S_2O_8$ (5.0 mM) ($[Ru^{II}(bpy)_3](NO_3)_2$: ●, 0 mM; □, 0.1 mM ;◆, 0.2 mM; ×, 0.6 mM; ■, 1.0 mM; ▲, 1.4 mM). (b) TOF as a function of the concentration of $[Ru^{II}(bpy)_3](NO_3)_2$.

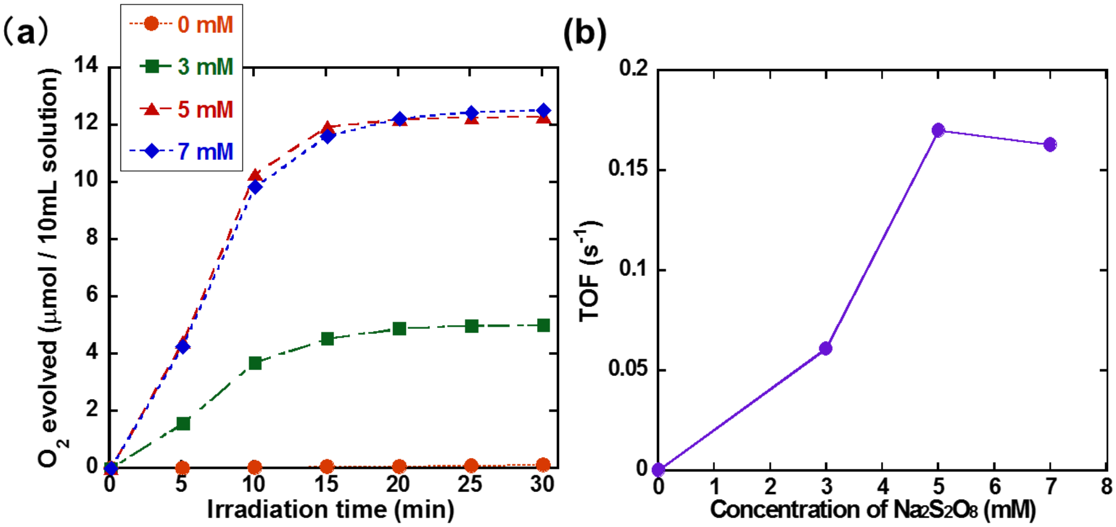

Figure S3. (a) Photo-initiated O_2 production from an aqueous $Na_2S_2O_8$ solution in 0.1 M pH 11 phosphate buffer containing **CoTPPS** (10 μM) and $[Ru^{II}(bpy)_3](NO_3)_2$ (1 mM) ($Na_2S_2O_8$ concentration: ●, 0 mM; ■, 3 mM; ▲, 5 mM; ◆, 7 mM).

(b) TOF as a function of the concentration of $Na_2S_2O_8$.

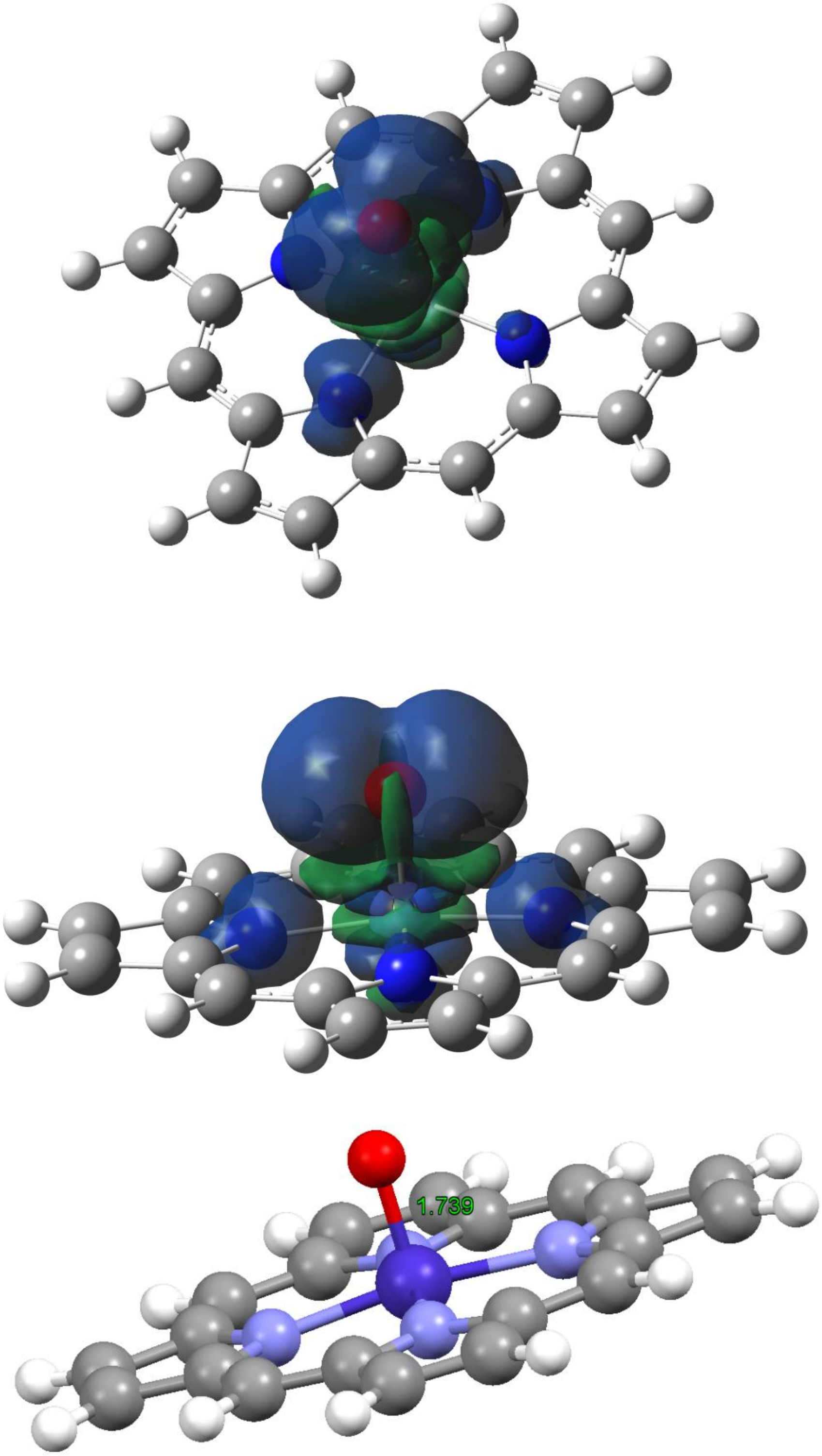

Figure S4. DFT calculated spin-densities (top and middle) and structure (bottom) of a Co(III) oxyl (Co^{III}-O•) porphyrin doublet (formally [Co(IV)(O)(porphyrin)]) using coordinates in Table S2. Selected bond lengths: Co-O 1.739 Å; Co-N 1.991, 2.002, 1.991, 2.002 Å.

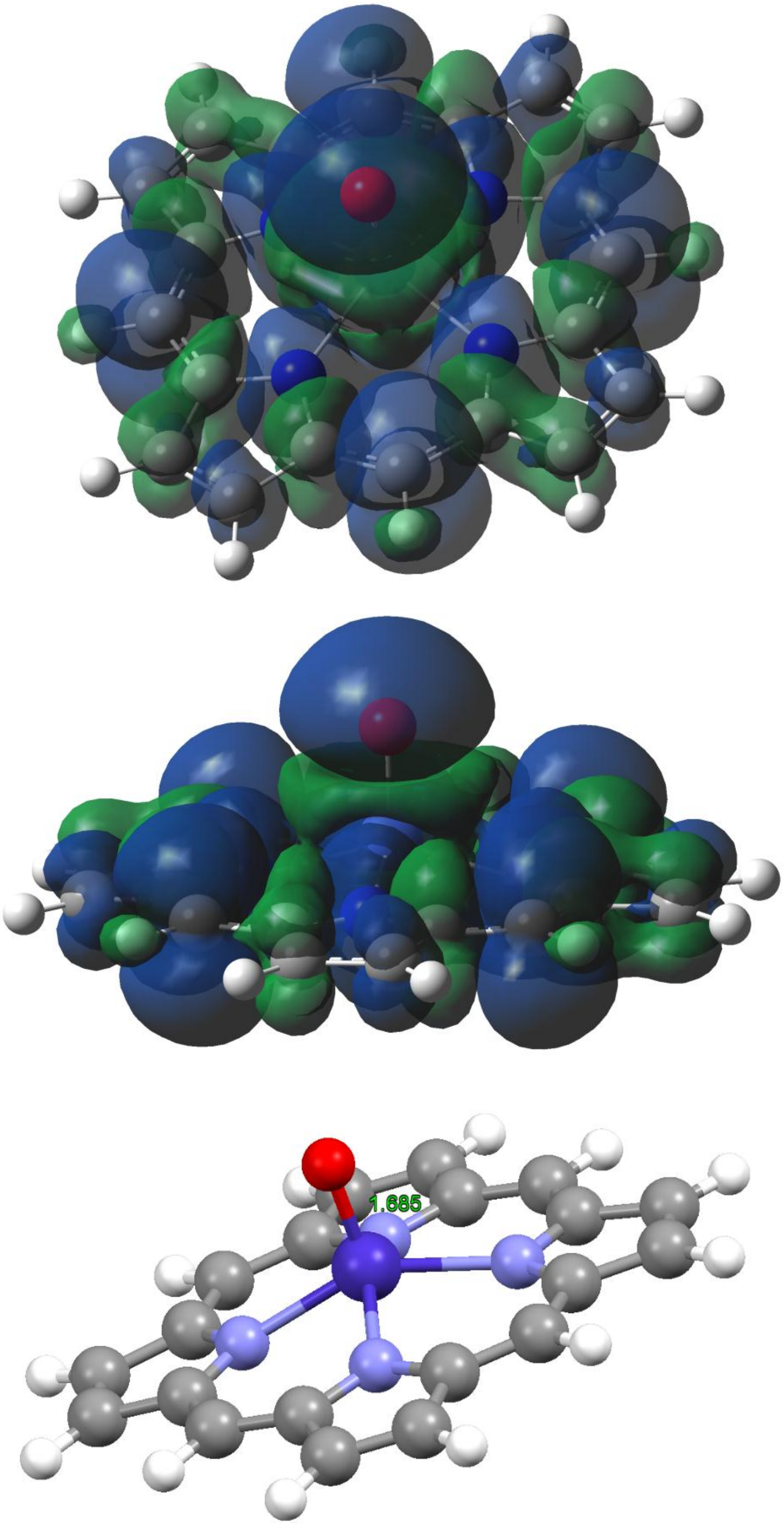

Figure S5. DFT calculated spin-densities (top and middle) and structure (bottom) of a Co(III) oxyl (Co^{III}-O•) porphyrin hextet (formally [Co(IV)(O)(porphyrin)]) using coordinates in Table S3. Selected bond lengths: Co-O 1.685 Å; Co-N 2.140, 2.140, 2.140, 2.139 Å.

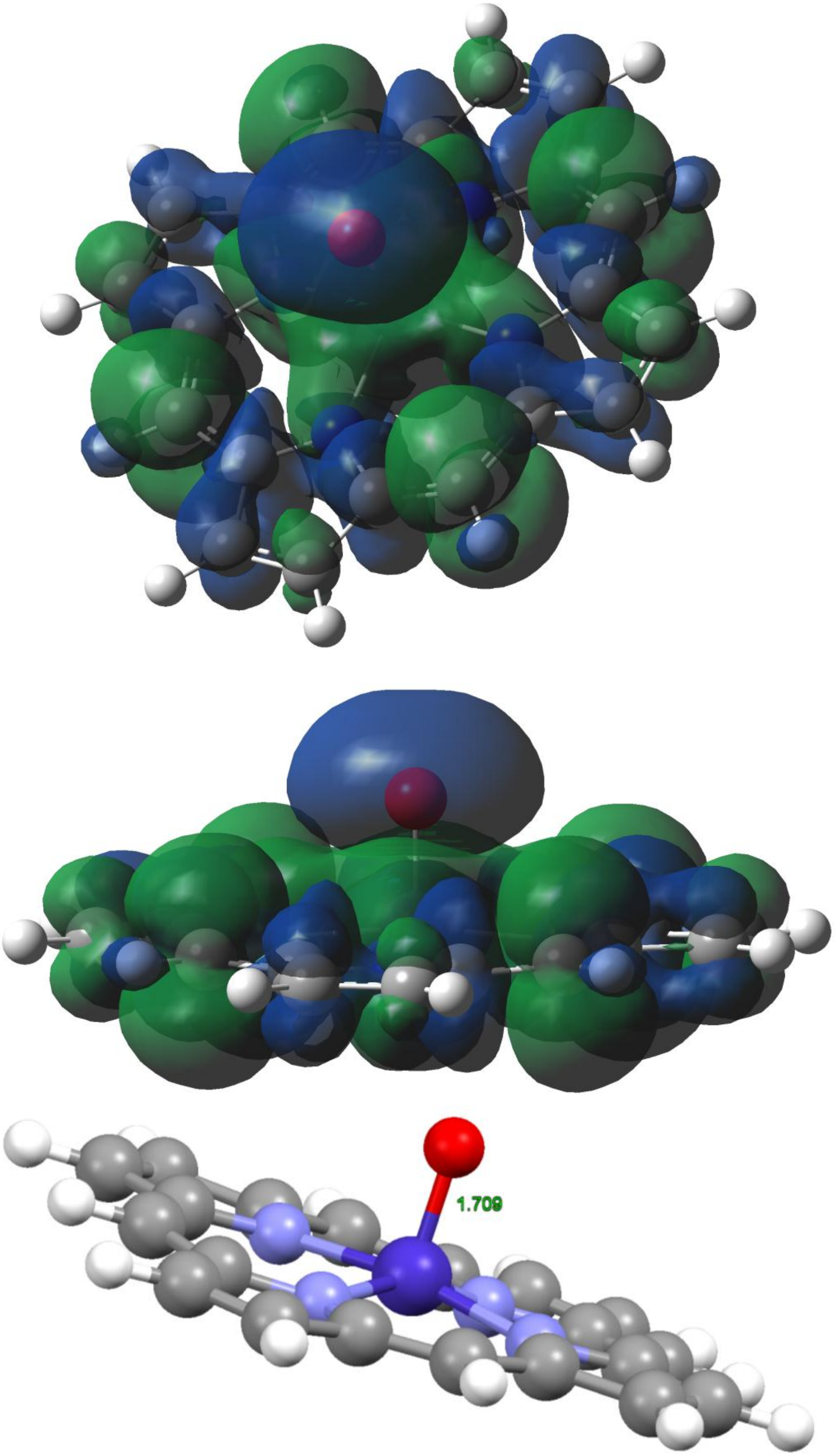

Figure S6. DFT calculated spin-densities (top and middle) and structure (bottom) of a Co(IV) oxyl (Co^{IV}-O•) porphyrin triplet (formally [Co(V)(O)(porphyrin)]) using coordinates in Table S4. Selected bond lengths: Co-O 1.709 Å; Co-N 1.987, 2.050, 1.987, 2.050 Å.

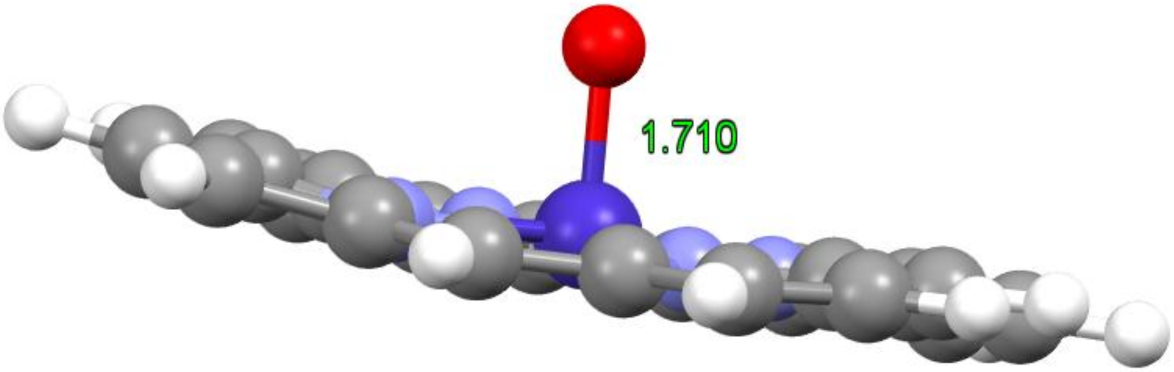

Figure S7. DFT calculated structure of a Co(V) oxo (Co^V=O) porphyrin singlet (formally [Co(V)(O)(porphyrin)]) using coordinates in Table S5. Selected bond lengths: Co-O 1.710 Å; Co-N 1.956, 1.997, 2.026, 2.000 Å.

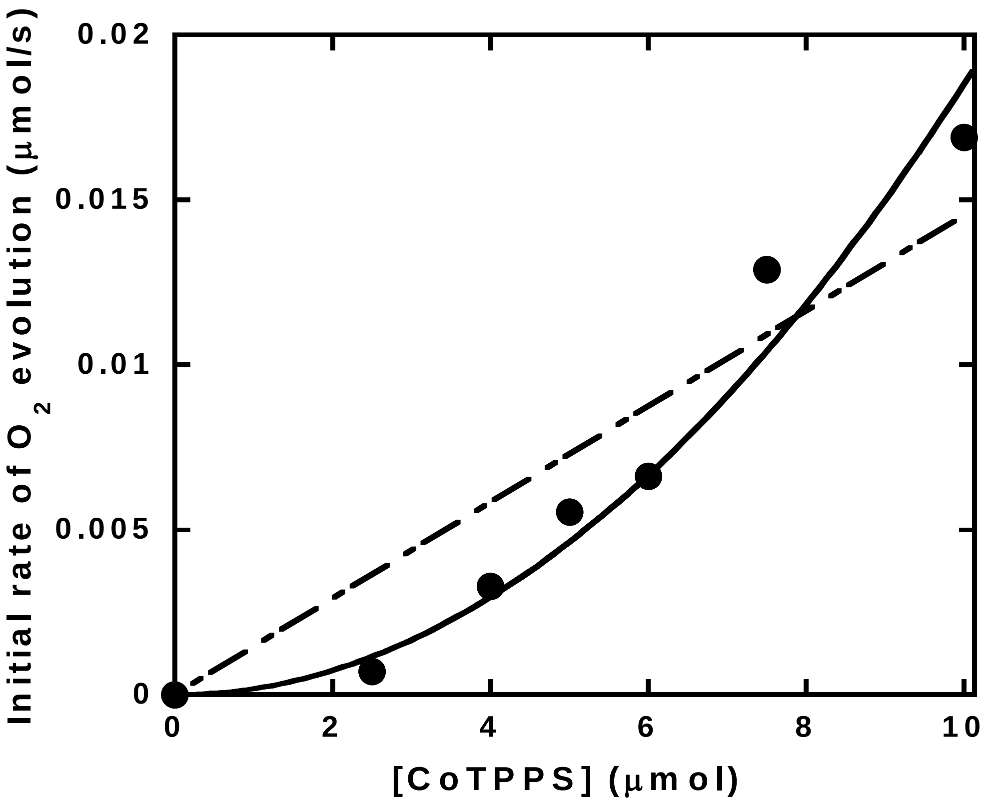

Figure S8. First (dashed) and second (solid) order fitting of the rate data shown in Fig. 3, showing the second order model better fits the observed data. First order $R^2 = 0.865$, second order $R^2 = 0.958$.

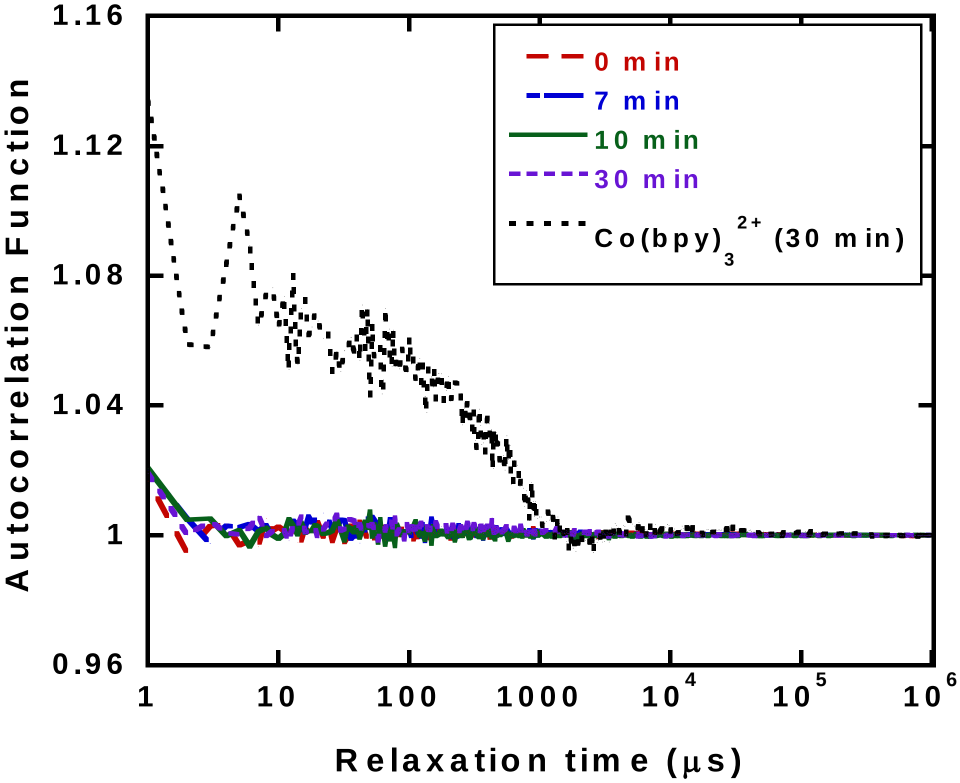

Figure S9. Autocorrelation function obtained by DLS measurements of an aqueous **CoTPPS** and $Co^{II}(bpy)_3^{2+}$ (10 μM) in 0.1 M pH 11 phosphate buffer containing $Na_2S_2O_8$ (5.0 mM) and $[Ru^{II}(bpy)_3](NO_3)_2$ (1 mM) under Ar atmosphere.

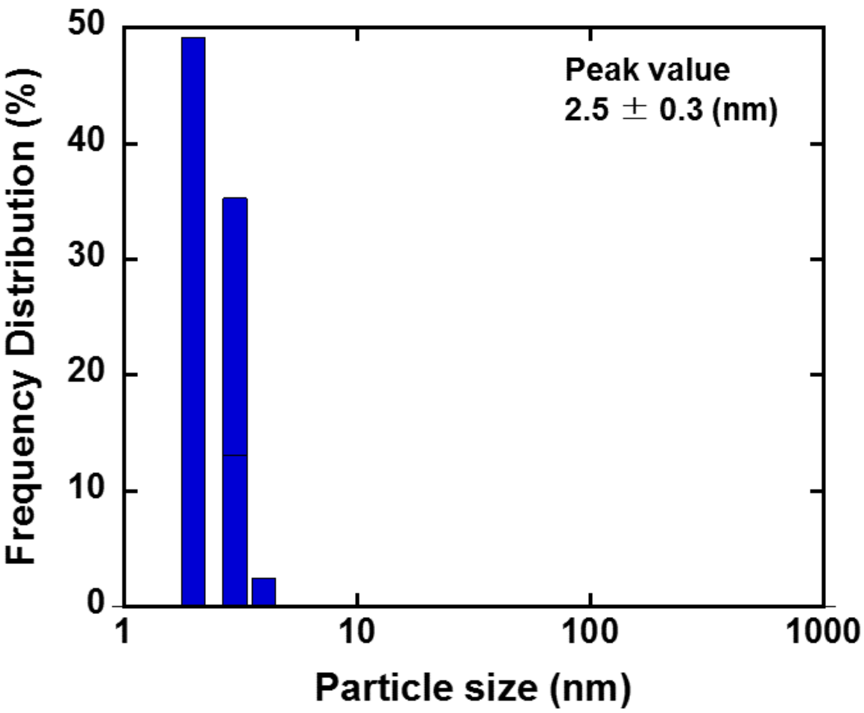

Figure S10. Particle size distribution observed via DLS measurement after 30 min of irradiation by a 300 W Xe lamp on an aqueous $[Co^{II}(bpy)_3](NO_3)_2$ solution (10 μM) in 0.1 M pH 11 phosphate buffer containing $Na_2S_2O_8$ (5.0 mM) and $[Ru^{II}(bpy)_3](NO_3)_2$ (1 mM) under Ar atmosphere.

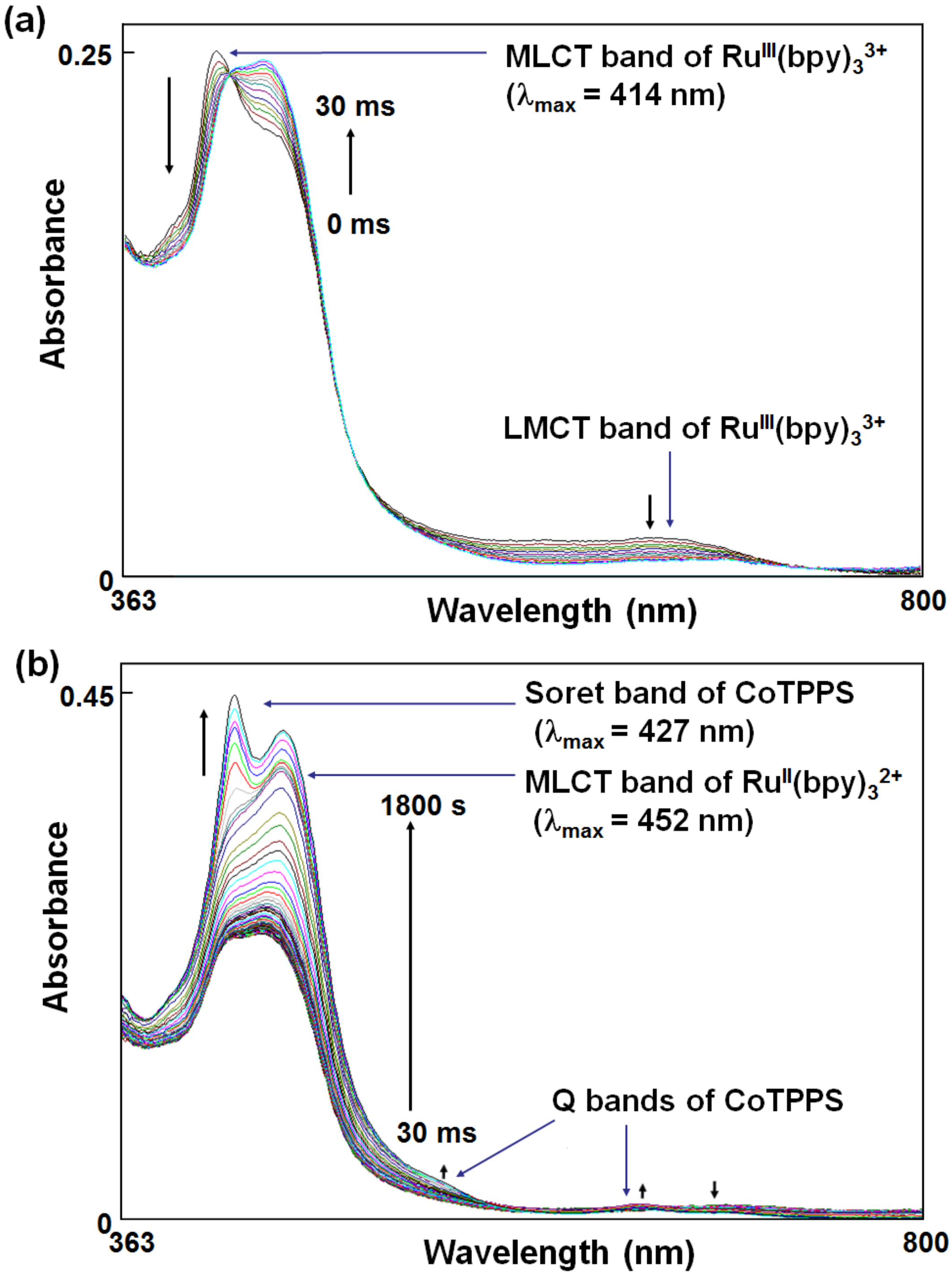

Figure S11. Spectral changes after mixing a 5 µM **CoTPPS** solution and a 50 µM Ru^{III}(bpy)$_3^{3+}$ solution in a stopped-flow apparatus under Ar at 5 °C, pH = 5. (a) Data points from 0 - 30 ms were recorded at 0, 1, 2, 3, 4, 6, 8, 10, 12, 14, 18, 22, 26, and 30 ms. (b) Data points were recorded every 1 ms during 30 - 41 ms, every 2 ms during 41 - 65 ms, and every 4 ms during 65 - 97 ms, recorded at 102 ms, every 8 ms during 102 - 126 ms and every 16 ms during 126 - 190 ms, recorded at 215 ms, and every 40 ms during 215 - 495 ms. Data points from 495 ms - 1800 s (b) were recorded at 0.65, 0.81, 0.97, 1.26, 1.58, 1.90, 2.55, 3.35, 4.15, 4.95, 6.50, 8.10, 12.6, 19.0, 33.5, 49.5, 81.0, 125, 190, 335, 495, 810, 1260, and 1800 s.

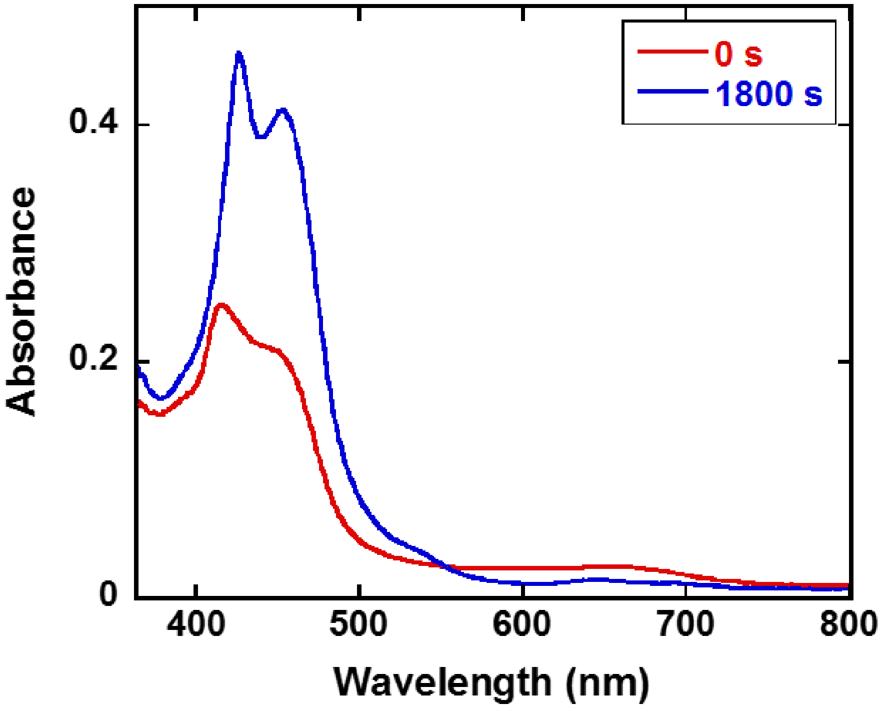

Figure S12. Initial and final spectra after mixing a 5 µM **CoTPPS** solution and a 50 µM $Ru^{III}(bpy)_3^{3+}$ solution in a stopped-flow apparatus taken from Fig. S10, showing the recovery of the Soret and Q bands after completion of the catalysis.

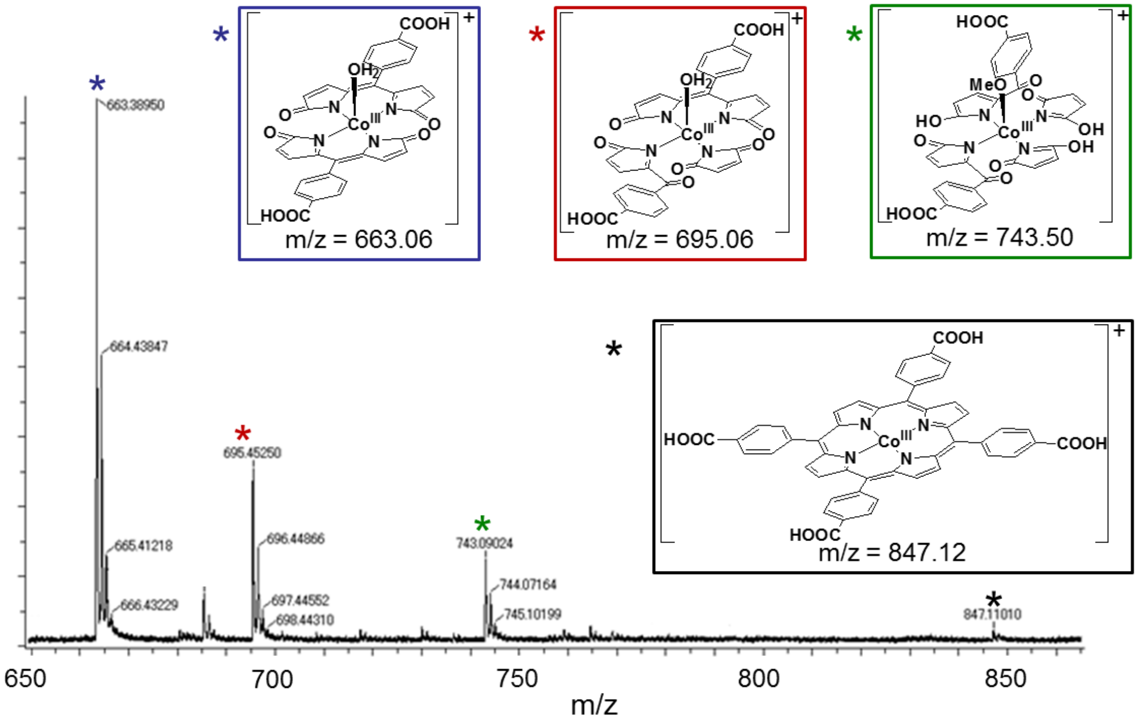

Figure S13. ESI-MS observed for the decomposition products of **CoTCPP** after photolysis. The decomposition products were isolated via acidification by addition of concentrated HCl to the reaction solution after 30 min of irradiation and dissolved in methanol prior to the MS analysis. Insets show possible species responsible for the observed ESI-MS peaks.

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