Supplementary Information

Ambiphilicity of a Mononuclear Cobalt(III) Superoxo Complex

Ting-Yi Chen,[a,c] Po-Hsun Ho,[a] Can-Jerome Spyra,[c] Franc Meyer,*[,c] Eckhard Bill,[d] Shengfa Ye,*[,e,f] and Way-Zen Lee*[,a,b]

[a]*Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan*

[b]*Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan*

[c]*Universität Göttingen, Institut für Anorganische Chemie, Göttingen D-37077, Germany*

[d]*Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr D-45470, Germany*

[e]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

[f]*Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr D-45470, Germany*

*Corresponding author. Email: wzlee@ntnu.edu.tw (W.-Z.L); shengfa.ye@dicp.ac.cn, shengfa.ye@kofo.mpg.de (S.Y.); franc.meyer@chemie.uni-goettingen.de (F.M.)

Contents

Materials and Instrumentation.

All Manipulations were performed under nitrogen or argon condition with standard Schlenk techniques or in a nitrogen-filled glove box. Dichloromethane was dried by CaH_2 under nitrogen atmosphere and was distilled prior to use. THF, Pentane and diethyl ether were dried by sodium/benzophenone under nitrogen atmosphere and distilled prior to use. n-PrCN was dried by $Na_2CO_3/KMnO_4$ and was distilled prior to use. Co^{II}(BDPP), Co^{III}(BDPP)($O_2^{\bullet}$) (**1**), and Co^{III}(BDPP)(OOH) (**3**) were synthesized according to the published procedures.[1] Other chemicals were purchased from commercial sources and used without further purification. UV-vis spectra were recorded with Agilent 8454 spectrophotometer equipped with cryostat from Unisoku Scientific Instruments, Osaka, Japan. X-Band CW EPR measurements were performed in the temperature range of 3.8 to 12 K using a Bruker E500 spectrometer equipped with a Bruker ER 4116DM resonator, Oxford Instruments ESR 935 gas flow cryostat and Oxford Instruments ITC503 temperature controller. Microwave power was in the range of 0.2 to 1 mW. Magnetic field modulation amplitude was 7.5 G.

Preparation of [Co^{III}(BDPP)($O_2^{\bullet}$)···H^+](OTf) (2)

One equiv of HOTf was gradually added into a THF solution of **1** through a microsyringe at −90 °C. The color of the reaction solution changed from marigold to gray-green indicating the formation of [Co^{III}(BDPP)($O_2^{\bullet}$)···H^+](OTf) (**2**).

Computational Details

All calculations were performed by using the ORCA quantum chemical program package.[2] Geometry optimizations and frequency analyses were performed with the B3LYP[3] density functional. The def2-TZVP for the first coordination sphere and def2-SVP basis sets[4] for the remaining atoms were applied in combination with the auxiliary basis sets def2/J.[5] The RIJCOSX[6] approximations were used to accelerate the calculations.

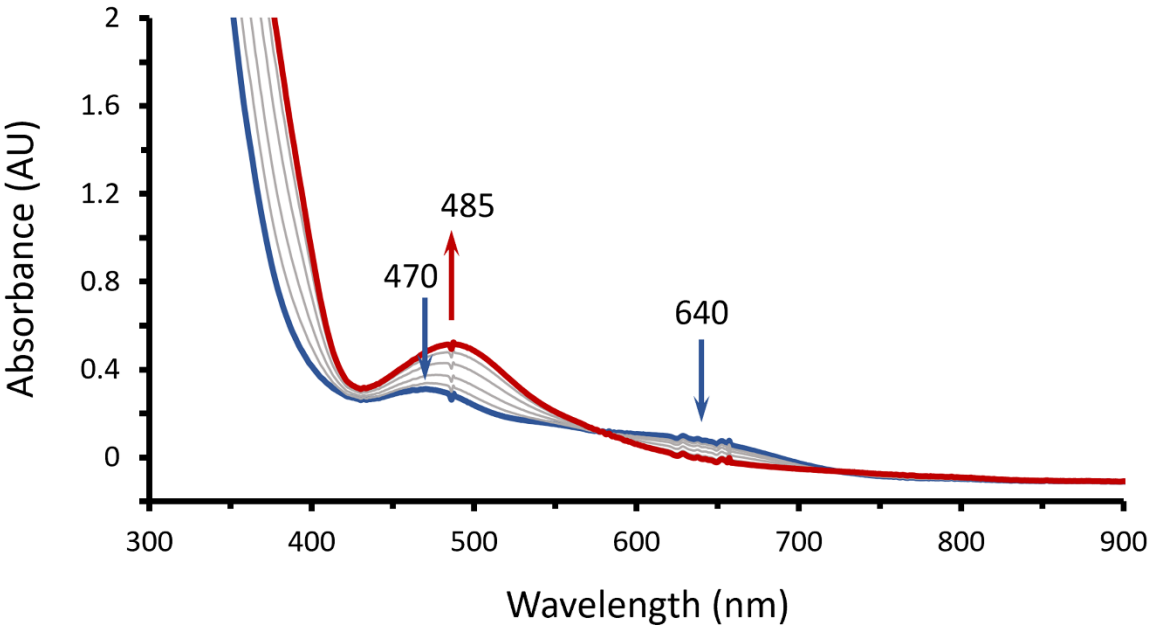

Figure S1. Conversion of [Co^{III}(BDPP)($O_2^{\bullet}$)···H^+](OTf) (**2**, 1.0 mM, blue trace) to Co^{III}(BDPP)($O_2^{\bullet}$) (**1**, red trace) by adding 1 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) into a THF solution of **2** at −90 °C. Two absorption bands at 470 and 640 nm decay with the growth of a band at 485 nm. The conversion yield is 80%.

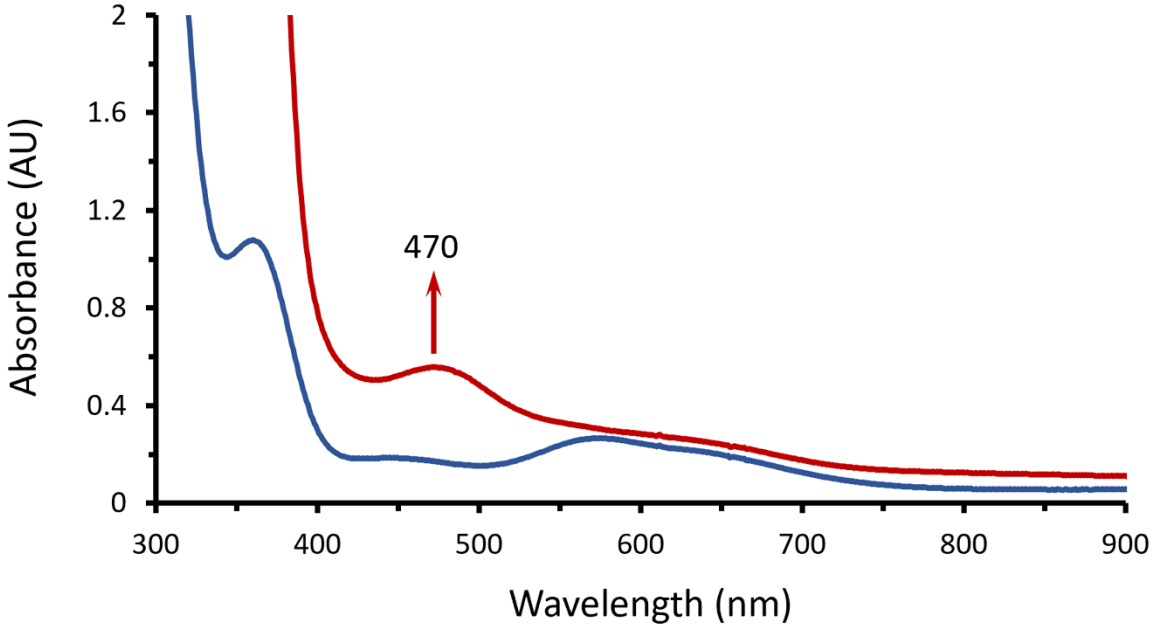

Figure S2. UV-vis spectra of Co^{III}(BDPP)(OOH) (**3**, blue trace) and **2** (red trace) which was converted from the reaction of **3** with 1 equiv of magic blue in n-PrCN (1.0 mM) at −90 °C.

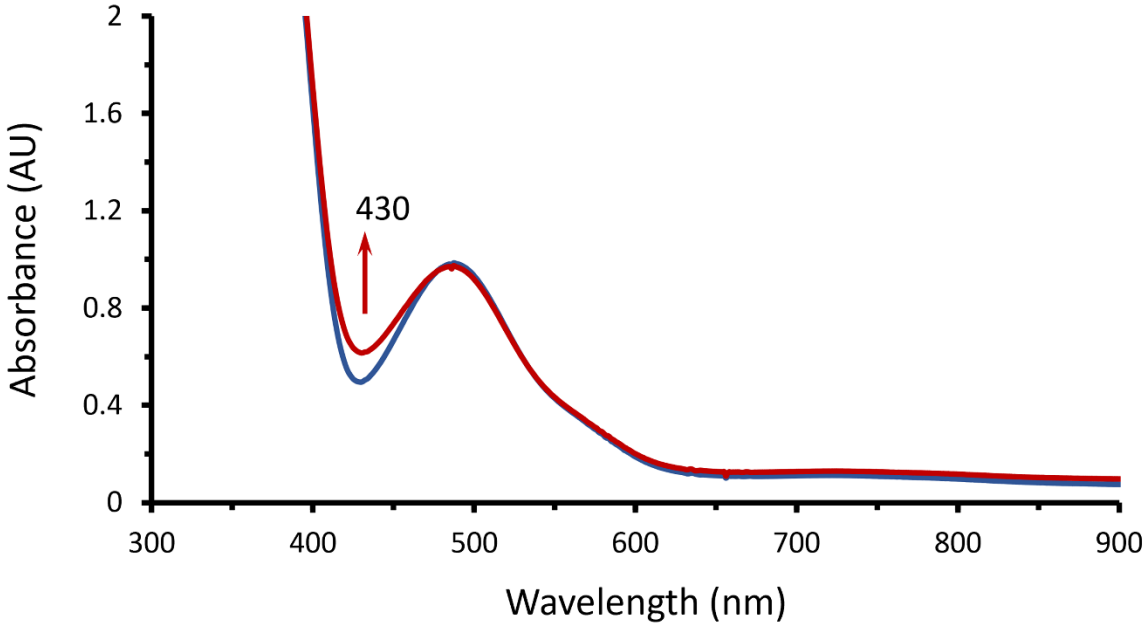

Figure S3. UV-vis spectra of **1** (blue trace) and **1** with addition of 1 equiv of decamethyl-ferrocene (Cp^*_2Fe) (red trace) in THF (1.0 mM) at −90 °C. The absorption band growth at 430 nm is the signal of Cp^*_2Fe indicating **2** cannot be reduced by Cp^*_2Fe.

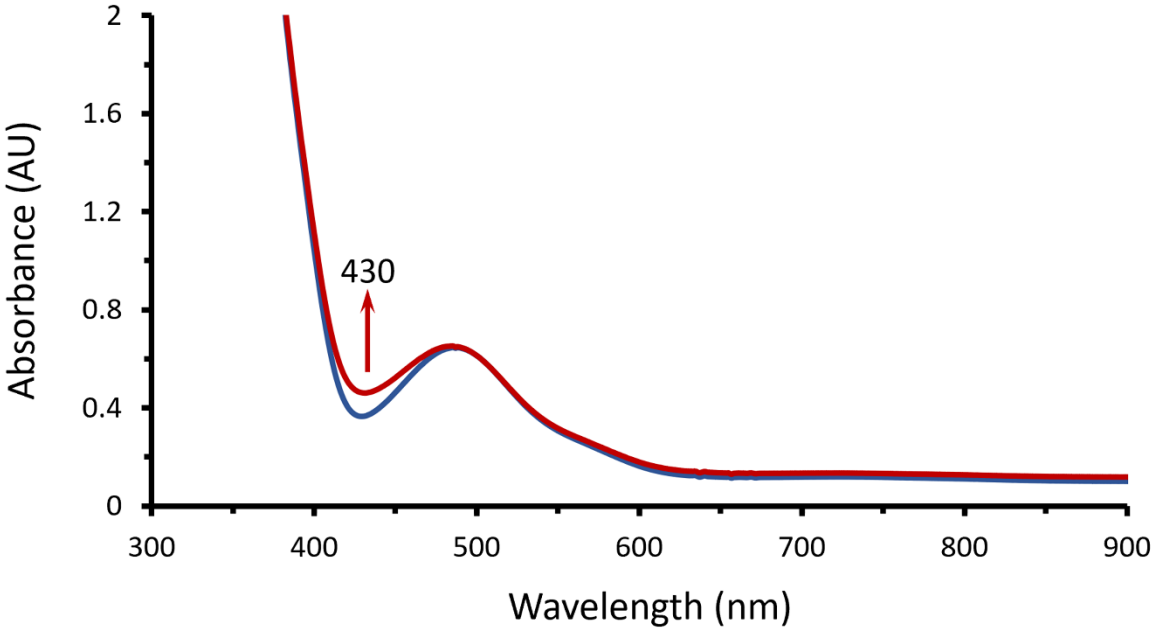

Figure S4. UV-vis spectra of **1** (blue trace) and **1** with addition of sodium naphthalenide ($NaC_{10}H_8$) (red trace) in THF (1.0 mM) at −90 °C.

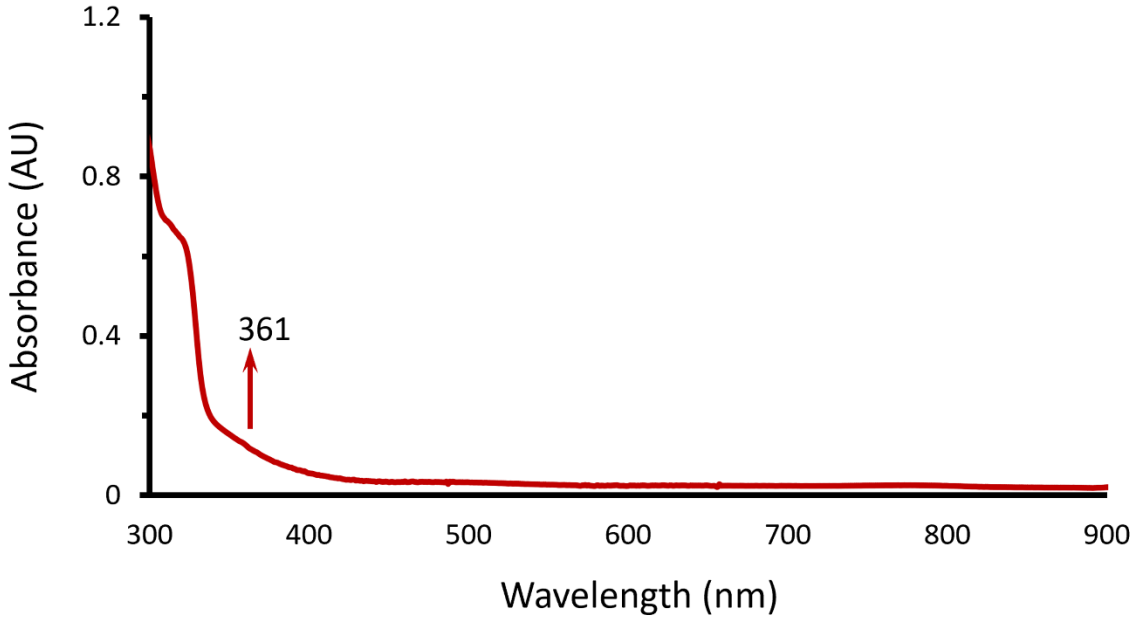

Figure S5. UV-vis spectrum of the produced I^{3-} from quantification for the yield of H_2O_2, which was carried out by the reaction of the mixture of **1** and Cp^*_2Fe with 1 equiv of HOTf in THF at −90 °C, and then warming up the reaction solution and subsequently adding into an acetone solution with excess NaI. The concentration of **1** is 3.2×10^{-5} M. The amount of the produced I_3^- (19% relative to **1**) was then quantified using its absorbance observed in the obtained UV-vis spectra (for I_3^-, λ_{max} = 361 nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}).

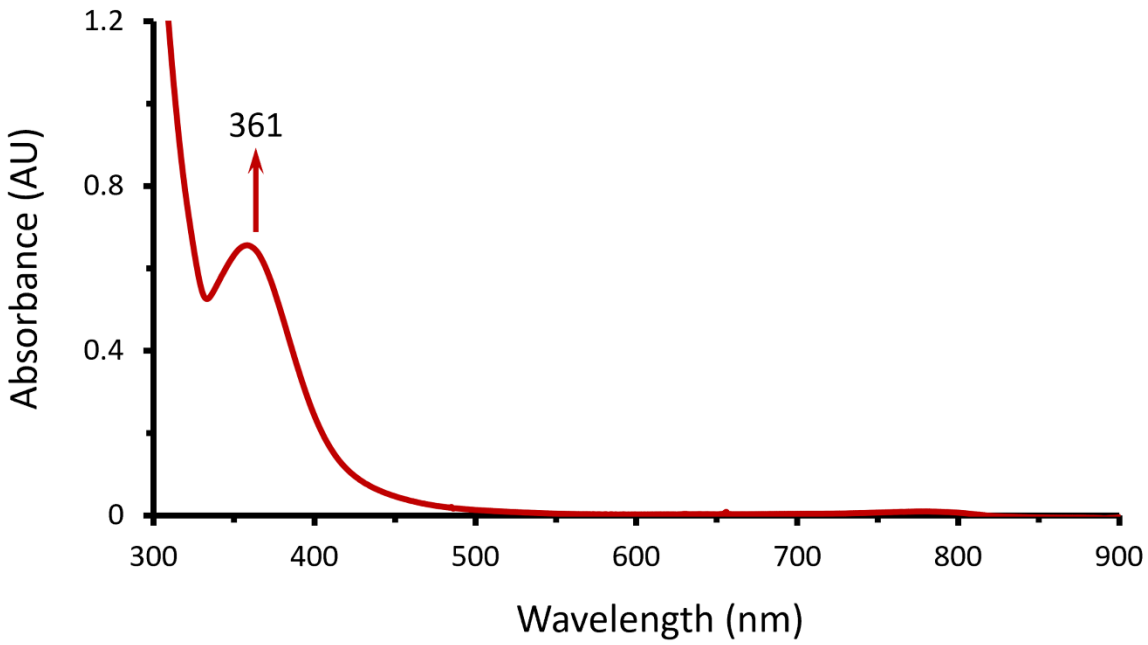

Figure S6. UV-vis spectrum of the produced I^{3-} from quantification for the yield of H_2O_2, which was carried out by the reaction of the mixture of **1** and Cp^*_2Fe with 2 equiv of HOTf in THF at −90 °C, and then warming up the reaction solution and subsequently adding into an acetone solution with excess NaI. The concentration of **1** is 3.2×10^{-5} M. The amount of the produced I_3^- (42% relative to **1**) was then quantified using its absorbance observed in the obtained UV-vis spectra (for I_3^-, λ_{max} = 361 nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}).

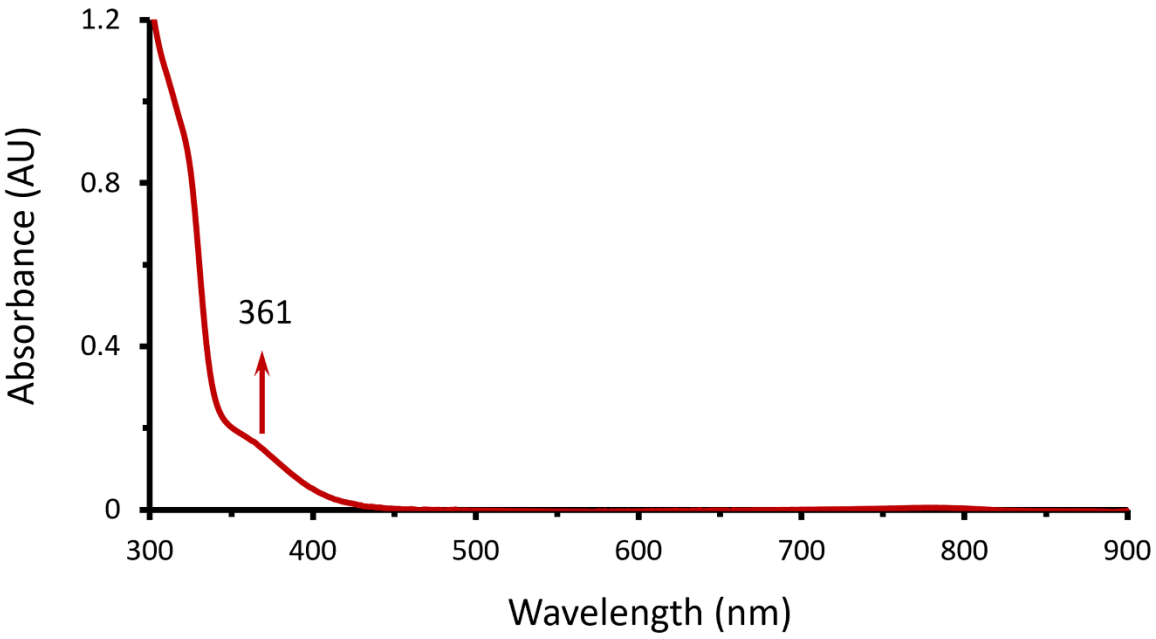

Figure S7. UV-vis spectrum of the produced I^{3-} from quantification for the yield of H_2O_2, which was carried out by the reaction of **2** with 1 equiv of Cp^*_2Fe in THF at −90 °C, and then warming up the reaction solution and subsequently adding into an acetone solution with excess NaI. The concentration of **1** is 3.2×10^{-5} M. The amount of the produced I_3^- (23% relative to **1**) was then quantified using its absorbance observed in the obtained UV-vis spectra (for I_3^-, λ_{max} = 361 nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}).

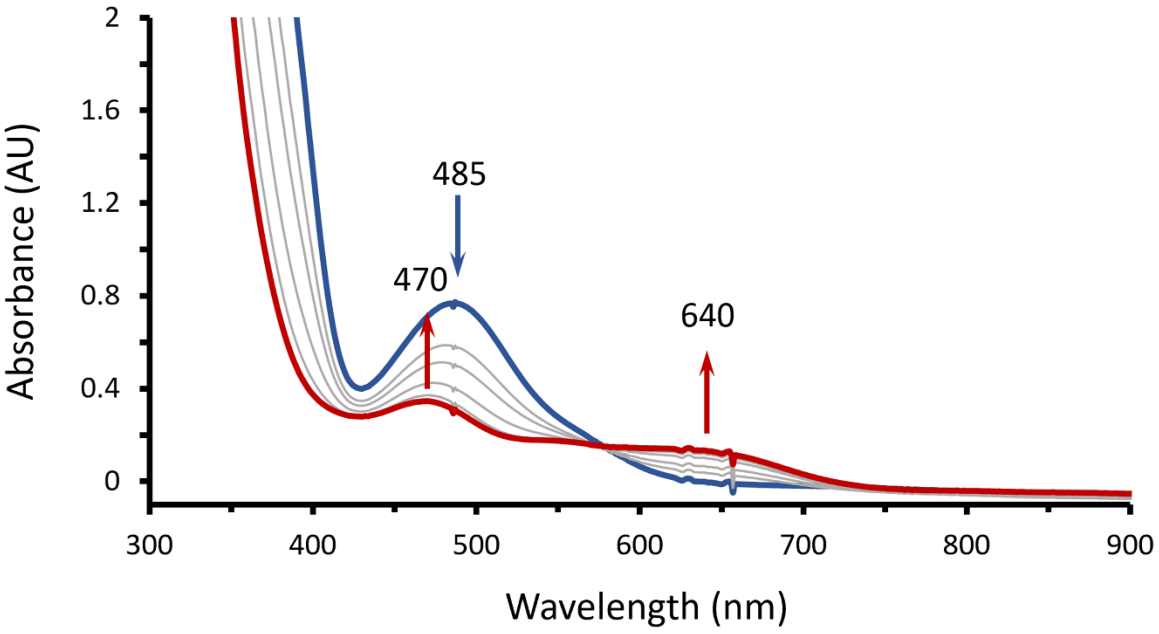

Figure S8. UV-vis spectral changes of the conversion of **1** (blue trace) to $[Co^{III}(BDPP)(O_2^{\bullet})\cdots Sc(OTf)_n]^{(3-n)+}$ (**4**, red trace) by adding $Sc(OTf)_3$ to a THF solution of **1** at −90 °C.

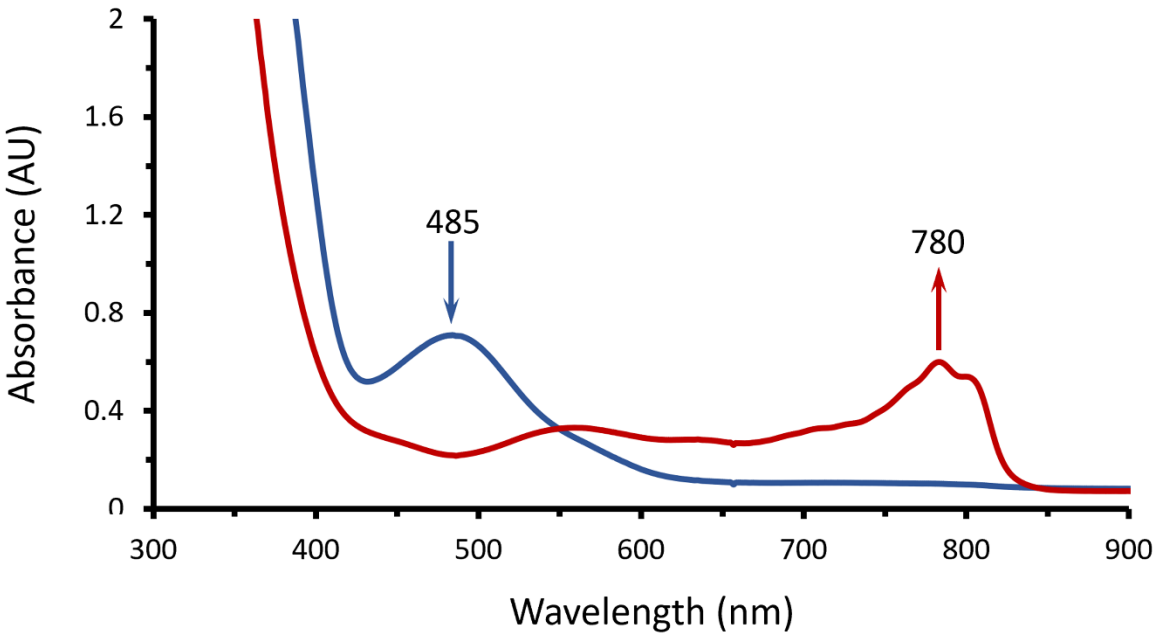

Figure S9. UV-vis spectra of **1** (blue trace) and $[Co^{III}(BDPP)(\mu\text{-}OO)Sc(OTf)_n]^{(2-n)+}$ (**5**, red trace) which was converted from the reaction of $Sc(OTf)_3$ with a THF solution of **1** in the presence of Cp^*_2Fe at −90 °C.

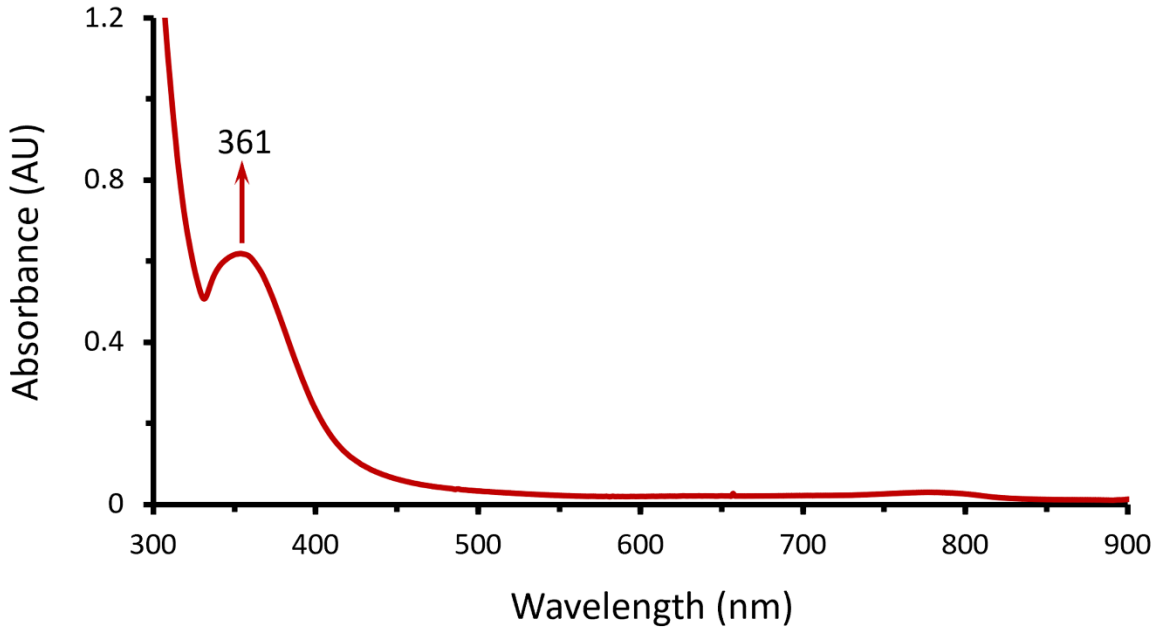

Figure S10. UV-vis spectrum of the produced I^{3-} from quantification for the yield of H_2O_2, which was carried out by adding 2 equiv of HOTf to a THF solution of **5** at −90 °C, and then warming up the reaction solution and subsequently adding into an acetone solution with excess NaI. The concentration of **1** is 3.2×10^{-5} M. The amount of the produced I_3^- (76% relative to **1**) was then quantified using its absorbance observed in the obtained UV-vis spectra (for I_3^-, λ_{max} = 361 nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}).

Table S1. Cartesian coordinates of optimized **A**

Co	1.970970	3.252119	18.220058
O	0.418822	4.322302	18.549289
O	-0.641344	3.630569	18.879876
H	0.093561	2.254552	19.101241
N	1.500153	2.935435	16.293245
N	3.465710	2.173163	17.859144
N	2.758975	3.405767	20.077510
O	2.907738	4.745202	17.657038
O	0.953498	1.717321	18.990326
C	3.123023	4.854358	16.268746
C	3.216562	6.347965	15.893686
C	3.167996	7.331895	16.885249
H	3.042047	7.027769	17.923367
C	3.274037	8.685139	16.546452
H	3.242617	9.442298	17.333822
C	3.415441	9.070510	15.212407
H	3.497828	10.127375	14.946891
C	3.458564	8.091381	14.215096
H	3.574719	8.381809	13.167955
C	3.370475	6.741192	14.555601
H	3.432706	5.992008	13.763792
C	4.467661	4.234413	15.823511
C	4.681821	3.678386	14.553230
H	3.865593	3.608957	13.832694
C	5.943542	3.213233	14.169965
H	6.082788	2.779981	13.176483
C	7.023379	3.304810	15.048968
H	8.009447	2.944522	14.745981
C	6.827990	3.875864	16.311233
H	7.669490	3.976382	17.001500
C	5.566213	4.337425	16.688328
H	5.417628	4.810300	17.660156
C	1.891432	4.221887	15.580782
H	2.087173	3.961671	14.530205
C	0.635241	5.089098	15.670574
H	0.667092	5.680339	16.592518
H	0.601408	5.795300	14.831999
C	-0.555139	4.115418	15.683784

H	-1.277689	4.386170	16.462642
H	-1.088470	4.112868	14.722806
C	0.051461	2.731004	15.944487
H	-0.436282	2.172403	16.752627
H	0.012779	2.111550	15.034455
C	2.272473	1.724897	15.876565
H	1.632739	0.851068	16.075761
H	2.479327	1.749273	14.796477
C	3.524601	1.558136	16.682020
C	4.643733	0.802264	16.350072
H	4.717972	0.315235	15.378019
C	5.670177	0.698490	17.290901
H	6.556994	0.106476	17.057344
C	5.571487	1.357294	18.520193
H	6.367023	1.287807	19.263191
C	4.437241	2.122582	18.766470
C	4.203126	3.042131	19.926646
H	4.741496	3.974613	19.703589
H	4.605517	2.637043	20.867354
C	2.661909	4.771300	20.691118
H	2.851253	5.510014	19.903116
H	3.453310	4.854567	21.454916
C	1.282683	4.856409	21.335894
H	0.567570	5.336495	20.659207
H	1.321227	5.454210	22.256153
C	0.873797	3.395925	21.611829
H	0.778648	3.180469	22.683380
H	-0.103293	3.172936	21.167016
C	1.980437	2.503097	21.011023
H	2.667208	2.199838	21.811780
C	1.452451	1.246393	20.271581
C	2.511267	0.168854	20.003564
C	2.405097	-0.634121	18.859110
H	1.598462	-0.443615	18.151847
C	3.310748	-1.669609	18.624986
H	3.213903	-2.277062	17.721991
C	4.327319	-1.940806	19.546136
H	5.028551	-2.758820	19.366395
C	4.423529	-1.167161	20.704924

H	5.199413	-1.379162	21.444490
C	3.521799	-0.123383	20.931470
H	3.620354	0.453778	21.851454
C	0.322905	0.565857	21.052994
C	0.523120	0.221365	22.398896
H	1.462851	0.463871	22.898740
C	-0.462543	-0.456883	23.114482
H	-0.283268	-0.726970	24.157642
C	-1.668646	-0.802394	22.495509
H	-2.441479	-1.334659	23.054412
C	-1.873446	-0.467386	21.156734
H	-2.807526	-0.740604	20.660305
C	-0.882888	0.210193	20.437123
H	-1.058552	0.442734	19.386830

Table S2. Cartesian coordinates of optimized **B**

Co	2.13269260364761	3.26061745657475	18.40403005418174
O	0.81592691681781	4.55525219520683	18.82536804653621
O	-0.43974226614941	4.25241859229925	18.90109536994466
N	1.56267256982905	2.93458535911309	16.48457776416421
N	3.62359376233516	2.17770258058361	17.96005978162098
N	2.96044423776597	3.33680705353943	20.23107600264566
O	3.07494136939447	4.87816613038664	17.65730432967670
O	1.20334324607255	1.77939349417475	18.97088959260599
C	3.10866080779085	4.94062679894791	16.18811913122132
C	3.10259108693289	6.42187725637915	15.76986853754473
C	2.39112590338606	7.38143724359303	16.51083998736117
H	1.81451047486522	7.11429058174658	17.40145523265052
C	2.36894438306492	8.72131919914571	16.11986005264220
H	1.80513385422137	9.44481792813865	16.71217130644404
C	3.05786367012506	9.12922626194755	14.97523155557980
H	3.03701758907314	10.17556778794734	14.66226423989091
C	3.77491742139017	8.18873894876789	14.23461315234093
H	4.32734961604065	8.49718254787166	13.34418868456943
C	3.79844545873971	6.84869630632034	14.63000751152832
H	4.37940723193870	6.13668897613549	14.04531078056139
C	4.41685438132534	4.28395107905496	15.74768081056963
C	4.54862500256205	3.66670574922087	14.49523311824397
H	3.69709408986176	3.59486707135103	13.81790697216849
C	5.77742044190128	3.15110022575539	14.07468244361401
H	5.85670355577360	2.67371038564238	13.09553041504152
C	6.89984420956807	3.25151494860384	14.89755039833262
H	7.85980164179143	2.84937274537567	14.56563817796597
C	6.78339067939318	3.88276200007496	16.13963835765636
H	7.65840330102057	3.98845007374145	16.78488749818469
C	5.55583465461901	4.39884634946931	16.55713280343875
H	5.47910900823374	4.90906836311296	17.51696778290877
C	1.83581056780363	4.19630821978091	15.69214738792257
H	1.98550537632949	3.91158708972414	14.64106701209136
C	0.53102184012587	4.98712553778772	15.79533837730771
H	0.48875888069085	5.55004114876148	16.73156982341746
H	0.44446169488840	5.70809565389808	14.97224509010317
C	-0.57166386207186	3.92653284490888	15.78661697136967
H	-1.42760398670970	4.24127436464325	16.39741332485678

H	-0.93684567873326	3.75077814142661	14.76420375480127
C	0.08002052171367	2.65726729631410	16.34487136492274
H	-0.29046159047307	2.36353318180728	17.33303164089978
H	-0.05307107092144	1.80902107554144	15.65954910375824
C	2.32938484828900	1.72853192450611	16.04074602763265
H	1.71311298289153	0.85752905750604	16.30278366536226
H	2.46775197028011	1.72909265812753	14.94964765016931
C	3.62071896003178	1.56026666962808	16.78340000882241
C	4.70061918941685	0.76379794907543	16.41799536749539
H	4.72542239514232	0.26966026901519	15.44682353855425
C	5.74013761127011	0.60218142623008	17.33858072816214
H	6.59039781541735	-0.03400776287257	17.08518847255266
C	5.68962375531564	1.23646086729431	18.58268501697096
H	6.47844747424393	1.09278038480304	19.32187250964126
C	4.59352949545662	2.04900580584925	18.85958982328404
C	4.38801836436946	2.90999669795847	20.07249621509638
H	4.98350882679230	3.82452554449166	19.92779385417115
H	4.75028026541283	2.42018029954011	20.98857505459533
C	2.93172394294613	4.64481435520934	20.96426779365560
H	3.14702420624584	5.45852674913694	20.25827909808143
H	3.74551613980873	4.62756527120234	21.70800689136308
C	1.57258420975713	4.74567351756914	21.65889414338928
H	0.91217291061955	5.44712221150536	21.13688377772582
H	1.70236212009035	5.11315920845974	22.68632876507144
C	0.98863956568446	3.32080254899041	21.61831114912094
H	0.66063719205036	2.96399122267755	22.60233714236143
H	0.11735299615189	3.28288705385936	20.95855735827764
C	2.09918391470903	2.41063672053855	21.07894306216410
H	2.72285150357090	2.06164586517392	21.91445087263210
C	1.58794344960141	1.23158130361326	20.21070644718814
C	2.63844143043680	0.10996609680985	20.03791478800522
C	2.55730629756824	-0.69725751636585	18.89293955633243
H	1.76281045212759	-0.49240442601907	18.17484505983710
C	3.45681297139100	-1.74137108790137	18.67798536821086
H	3.37392254106033	-2.35107427955845	17.77461608132802
C	4.45359422906926	-2.02002899832159	19.62048582345762
H	5.15324894483598	-2.84298695846066	19.45622590244986
C	4.52502337856922	-1.25057349164103	20.78289461586823
H	5.27903394559474	-1.47208281756683	21.54268741544948

C	3.62293614969183	-0.19979466312231	20.98873547983242
H	3.69938592719486	0.36748567002905	21.91817746793645
C	0.33568723752494	0.61378319812361	20.86985137155726
C	0.43964112104619	-0.26397103992796	21.95762059735971
H	1.41921463408285	-0.56745137400731	22.32961436952930
C	-0.70585366421864	-0.77664912115477	22.57204947980836
H	-0.60354412141737	-1.45840007762119	23.42006576966648
C	-1.97331683889406	-0.42315204387997	22.10108295005116
H	-2.86749333834899	-0.82888979146864	22.58013081261033
C	-2.08351551254607	0.44782887589611	21.01369083784656
H	-3.06802598474932	0.73714350665680	20.63644043564622
C	-0.93830518746849	0.96364731187377	20.40151900389990
H	-1.02161329025869	1.64993329827131	19.55975091339630
H	2.54370834216765	5.62343534445150	17.98098863709276

Table S3. Cartesian coordinates of optimized **C**

Co	1.994678	3.268206	18.326222
O	0.662038	4.422666	18.816900
O	-0.644111	3.941409	18.708865
N	1.479466	2.888128	16.411461
N	3.498812	2.196525	17.928659
N	2.826296	3.427483	20.139203
O	2.999505	4.699116	17.681957
O	1.156239	1.737175	18.931506
C	3.118183	4.802939	16.281774
C	3.154697	6.294355	15.889688
C	3.023972	7.287083	16.864584
H	2.899138	6.989817	17.905068
C	3.050308	8.639157	16.505549
H	2.955371	9.404905	17.279330
C	3.192179	9.011830	15.167914
H	3.210765	10.067530	14.886277
C	3.316862	8.022564	14.187636
H	3.435385	8.304255	13.138449
C	3.309749	6.674639	14.548228
H	3.438181	5.917377	13.772411
C	4.448254	4.192879	15.786355
C	4.610495	3.581883	14.534727
H	3.762207	3.464198	13.858883
C	5.860709	3.114706	14.116281
H	5.961199	2.637770	13.138441
C	6.977492	3.260097	14.939833
H	7.953932	2.898562	14.608605
C	6.832357	3.887986	16.181715
H	7.702164	4.033178	16.827086
C	5.582978	4.349851	16.595558
H	5.474007	4.862883	17.552270
C	1.856631	4.151644	15.661600
H	2.015801	3.874983	14.608456
C	0.596578	5.007748	15.773505
H	0.603804	5.533114	16.736203
H	0.571295	5.771089	14.986626
C	-0.566727	4.012524	15.686769
H	-1.408769	4.314992	16.320935

H	-0.943247	3.939647	14.656260
C	0.018236	2.662724	16.125272
H	-0.440176	2.230214	17.021042
H	-0.055920	1.923553	15.312486
C	2.234743	1.661132	16.020720
H	1.609992	0.802310	16.306939
H	2.383637	1.631271	14.931243
C	3.519205	1.540802	16.773810
C	4.633895	0.784955	16.428066
H	4.675961	0.266693	15.470449
C	5.693584	0.718491	17.334759
H	6.578032	0.128074	17.088965
C	5.625225	1.406117	18.549509
H	6.438353	1.356766	19.274694
C	4.491872	2.167299	18.812430
C	4.272162	3.092139	19.967651
H	4.789290	4.032565	19.727320
H	4.692802	2.698350	20.904787
C	2.705736	4.781578	20.776770
H	2.737744	5.532317	19.976865
H	3.585594	4.928245	21.421800
C	1.418213	4.780809	21.610111
H	0.683526	5.486752	21.203062
H	1.638682	5.097253	22.639447
C	0.887264	3.336800	21.564419
H	0.572360	2.963877	22.547082
H	0.019489	3.254116	20.905243
C	2.032664	2.477677	21.021122
H	2.688361	2.181453	21.851723
C	1.564547	1.247462	20.194358
C	2.656145	0.161719	20.043603
C	2.580955	-0.708808	18.945669
H	1.766137	-0.579187	18.232779
C	3.511229	-1.733698	18.771998
H	3.432804	-2.394490	17.904604
C	4.532178	-1.927049	19.709356
H	5.256342	-2.734361	19.576676
C	4.597818	-1.092766	20.826611
H	5.372397	-1.247377	21.582320

C	3.666901	-0.060627	20.990850
H	3.742729	0.558482	21.886642
C	0.343029	0.586034	20.868650
C	0.495914	-0.286176	21.955756
H	1.490975	-0.541237	22.322570
C	-0.619474	-0.859630	22.571227
H	-0.478544	-1.538100	23.415927
C	-1.905388	-0.574917	22.103208
H	-2.775824	-1.030449	22.580554
C	-2.064201	0.288666	21.016345
H	-3.063660	0.518954	20.636682
C	-0.948881	0.863417	20.401331
H	-1.071664	1.530751	19.550011
H	-1.153953	4.679459	19.088753

Reference

(1) C. C. Wang, H. C. Chang, Y. C. Lai, H. Fang, C. C. Li, H. K. Hsu, Z. Y. Li, T. S. Lin, T. S. Kuo, F. Neese, S. Ye, Y. W. Chiang, M. L. Tsai, W. F. Liaw and W. Z. Lee, *J. Am. Chem. Soc.,* 2016, **138**, 14186-14189.

(2) (a) F. Neese, *WIREs Comput. Mol. Sci.* 2012, **2**, 73-78; (b) F. Neese, *WIREs Comput. Mol. Sci* 2018, **8**, e1327.

(3) (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652; (b) C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785-789.

(4) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297-3305.

(5) F. Weigend, *Phys. Chem. Chem. Phys.,* 2006, **8**, 1057-1065.

(6) F.Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.,* 2009, **356**, 98-109.