Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Bimetallic Cooperative Effect on O-O Bond Formation: Copper polypyridyl Complexes Catalyze Water Oxidation

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General Information. All chemicals used in this work except the ligand of BPMAN and the complexes were commercial products of the highest available purity and were further purified by the standard methods, if necessary. Distilled water was further purified using a Milli-Q Ultrapure water purification system. ESI-MS analysis was conducted by Bruker Daltonics ESI-Q-ToF LC/MS. UV-Vis measurements were recorded by Agilent Cary 100 UV-Vis. Electrochemical experiments were performed on a CHI-660E electrochemical workstation. Oxygen evolution was recorded by a calibrated Ocean Optics FOXY probe.

Titration Procedure. In 100 ml of titration vessel, 427 mg of $NaNO_3$ (5.024 mmol) was added to 49.55 ml of water, 0.10 ml of a 0.1000 M solution of $Cu(CF_3SO_3)_2$ (10 μmol), 0.75 ml of a 0.0400 M TPA containing 0.0200 M HNO_3 (30 μmol of TPA, 15 μmol HNO_3), and 0.15 ml of 0.1000 N NaOH was added to the solution in sequence. The mixture was stirred for 30 min and no precipitated was observed. The temperature was maintained at 24 ºC and the initial pH was 6.730 with the ionic strength is 0.1000 M. Then pH value of the mixture was titrated to 2.150 with 0.1000 N HNO_3. The aliquot size was 0.04 ml/min of 0.100 N NaOH.

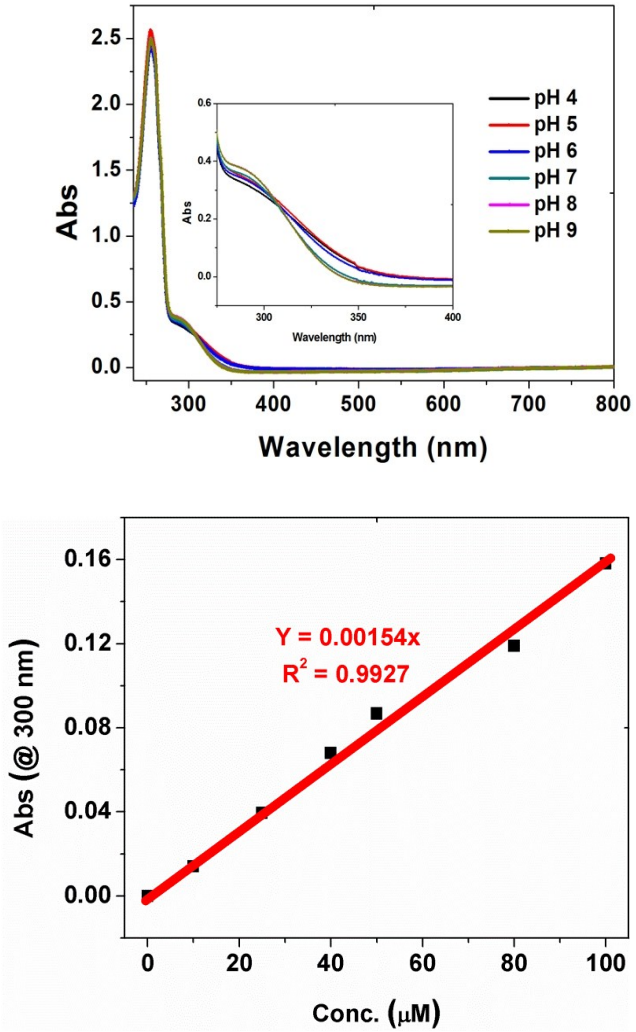

Figure S1. (Top) UV-visible spectra of $[TPA(Cu^{II})(OH_2)]^{2+}$ in different pH solution. (Bottom) Dependence of the absorption at 300 nm versus the concentration of $[TPA(Cu^{II})(OH_2)]^{2+}$ in pH = 7 phosphate buffer solution.

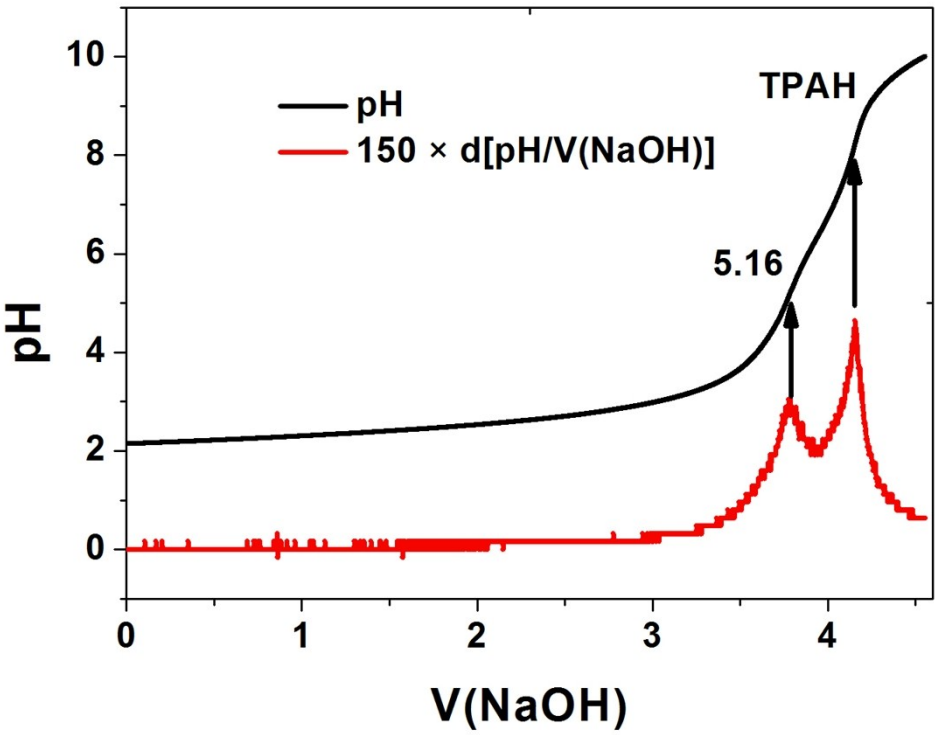

Figure S2. Acid-base titration of Cu(II)-TPA complexes. Conditions: 0.2 mM Cu^{2+}; 0.6 mM TPA, 23 ºC, *I* = 0.100 M, dropping rate = 0.04 ml/min.

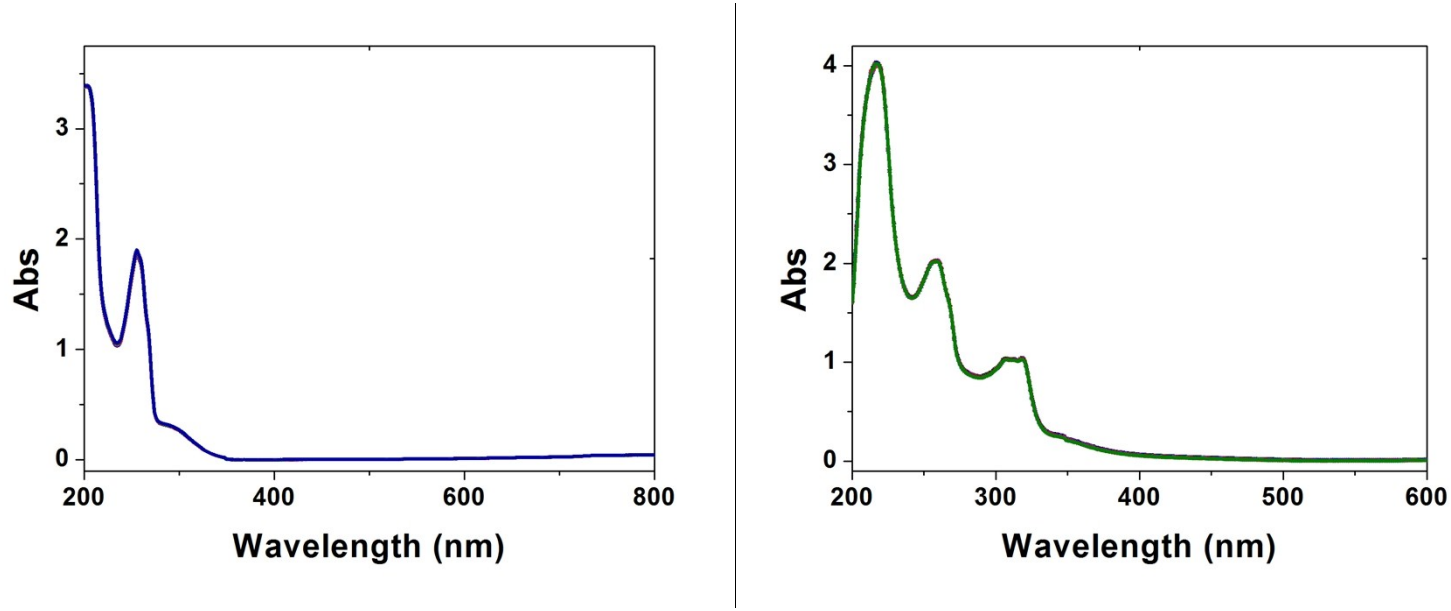

Figure S3. UV-visible spectra of $[TPA(Cu^{II})(OH_2)]^{2+}$ (Left) and $[Cu_2(BPMAN)(\mu\text{-}OH)]^{3+}$ (Right) in 0.1 M phosphate buffer at pH 7.0 after immersion for 5 days.

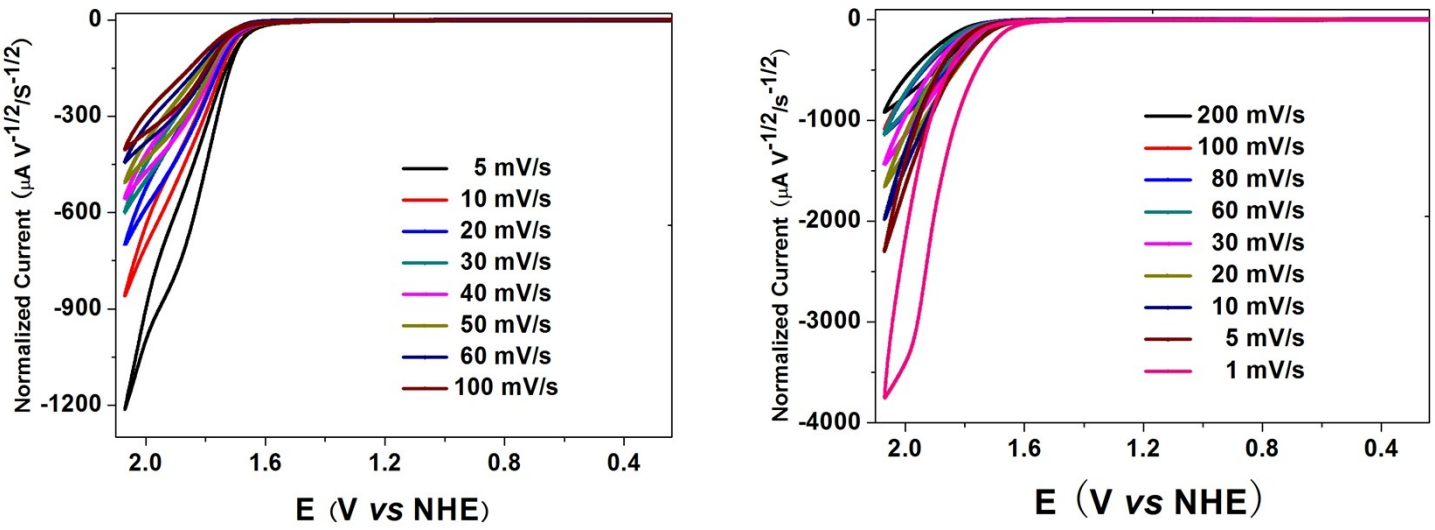

Figure S4. Normalized CVs of $[TPA(Cu^{II})(OH_2)]^{2+}$ (Left) and $[Cu_2(BPMAN)(\mu\text{-}OH)]^{3+}$ (Right) in 0.1 M phosphate buffer at pH 7.0 at different scan rate at a BDD working electrode at room temperature.

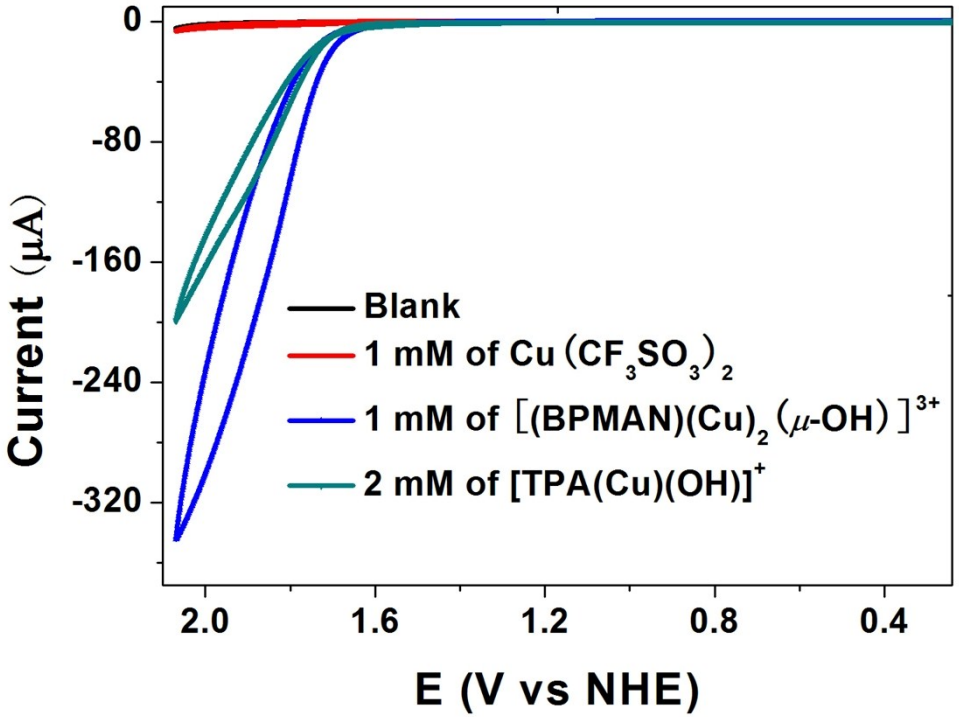

Figure S5. CVs of $Cu(CF_3SO_3)_2$ (red line), $[Cu_2(BPMAN)(\mu\text{-}OH)]^{3+}$ (blue line) and $[TPA(Cu^{II})(OH_2)]^{2+}$ (green line) in 0.1 M phosphate buffer at pH 7.0 at 100 mV/s at a BDD working electrode at room temperature.

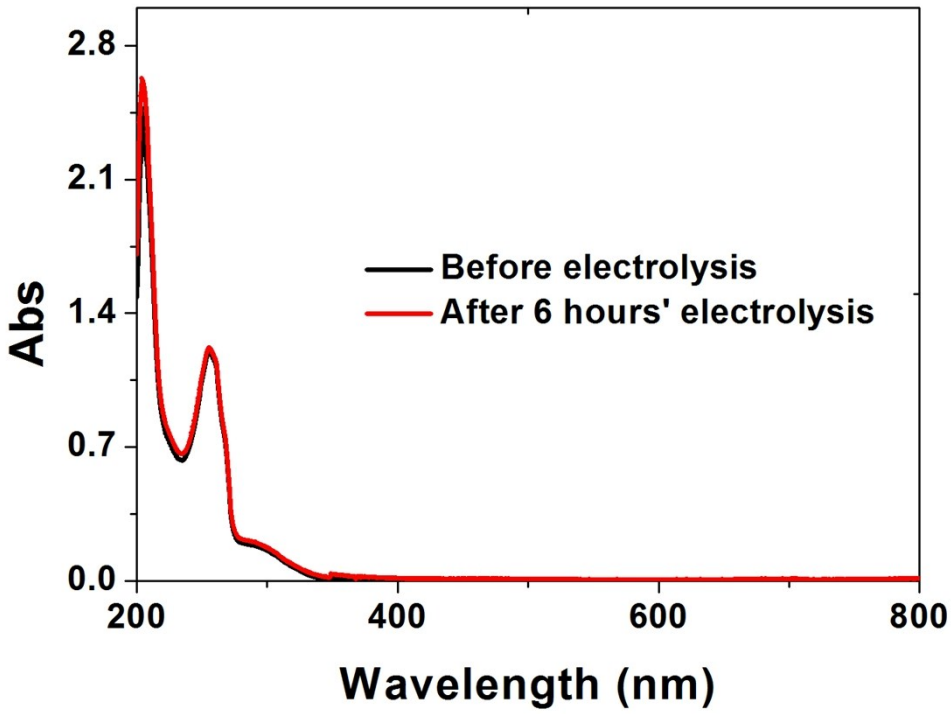

Figure S6. UV-visible spectra of 0.12 mM $[TPA(Cu^{II})(OH_2)]^{2+}$ before and after electrolysis for 6 hours in 0.1 M phosphate buffer at pH 7.0.

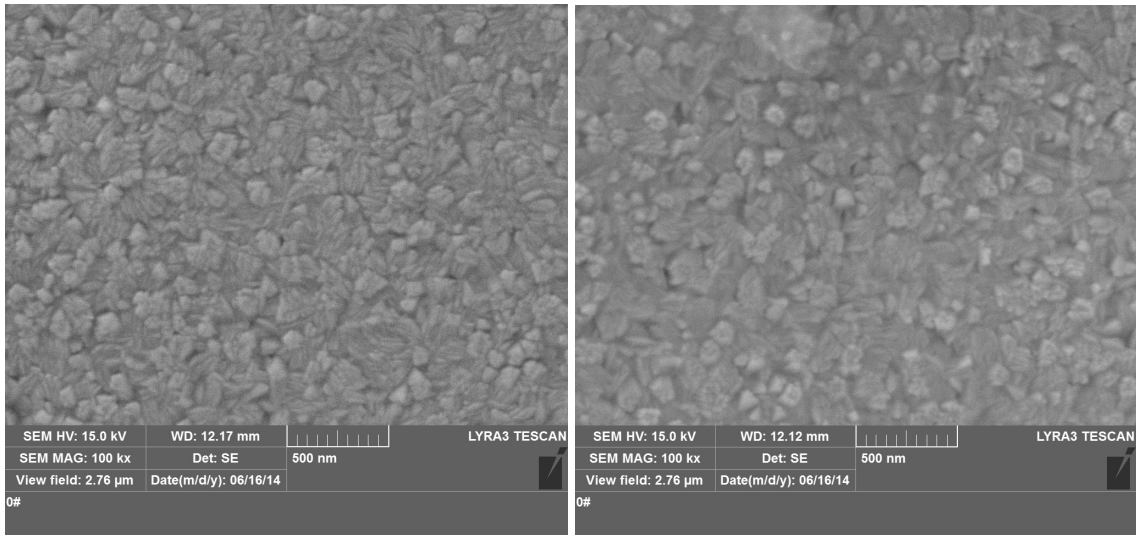

Figure S7. Scanning electron microscopes for blank ITO (Left) and ITO after electrolysis 6 hours in 0.1 M phosphate buffer at pH 7.0 (Right).

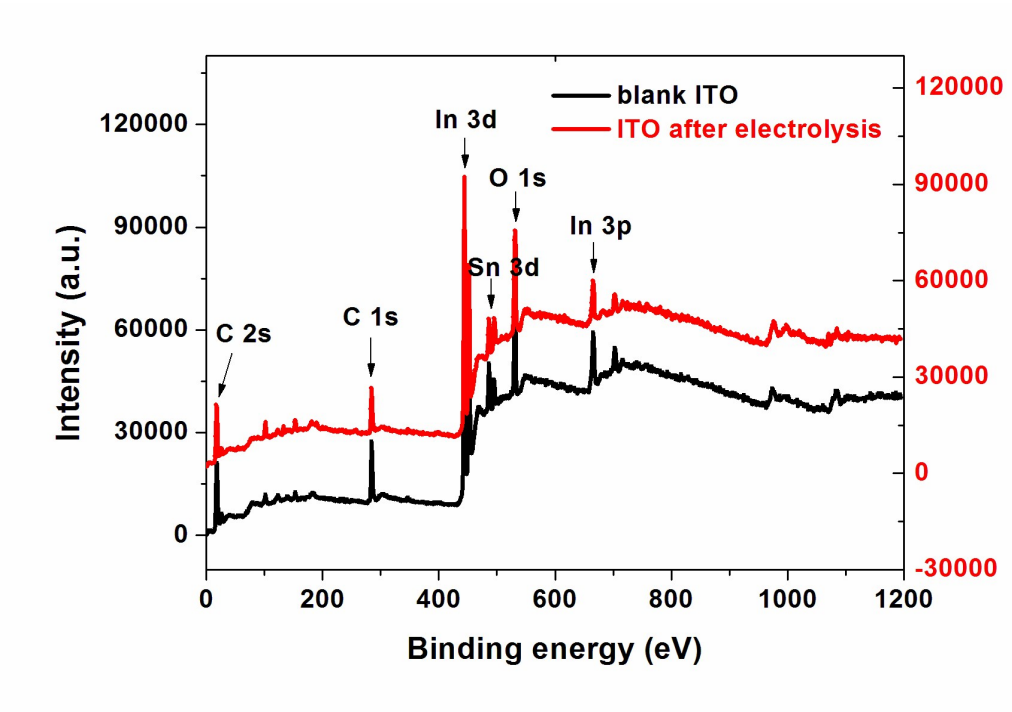

Figure S8. X-ray photoelectron spectroscopy data for blank ITO (black) and ITO after electrolysis 6 hours in 0.1 M phosphate buffer at pH 7.0 (Red).

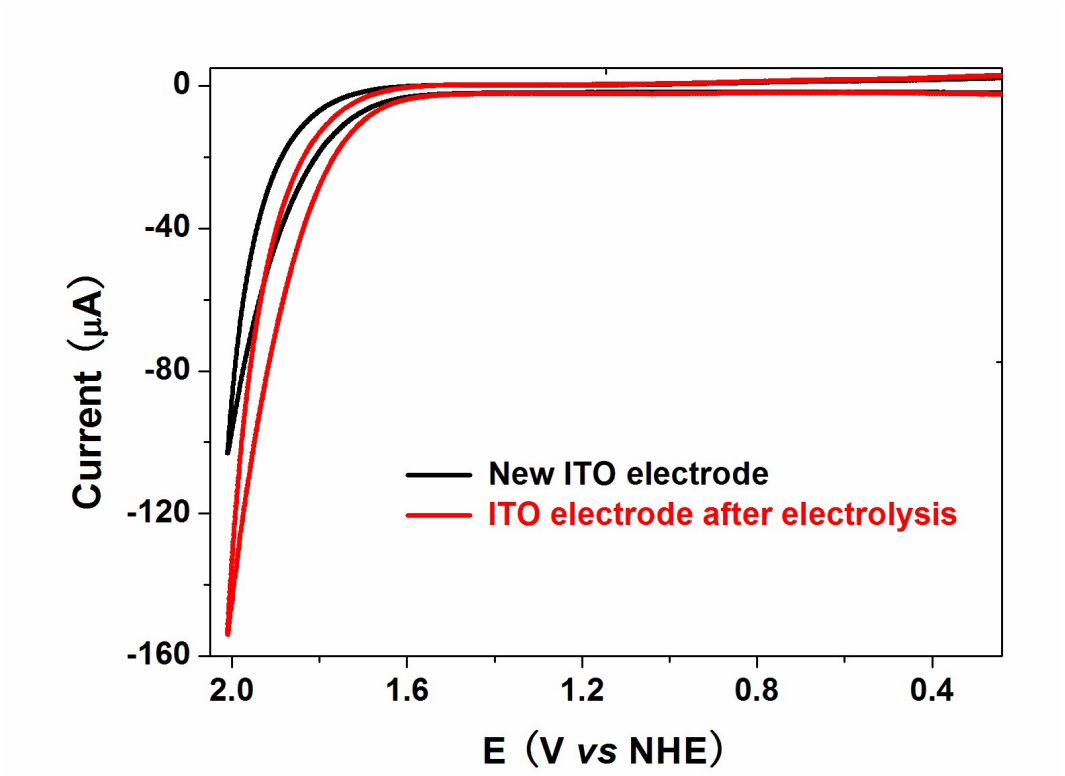

Figure S9. CVs of new ITO and ITO after electrolysis for 6 hours in 0.1 M phosphate buffer at pH 7.0 (electrode area: ~1 cm^2, scan rate: 100 mV/s).

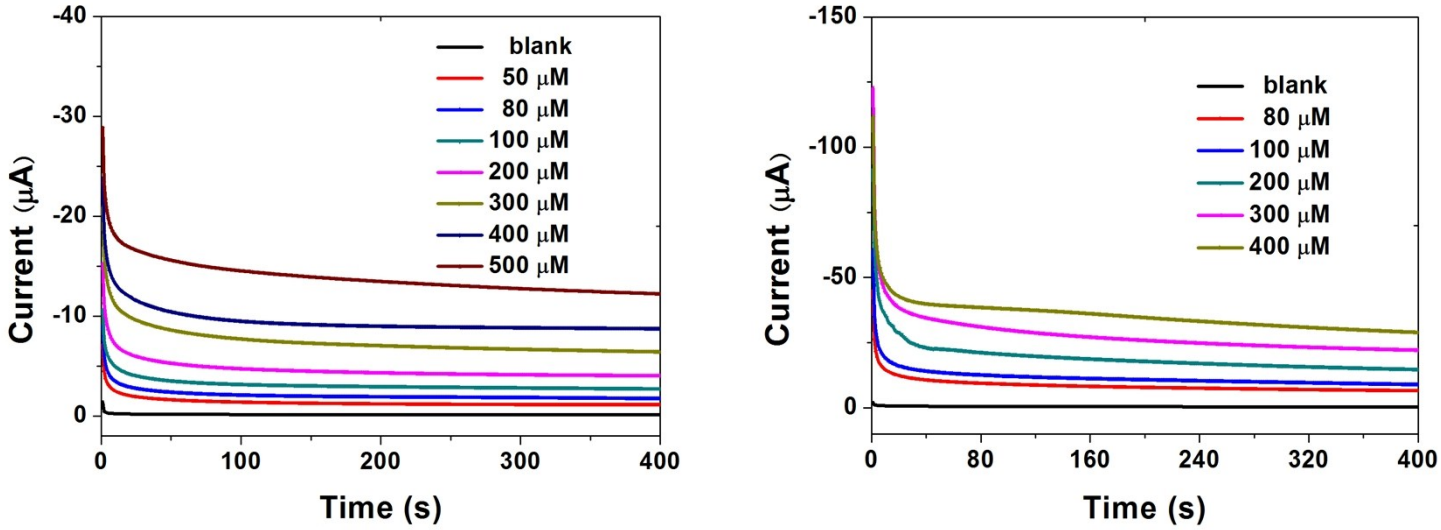

Figure S10. Controlled potential electrolysis of **1** at 2.04 V *vs* NHE (Left) and **2** at 1.87 V *vs* NHE (Right) with different concentrations in 0.1 M phosphate buffer, pH 7.0, at a boron doped diamond (BDD) electrode (0.07cm^2).

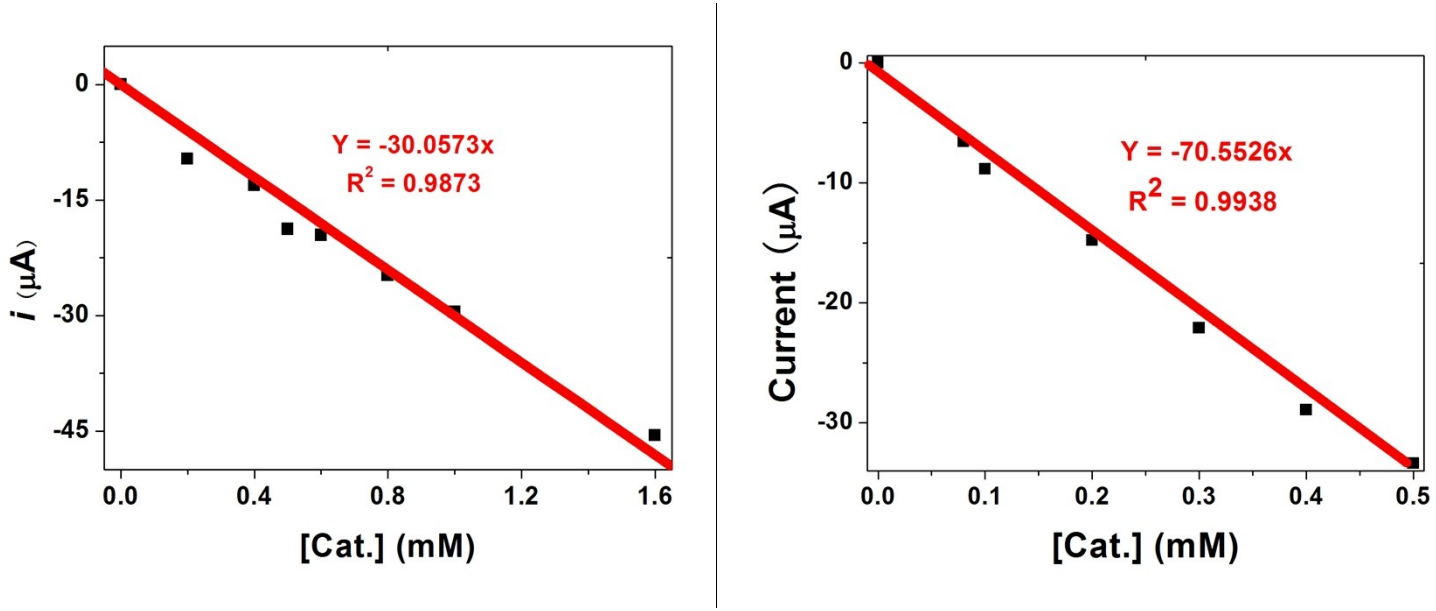

Figure S11. Plot of i_{cat} (background current was subtracted) versus [Cat.] of **1** (Left) and **2** (Right) in 0.1 M phosphate buffer at pH 7.0 at a boron doped diamond (BDD) electrode (0.07cm^2).

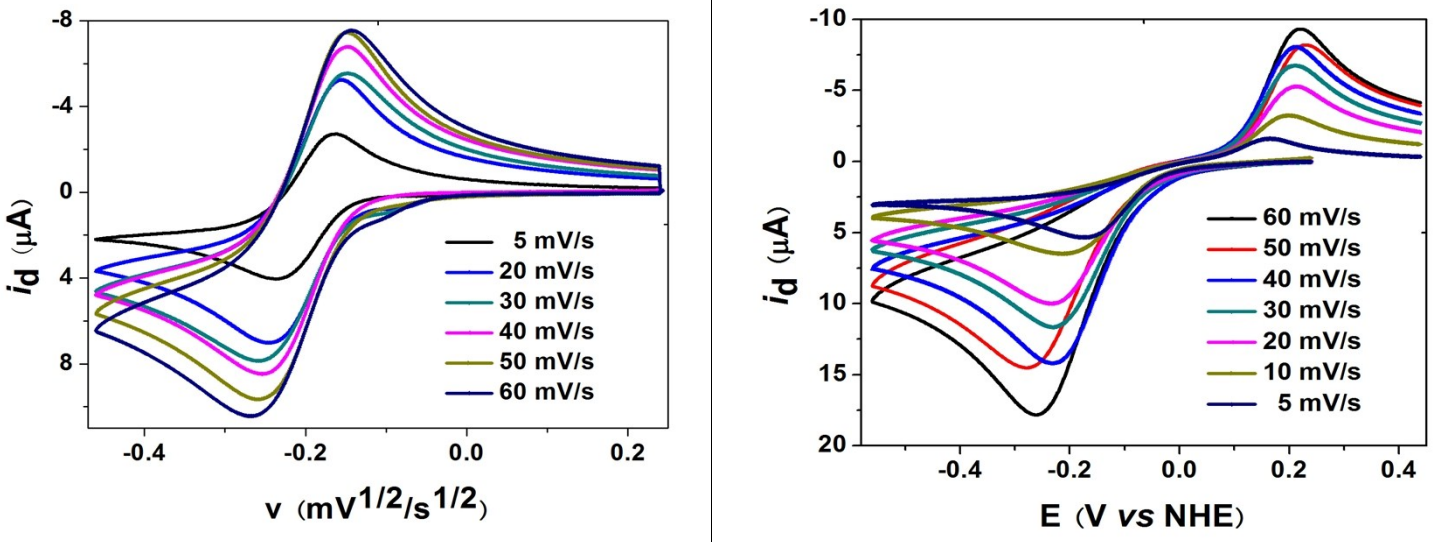

Figure S12. CVs of different scan rates for Cu(II/I) redox couple of 0.8 mM $[TPA(Cu^{II})(OH_2)]^{2+}$ (Left) and 1.2 mM $[BPMAN(Cu)_2(\mu\text{-}OH)]^{3+}$ (Right) in 0.1 M phosphate buffer at pH 7.0 at a BDD working electrode at room temperature.

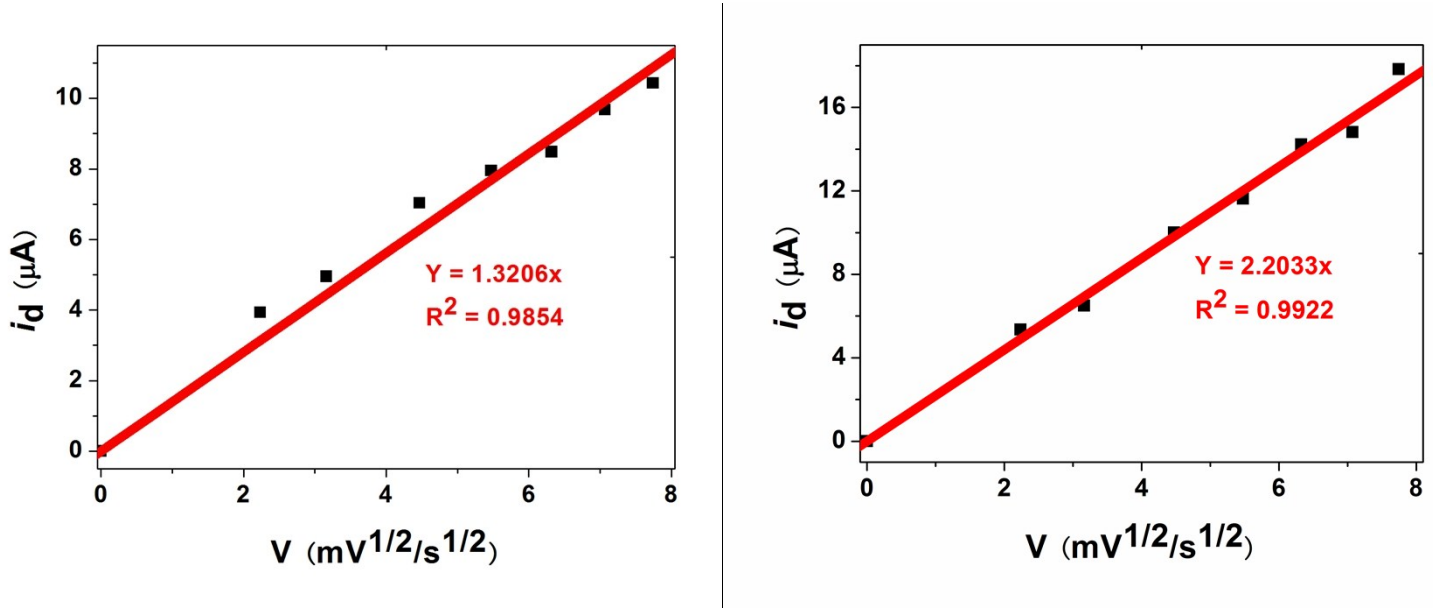

Figure S13. Dependence of the peak current for the Cu(II/I) couple versus $v^{1/2}$ of 0.5 mM of $[TPA(Cu^{II})(OH_2)]^{2+}$ (Left) and 1.2 mM of $[BPMAN(Cu)_2(\mu\text{-}OH)]^{3+}$ (Right).

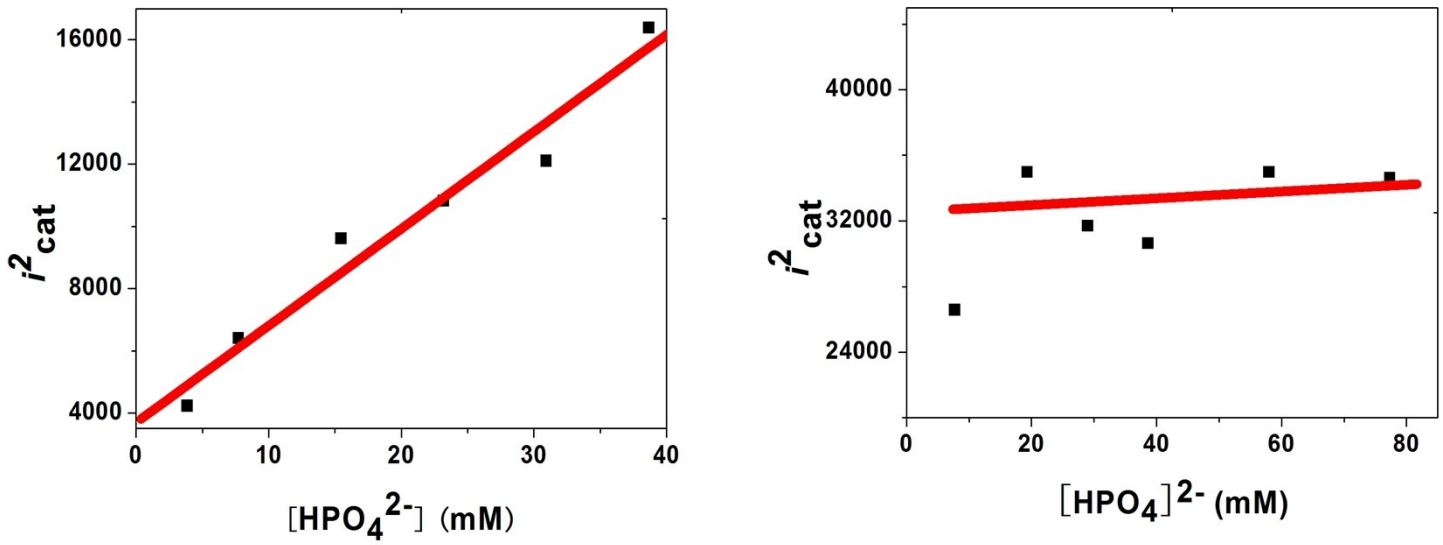

Figure S14. Plot of i^2_{cat} versus $[HPO_4^{2-}]$ for 1 mM of $[TPA(Cu^{II})(OH_2)]^{2+}$ at 2.04 V vs. NHE (Left) and 0.5 mM of $[BPMAN(Cu)_2(\mu\text{-}OH)]^{3+}$ at 1.87 V vs. NHE (Right) at 0.1 M PBS buffer at pH 7.0 (μ= 0.225 M with added $LiClO_4$. Data collected from the corresponding CVs respectively.

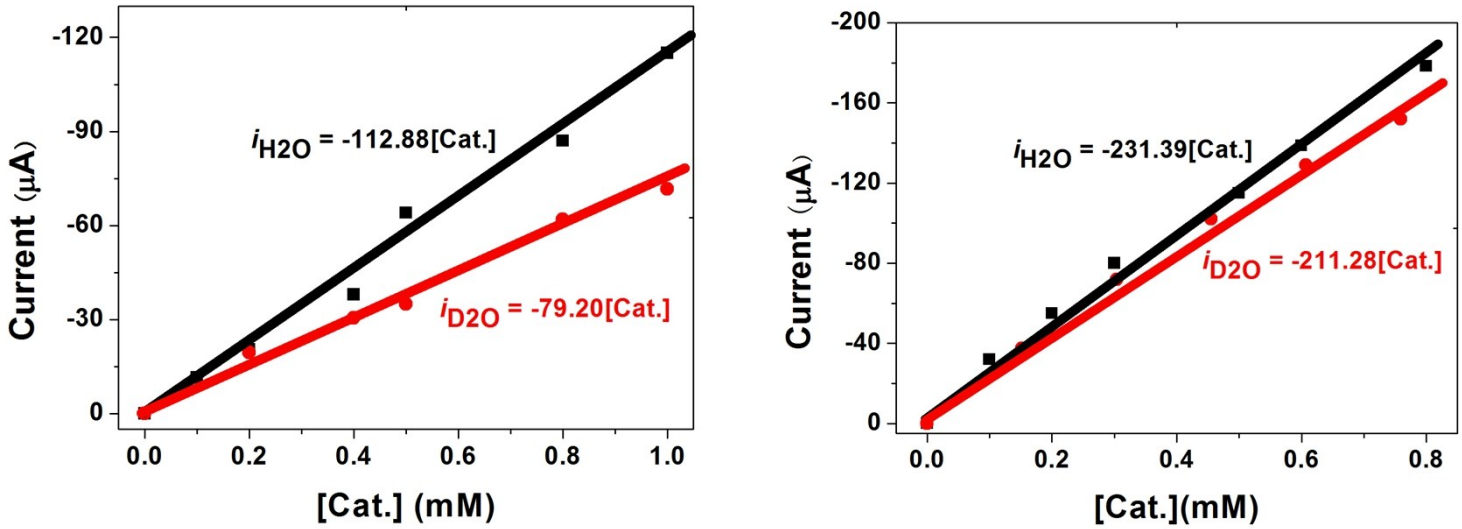

Figure S15. Plot of i^2_{cat} versus concentration for $[TPA(Cu^{II})(OH_2)]^{2+}$ at 2.04 V vs. NHE (Left) and $[BPMAN(Cu)_2(\mu\text{-}OH)]^{3+}$ at 1.87 V vs. NHE (Right) at 0.1 M PBS H_2O (pH 7.0) and D_2O (pD7.4). Data collected from the corresponding CVs respectively.

Computational details.

The density functional calculations presented were performed with the hybrid functional B3LYP,[1] as implemented in the Gaussian 09 program package.[2] Geometries were optimized using the 6-31G(d,p) basis set on all elements except for Ir, which were described by the SDD [3]pseudopotential and its corresponding basis sets. The final and the solvation energies were calculated as single-point corrections on the optimized structures using the SMD[4] continuum solvation model at the B3LYP* (15% HF exact exchange)[5] level employing a larger basis set, where all elements, except Cu, were described by 6-311+G(2df,2p). D3 dispersion corrections proposed by Grimme[6] were also added at single points. For water, the experimental solvation free energy of -6.3 kcal/mol was used.[7] Analytic frequency calculations were performed on all the optimized structures at the same level of theory, to identify all the stationary points and to obtain Gibbs free energy corrections at 298.15 K. The concentration correction of 1.9 kcal/mol at room temperature (derived from the free-energy change of 1 mol of an ideal gas from 1 atm (24.5 L/mol, 298.15 K) to 1 M was added for all species except water, for which the corresponding value is 4.3 kcal/mol as the standard state of water is 55.6 M. Unless otherwise specified, the B3LYP*-D3 energies are reported, including Gibbs free energy corrections and D3 dispersion from B3LYP.

The calculation methodology for the redox potentials and pKas is the same as that in our previous study on the dinuclear copper water oxidation catalyst[8] and details of the methodology have been discussed in our recent review.[9] Therefore, only some critical features are described here. The total exergonicity of 72.3 kcal/mol derived from the experimental over-potential (reference potential of 1.6 V, and 0.816 V for water oxidation at pH=7.0) was used to construct the energy diagram for the full catalytic cycle. From this experimental parameter, the reference energy for proton-coupled electron transfer (potential of 1.6 V) can be estimated to be 413.5 kcal/mol, which includes correction for the pH of the solution. To calculate pKas of various species, the experimental solvation free energy of a proton (-264.0 kcal/mol, corresponding to 1 atm in the gas phase and 1 M in the solution phase) was used.[7] In this methodology, the reference energy for one electron oxidation (1.8 V) was estimated to be 138.4 kcal/mol. Compared to the experimental absolute onsite potential (1.8 + 4.281 V),[10] which corresponds to an electron affinity of 135.9 kcal/mol, an error of 1.9 kcal/mol (0.086 V) is present for each oxidation step. The error originates from the difference between the experimental and calculated redox potential for the uncatalyzed water oxidation, in which the experimental value is 0.816 V (pH=7) and the calculated value is 0.730 V.

References:

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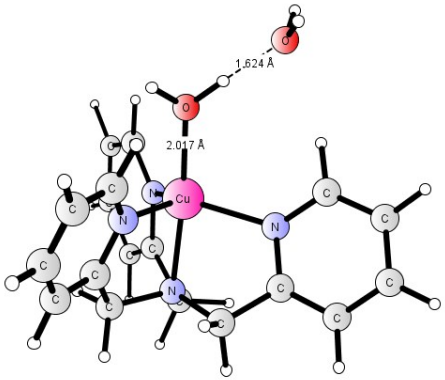
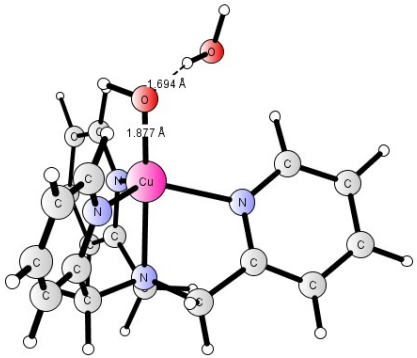
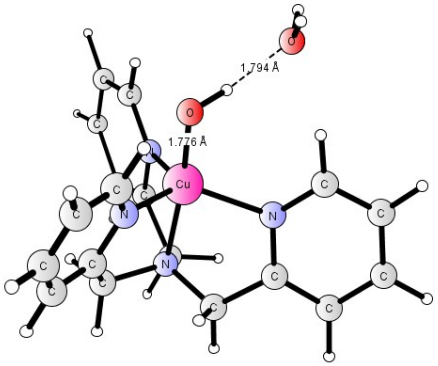
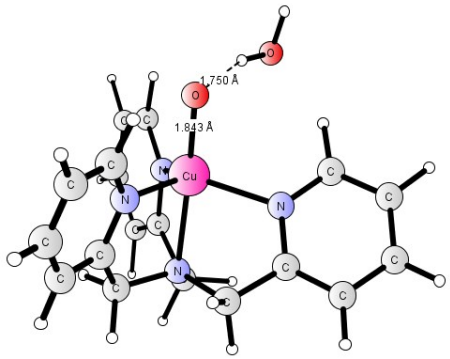
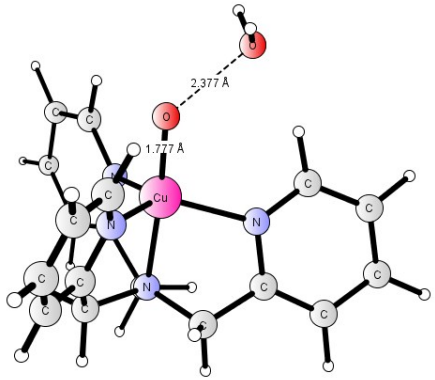
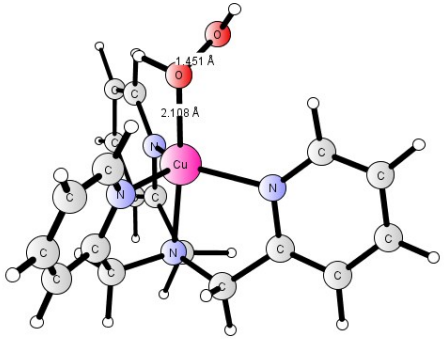
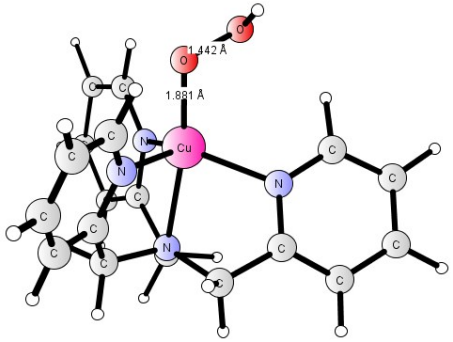
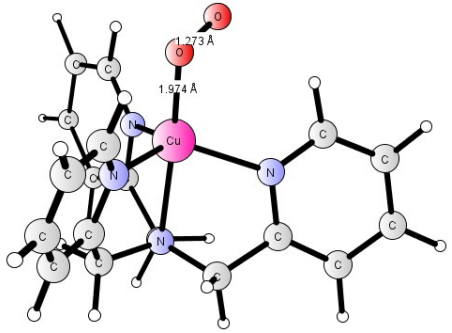
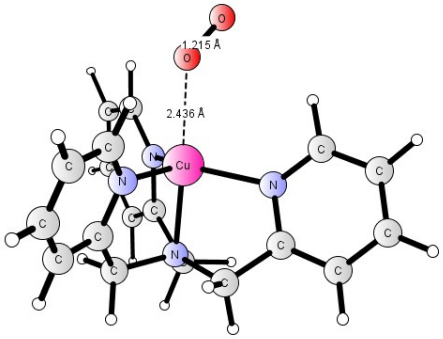
Structures of various species

			
$Cu(II)\text{-}OH_2\text{-}OH_2$ Doublet	$Cu(II)\text{-}OH\text{-}OH_2$ Doublet	$Cu(III)\text{-}OH\text{-}OH_2$ Singlet (0.0) Triplet(10.4 kcal/mol)	$Cu(III)\text{-}O\text{-}OH_2$ Triplet(0.0) Singlet(1.7 kcal/mol)
			
$Cu(IV)\text{-}O\text{-}OH_2$ Doublet	$Int1_{pt}$ Doublet	Int1 Doublet	Int2 Triplet(0.0) Singlet(19.9 kcal/mol)

			
Int3 Quartet(0.0) Doublet(4.0 kcal/mol)			

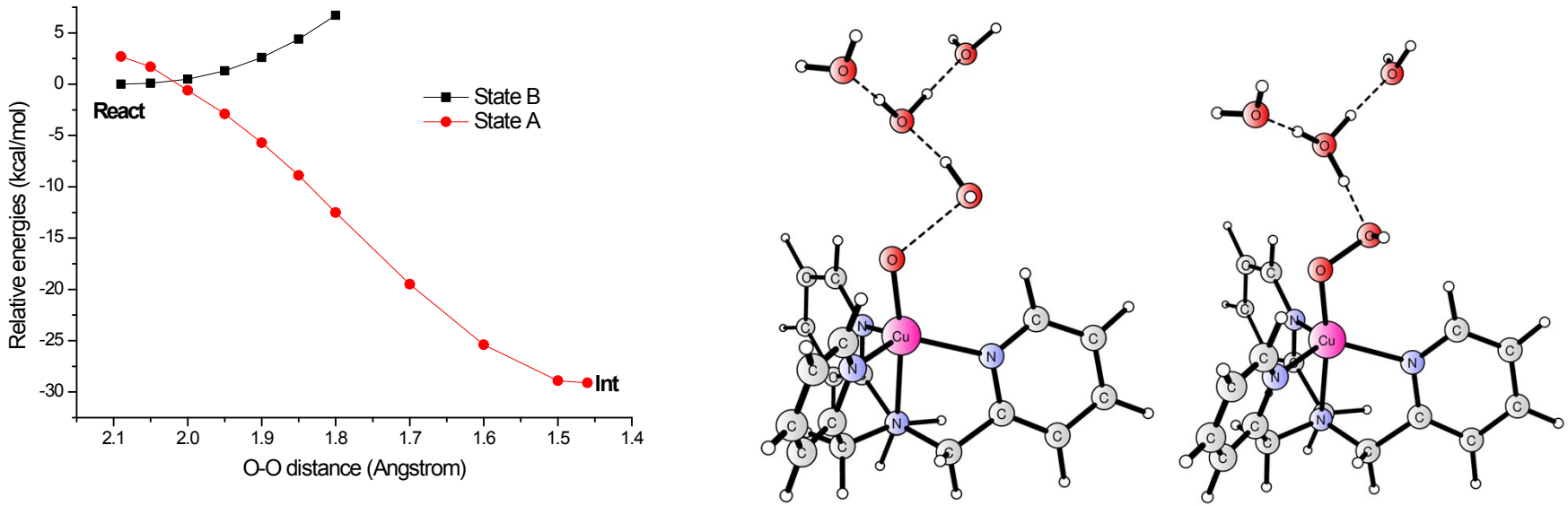


Figure S16. Potential energy surface scan along the O-O bond formation.

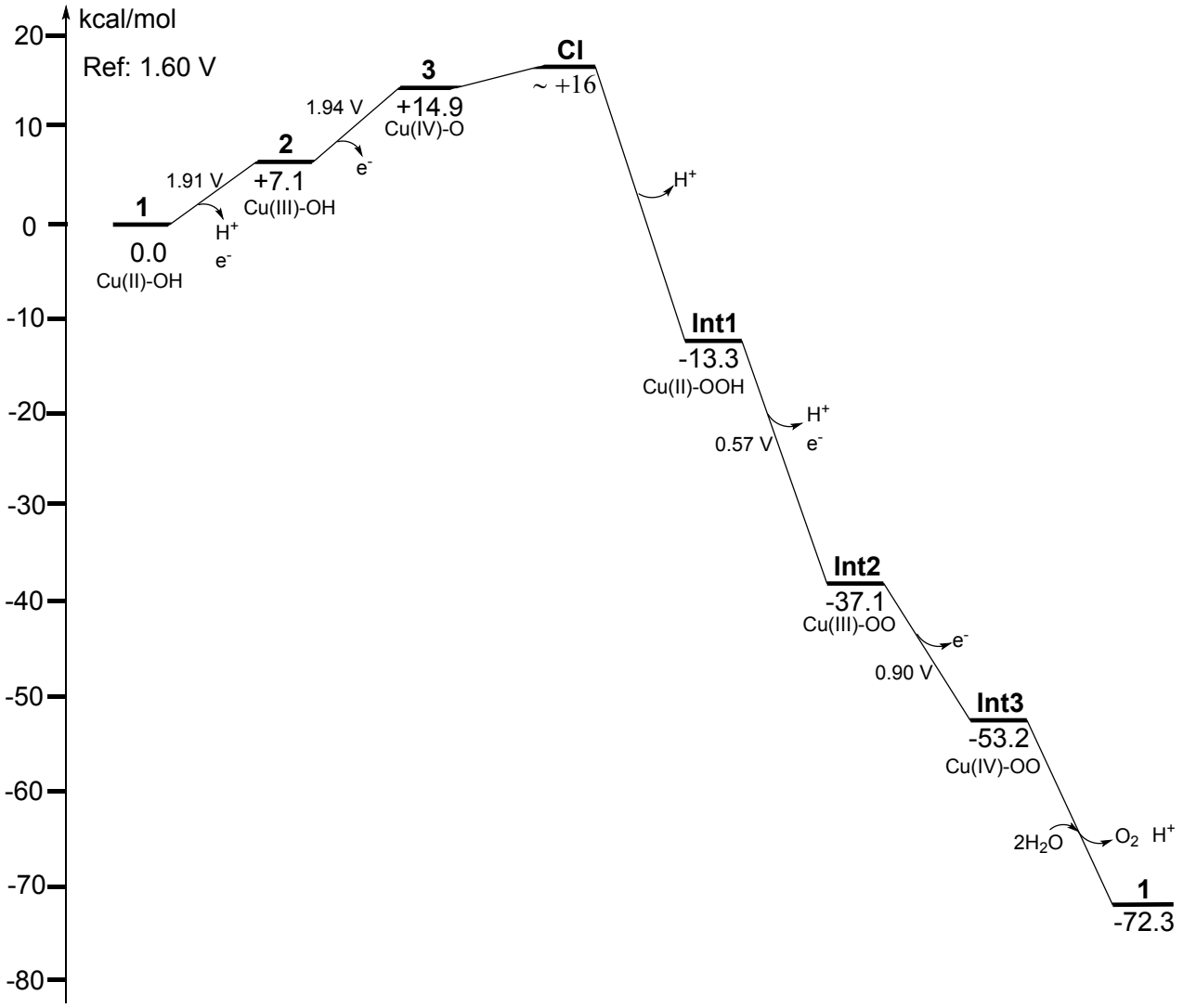


Figure S17. Gibbs free energy diagram for water oxidation catalyzed by mononuclear copper complex 1.

Coordinates for all structures

Cu(II)-OH_2-OH_2 E_{opt}= -1265.57769

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.494190	3.585211	-0.266138
2	6	0	-1.862278	2.536824	0.396934
3	1	0	-2.689570	4.601149	-2.162582
4	6	0	-2.208610	3.797450	-1.614255
5	6	0	-0.695554	1.935476	-1.521519
6	6	0	-1.297132	2.955350	-2.253677
7	1	0	-1.055268	3.091049	-3.302850
8	7	0	-0.976847	1.727731	-0.215580
9	29	0	-0.010044	-0.024907	0.517605
10	6	0	0.359874	1.030450	-2.119985
11	1	0	1.349049	1.460918	-1.931799
12	1	0	0.243154	0.946071	-3.206924
13	7	0	0.329544	-0.318595	-1.486655
14	6	0	1.643934	-1.015293	-1.583632
15	1	0	1.476902	-2.070036	-1.338769
16	1	0	2.025369	-0.975455	-2.611137
17	6	0	-0.787773	-1.155987	-2.009287
18	1	0	-1.631892	-0.487860	-2.212059
19	1	0	-0.505880	-1.621702	-2.961109
20	6	0	-1.212018	-2.189544	-0.989659
21	6	0	-1.795361	-3.402595	-1.344882

22	6	0	-1.460999	-2.661121	1.275612
23	6	0	-2.230927	-4.261559	-0.333921
24	1	0	-1.910846	-3.669291	-2.390425
25	6	0	-2.063971	-3.883944	0.998771
26	1	0	-1.302811	-2.319317	2.292484
27	1	0	-2.690337	-5.212300	-0.584856
28	1	0	-2.388090	-4.524168	1.811501
29	6	0	2.636268	-0.422479	-0.606777
30	6	0	4.009360	-0.419699	-0.839181
31	6	0	4.858057	0.106650	0.136318
32	1	0	4.407983	-0.822133	-1.764801
33	6	0	2.924407	0.601925	1.459767
34	6	0	4.306403	0.630218	1.306198
35	1	0	5.931976	0.116441	-0.020168
36	1	0	2.450407	1.017715	2.343442
37	1	0	4.930013	1.059372	2.082367
38	7	0	2.104682	0.077752	0.530306
39	7	0	-1.044604	-1.831414	0.301851
40	8	0	-0.280339	0.090430	2.513260
41	1	0	0.437288	-0.191361	3.094221
42	1	0	-0.856237	0.743290	3.007212
43	1	0	-3.198847	4.214387	0.266020
44	1	0	-2.061286	2.336039	1.445058
45	8	0	-1.863378	1.772249	3.757903
46	1	0	-2.642994	1.426270	4.215067
47	1	0	-1.543429	2.509487	4.296693

Cu(II)-OH-OH_2 E_{opt}= -1265.258676

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.996680	-3.211068	0.442479
2	6	0	-2.131737	-2.225027	0.910286
3	1	0	-3.745518	-4.190472	-1.330027
4	6	0	-3.091252	-3.420910	-0.932532
5	6	0	-1.515844	-1.639146	-1.254201
6	6	0	-2.344233	-2.619163	-1.797161
7	1	0	-2.413177	-2.743321	-2.873264
8	7	0	-1.396819	-1.471455	0.076366
9	29	0	0.118118	-0.114525	0.654402
10	6	0	-0.797216	-0.620783	-2.119352
11	1	0	-1.482311	0.219550	-2.275395
12	1	0	-0.568056	-1.033597	-3.110300
13	7	0	0.422513	-0.082607	-1.467859
14	6	0	0.664888	1.340415	-1.821488
15	1	0	1.690779	1.580986	-1.521720
16	1	0	0.601309	1.494482	-2.907126
17	6	0	1.612480	-0.930874	-1.720765
18	1	0	1.283717	-1.975888	-1.674898
19	1	0	2.019497	-0.762749	-2.727302
20	6	0	2.671000	-0.703063	-0.660164
21	6	0	4.036129	-0.852884	-0.892394
22	6	0	3.039839	-0.191599	1.581979
23	6	0	4.920143	-0.668714	0.172998
24	1	0	4.399679	-1.107866	-1.882686
25	6	0	4.417098	-0.332530	1.429953

26	1	0	2.568694	0.075340	2.523089
27	1	0	5.988896	-0.780420	0.019497
28	1	0	5.075213	-0.175518	2.277191
29	6	0	-0.295048	2.257977	-1.086556
30	6	0	-0.725138	3.470151	-1.620741
31	6	0	-1.573123	4.273436	-0.855212
32	1	0	-0.405154	3.779225	-2.610891
33	6	0	-1.519939	2.594721	0.861382
34	6	0	-1.980873	3.827806	0.400396
35	1	0	-1.920297	5.225809	-1.243779
36	1	0	-1.848290	2.163621	1.805067
37	1	0	-2.655362	4.414404	1.014221
38	7	0	-0.681369	1.838583	0.132989
39	7	0	2.195380	-0.378501	0.556166
40	8	0	0.024691	-0.137495	2.528680
41	1	0	0.230048	-1.025201	2.852776
42	1	0	-1.592170	0.189901	2.915800
43	1	0	-3.579368	-3.796561	1.144636
44	1	0	-2.040103	-1.988228	1.964572
45	8	0	-2.568882	0.355160	2.911965
46	1	0	-2.800817	0.581810	3.820644

Cu(III)-OH-OH_2 E_{opt}= -1264.888689

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.899165	-1.965934	-0.156875

2	6	0	-2.822470	-1.247529	-0.673440
3	1	0	-4.642334	-3.037598	1.563854
4	6	0	-3.815736	-2.479463	1.135841
5	6	0	-1.611365	-1.548278	1.300820
6	6	0	-2.653954	-2.261833	1.881052
7	1	0	-2.559620	-2.644636	2.892066
8	7	0	-1.702008	-1.049042	0.044485
9	29	0	0.027599	0.001024	-0.462102
10	6	0	-0.284876	-1.329111	1.982327
11	1	0	0.391957	-2.156795	1.745577
12	1	0	-0.382820	-1.284018	3.073090
13	7	0	0.357391	-0.069568	1.479833
14	6	0	1.847677	-0.095566	1.682556
15	1	0	2.207093	0.935517	1.599843
16	1	0	2.075877	-0.447020	2.695094
17	6	0	-0.268591	1.158674	2.082871
18	1	0	-1.337759	0.955500	2.202406
19	1	0	0.149082	1.333736	3.080636
20	6	0	-0.073345	2.339529	1.163932
21	6	0	-0.002402	3.662972	1.583714
22	6	0	0.133512	2.971088	-1.082883
23	6	0	0.128037	4.665656	0.617101
24	1	0	-0.046582	3.908983	2.639671
25	6	0	0.198998	4.317840	-0.732031
26	1	0	0.201888	2.620779	-2.107703
27	1	0	0.183527	5.706618	0.919488
28	1	0	0.311141	5.070823	-1.504105
29	6	0	2.494302	-0.942194	0.614406
30	6	0	3.716580	-1.590504	0.745941

31	6	0	4.239930	-2.259114	-0.366331
32	1	0	4.253481	-1.569255	1.688670
33	6	0	2.304933	-1.601549	-1.626953
34	6	0	3.531363	-2.261353	-1.568032
35	1	0	5.193820	-2.771520	-0.291128
36	1	0	1.694541	-1.551272	-2.523422
37	1	0	3.913909	-2.765499	-2.448345
38	7	0	1.814821	-0.969423	-0.553243
39	7	0	-0.010717	2.019479	-0.148736
40	8	0	-0.067259	0.072252	-2.233738
41	1	0	-0.985375	0.223598	-2.561887
42	1	0	-4.784864	-2.110990	-0.765293
43	1	0	-2.852802	-0.819392	-1.670910
44	8	0	-2.503891	0.279495	-3.515145
45	1	0	-2.963951	1.089925	-3.773517
46	1	0	-2.448347	-0.251253	-4.322515

Cu(III)-O-OH_2 E_{opt}= -1264.580959

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.658329	-3.446721	0.455726
2	6	0	1.988482	-2.306730	0.897383
3	1	0	2.836975	-4.867946	-1.159625
4	6	0	2.328606	-3.984207	-0.786888
5	6	0	0.711955	-2.231174	-1.049815
6	6	0	1.348543	-3.359233	-1.560772

7	1	0	1.085029	-3.739182	-2.542735
8	7	0	1.023793	-1.727614	0.161035
9	29	0	-0.100731	0.004433	0.664813
10	6	0	-0.388456	-1.505878	-1.801649
11	1	0	-1.359744	-1.917269	-1.503825
12	1	0	-0.288785	-1.662456	-2.884408
13	7	0	-0.399798	-0.061106	-1.462891
14	6	0	-1.711279	0.571529	-1.740483
15	1	0	-1.552570	1.656030	-1.755756
16	1	0	-2.091617	0.287206	-2.730939
17	6	0	0.722618	0.679185	-2.088189
18	1	0	1.568177	-0.012619	-2.167736
19	1	0	0.471491	0.997374	-3.108585
20	6	0	1.165948	1.859161	-1.242570
21	6	0	1.762852	2.987814	-1.799950
22	6	0	1.524172	2.653618	0.912328
23	6	0	2.258368	3.975835	-0.947232
24	1	0	1.847038	3.086900	-2.877543
25	6	0	2.147258	3.802643	0.431316
26	1	0	1.430560	2.452450	1.973400
27	1	0	2.729082	4.864366	-1.356113
28	1	0	2.532656	4.539971	1.126394
29	6	0	-2.719173	0.249563	-0.654828
30	6	0	-4.093642	0.211954	-0.878110
31	6	0	-4.942110	-0.012066	0.208218
32	1	0	-4.491608	0.358548	-1.877159
33	6	0	-3.009198	-0.159256	1.619370
34	6	0	-4.394222	-0.197111	1.477550
35	1	0	-6.017265	-0.044093	0.062215

36	1	0	-2.503885	-0.297858	2.570261
37	1	0	-5.023038	-0.373158	2.343088
38	7	0	-2.199847	0.059221	0.571601
39	7	0	1.035204	1.711952	0.089874
40	8	0	-0.025107	0.020650	2.506082
41	1	0	1.674840	0.152709	2.899691
42	1	0	3.430264	-3.890044	1.074751
43	1	0	2.243173	-1.804522	1.828030
44	8	0	2.657700	0.152637	2.846872
45	1	0	2.969908	0.088025	3.757629

Cu(IV)-O-OH_2 E_{opt}= -1264.197794

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.209538	-2.926468	0.259930
2	6	0	2.322493	-1.976563	0.764922
3	1	0	3.762767	-4.074663	-1.482233
4	6	0	3.080636	-3.341463	-1.063682
5	6	0	1.203330	-1.864914	-1.287224
6	6	0	2.063355	-2.797846	-1.853920
7	1	0	1.940376	-3.097901	-2.889510
8	7	0	1.340612	-1.465124	0.000709
9	29	0	-0.035065	0.011877	0.475565
10	6	0	0.024800	-1.272926	-2.019943
11	1	0	-0.862534	-1.892593	-1.852662
12	1	0	0.193613	-1.223170	-3.101736

13	7	0	-0.278312	0.097176	-1.489772
14	6	0	-1.711183	0.482769	-1.720172
15	1	0	-1.783686	1.568301	-1.593803
16	1	0	-1.997986	0.250109	-2.752112
17	6	0	0.674599	1.128731	-2.022412
18	1	0	1.651528	0.645740	-2.129926
19	1	0	0.353807	1.450764	-3.019588
20	6	0	0.787248	2.282127	-1.055606
21	6	0	1.131107	3.579116	-1.420487
22	6	0	0.713740	2.868384	1.209490
23	6	0	1.277267	4.541165	-0.416101
24	1	0	1.284988	3.834604	-2.463859
25	6	0	1.067751	4.183110	0.916008
26	1	0	0.527949	2.519505	2.219974
27	1	0	1.547407	5.559988	-0.675181
28	1	0	1.170232	4.905763	1.717788
29	6	0	-2.600717	-0.204505	-0.712649
30	6	0	-3.940526	-0.505518	-0.929820
31	6	0	-4.677895	-1.077757	0.111650
32	1	0	-4.401497	-0.294721	-1.889271
33	6	0	-2.706708	-1.026905	1.479626
34	6	0	-4.055260	-1.340840	1.331995
35	1	0	-5.726349	-1.318150	-0.033423
36	1	0	-2.158960	-1.209894	2.397906
37	1	0	-4.597316	-1.785258	2.159166
38	7	0	-2.009788	-0.470458	0.475797
39	7	0	0.584170	1.950982	0.239562
40	8	0	0.044280	-0.002286	2.250482
41	1	0	1.329259	-1.129969	4.212636

42	1	0	3.987081	-3.323670	0.902897
43	1	0	2.382431	-1.612799	1.786386
44	8	0	1.898400	-0.671122	3.578452
45	1	0	2.234100	0.104627	4.049983

$Int1_{pt}$ E_{opt}= -1264.238298

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.158251	-1.459499	1.069447
2	6	0	2.901940	-0.927513	1.339985
3	1	0	5.388671	-2.360800	-0.459817
4	6	0	4.417382	-1.944107	-0.212989
5	6	0	2.178283	-1.337780	-0.835290
6	6	0	3.415134	-1.873164	-1.182992
7	1	0	3.592794	-2.227718	-2.193103
8	7	0	1.926309	-0.878875	0.412302
9	29	0	0.007404	-0.054052	0.548298
10	6	0	1.019234	-1.256822	-1.804869
11	1	0	0.404567	-2.159896	-1.719434
12	1	0	1.370417	-1.197415	-2.841957
13	7	0	0.146811	-0.090461	-1.482805
14	6	0	-1.236981	-0.251455	-2.013060
15	1	0	-1.694147	0.743483	-2.042034
16	1	0	-1.208885	-0.626936	-3.042697
17	6	0	0.758052	1.211820	-1.882375
18	1	0	1.839420	1.129667	-1.730410

19	1	0	0.592603	1.396580	-2.950307
20	6	0	0.217038	2.346459	-1.036478
21	6	0	0.135872	3.653212	-1.509133
22	6	0	-0.585217	2.986059	1.051195
23	6	0	-0.312445	4.655647	-0.646292
24	1	0	0.420178	3.884803	-2.530517
25	6	0	-0.680238	4.316550	0.655685
26	1	0	-0.880593	2.667786	2.044685
27	1	0	-0.380797	5.682830	-0.989969
28	1	0	-1.042361	5.063776	1.352844
29	6	0	-2.070656	-1.144921	-1.120209
30	6	0	-3.148542	-1.878992	-1.607242
31	6	0	-3.937475	-2.599108	-0.708527
32	1	0	-3.371909	-1.881524	-2.669186
33	6	0	-2.521235	-1.819512	1.059730
34	6	0	-3.622050	-2.563736	0.649814
35	1	0	-4.784710	-3.176569	-1.064388
36	1	0	-2.250056	-1.758636	2.108027
37	1	0	-4.212847	-3.102649	1.381911
38	7	0	-1.755408	-1.126066	0.195279
39	7	0	-0.137665	2.020690	0.227061
40	8	0	0.067461	-0.161838	2.653018
41	1	0	4.914276	-1.483062	1.846251
42	1	0	2.663574	-0.517311	2.316171
43	8	0	-1.147724	0.361955	3.248288
44	1	0	-0.792682	0.817265	4.036419
45	1	0	0.081473	-1.082956	2.975175

Int1 E_{opt}= -1263.952724

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.186904	-1.402753	1.021103
2	6	0	-2.883184	-1.011189	1.314638
3	1	0	-5.642475	-1.602262	-0.561171
4	6	0	-4.635249	-1.297142	-0.295314
5	6	0	-2.487361	-0.408842	-0.897041
6	6	0	-3.773148	-0.794822	-1.271466
7	1	0	-4.094494	-0.697976	-2.303651
8	7	0	-2.057072	-0.528995	0.372756
9	29	0	-0.038062	-0.026676	0.683142
10	6	0	-1.516146	0.242131	-1.864704
11	1	0	-1.657192	1.327761	-1.809973
12	1	0	-1.735241	-0.058469	-2.898766
13	7	0	-0.109246	-0.036270	-1.501986
14	6	0	0.815304	1.020772	-1.974392
15	1	0	1.826983	0.600008	-1.961215
16	1	0	0.601537	1.307005	-3.013413
17	6	0	0.322910	-1.391979	-1.903278
18	1	0	-0.530877	-2.064108	-1.758743
19	1	0	0.589014	-1.435511	-2.968678
20	6	0	1.474378	-1.880635	-1.044312
21	6	0	2.445624	-2.753052	-1.531584
22	6	0	2.446301	-1.879056	1.065494
23	6	0	3.441900	-3.205359	-0.665027
24	1	0	2.421499	-3.072015	-2.568787

25	6	0	3.443831	-2.760903	0.656070
26	1	0	2.397023	-1.474485	2.071233
27	1	0	4.208281	-3.886836	-1.020766
28	1	0	4.205698	-3.080189	1.358429
29	6	0	0.791030	2.234827	-1.062216
30	6	0	1.058409	3.524896	-1.516472
31	6	0	1.094522	4.567161	-0.587658
32	1	0	1.237766	3.710449	-2.570877
33	6	0	0.577912	2.977921	1.131003
34	6	0	0.853999	4.291953	0.758275
35	1	0	1.303358	5.581161	-0.914174
36	1	0	0.365941	2.686782	2.155633
37	1	0	0.871700	5.076713	1.506298
38	7	0	0.552580	1.979656	0.236074
39	7	0	1.479867	-1.455223	0.234857
40	8	0	-0.231460	0.156521	2.545095
41	1	0	-4.828533	-1.784891	1.807149
42	1	0	-2.466222	-1.066660	2.315332
43	8	0	1.035624	0.001199	3.216492
44	1	0	0.829059	-0.712388	3.841703

Int2 E_{opt}= -1263.33708

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.392150	-0.385740	1.045768
2	6	0	-3.035471	-0.279291	1.340120

3	1	0	-5.851124	-0.290296	-0.543523
4	6	0	-4.802982	-0.205912	-0.274337
5	6	0	-2.508665	0.185522	-0.875727
6	6	0	-3.847264	0.080559	-1.249895
7	1	0	-4.135356	0.224528	-2.286431
8	7	0	-2.116573	-0.000148	0.400927
9	29	0	-0.040906	-0.000181	0.684510
10	6	0	-1.425550	0.582988	-1.865112
11	1	0	-1.310188	1.672470	-1.823008
12	1	0	-1.735621	0.335726	-2.890622
13	7	0	-0.119747	-0.010676	-1.524876
14	6	0	1.025440	0.801779	-1.975210
15	1	0	1.908893	0.153031	-1.969405
16	1	0	0.897644	1.153406	-3.008913
17	6	0	-0.008944	-1.432421	-1.901351
18	1	0	-0.999492	-1.884087	-1.771327
19	1	0	0.260651	-1.557846	-2.960009
20	6	0	0.975547	-2.177882	-1.014855
21	6	0	1.710761	-3.264448	-1.485895
22	6	0	1.873181	-2.420670	1.113554
23	6	0	2.544448	-3.951589	-0.602604
24	1	0	1.629047	-3.567394	-2.524999
25	6	0	2.627406	-3.523915	0.721432
26	1	0	1.911355	-2.031709	2.126612
27	1	0	3.123905	-4.802549	-0.946619
28	1	0	3.266971	-4.025277	1.439201
29	6	0	1.300726	1.974721	-1.047729
30	6	0	1.862499	3.161972	-1.515566
31	6	0	2.179547	4.167257	-0.601388

32	1	0	2.052550	3.293465	-2.576152
33	6	0	1.346022	2.750281	1.140179
34	6	0	1.922006	3.957270	0.752512
35	1	0	2.619019	5.099193	-0.942812
36	1	0	1.122395	2.536329	2.180509
37	1	0	2.154735	4.710680	1.496689
38	7	0	1.040488	1.782209	0.260637
39	7	0	1.062607	-1.766090	0.266116
40	8	0	-0.141075	0.032448	2.655261
41	1	0	-5.101867	-0.610293	1.834038
42	1	0	-2.656863	-0.416281	2.348571
43	8	0	1.001430	-0.050921	3.210289

Int3 E_{opt}= -1262.980089

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.355573	-0.121499	1.032702
2	6	0	2.997250	-0.001523	1.307945
3	1	0	5.802573	-0.551158	-0.511675
4	6	0	4.750490	-0.456543	-0.262429
5	6	0	2.434360	-0.540801	-0.889410
6	6	0	3.774706	-0.663075	-1.240811
7	1	0	4.052892	-0.919881	-2.257807
8	7	0	2.054820	-0.212486	0.368593
9	29	0	0.008865	-0.009624	0.486236
10	6	0	1.309584	-0.828424	-1.862747

11	1	0	1.036301	-1.887300	-1.800198
12	1	0	1.612687	-0.628112	-2.897106
13	7	0	0.090925	-0.033135	-1.526344
14	6	0	-1.177584	-0.682764	-1.973592
15	1	0	-1.958143	0.085552	-1.968824
16	1	0	-1.071670	-1.035816	-3.006066
17	6	0	0.192801	1.399043	-1.936983
18	1	0	1.242551	1.694530	-1.836063
19	1	0	-0.076941	1.503655	-2.994449
20	6	0	-0.665991	2.285642	-1.057710
21	6	0	-1.210916	3.480224	-1.517893
22	6	0	-1.523941	2.647234	1.076911
23	6	0	-1.925959	4.284155	-0.626894
24	1	0	-1.075699	3.781135	-2.551744
25	6	0	-2.084091	3.861174	0.692659
26	1	0	-1.634893	2.278071	2.090736
27	1	0	-2.356150	5.222683	-0.961590
28	1	0	-2.634971	4.453525	1.414570
29	6	0	-1.575914	-1.808882	-1.041737
30	6	0	-2.320614	-2.902637	-1.471131
31	6	0	-2.715948	-3.860255	-0.533888
32	1	0	-2.591785	-3.003705	-2.517026
33	6	0	-1.584553	-2.589330	1.154236
34	6	0	-2.342880	-3.700648	0.800583
35	1	0	-3.301277	-4.719785	-0.844615
36	1	0	-1.261168	-2.433871	2.177943
37	1	0	-2.625682	-4.423653	1.557411
38	7	0	-1.213426	-1.658178	0.254290
39	7	0	-0.823630	1.875503	0.223326

40	8	0	0.018233	-0.058673	2.921709
41	1	0	5.082039	0.050381	1.818959
42	1	0	2.646531	0.267769	2.298524
43	8	0	-0.771154	0.300746	3.772074
