Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Photosensitization Mechanism of Cu(II) Porphyrins

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Comparisons between M06-2X and B3LYP

Table S1: Relative enthalpy (kcal/mol), Gibbs free energy (kcal/mol) and entropy ($cal/(mol \cdot K)$) for the different steps along the reaction cycle.

	B3LYP			M062X		
step	$\triangle H$	$\triangle G$	$\triangle S$	$\triangle H$	$\triangle G$	$\triangle S$
2	-52.5	-51.8	-2.3	-28.2	-29.2	3.4
3b	-16.0	-13.5	-8.0	-10.5	-9.9	-2.0
4a	29.2	24.6	15.5	11.7	10.0	5.6
4c	-24.4	-25.2	3.0	-19.8	-21.6	6.0
5a	18.3	11.3	23.2	-7.9	-9.0	4.0
5c	7.5	3.7	12.6	-1.2	-1.6	1.3

The main differences between B3YLP and M06-2X results arise from the much larger presence of exact exchange in the latter (54%), which has been shown to be crucial to properly describe the coordination of Cu(II) in water solution [J. Phys. Chem. B, 118 (2014) 4840]. Additionally, the ability of M06-2X to (partially) capture non-covalent interactions (dispersion forces) can result in larger relative stabilization of complexes with such interactions. In particular, the smaller amount of exact exchange in B3LYP results in an underestimation of the coordination strength of water molecules to Cu^{2+}. This behavior is clear in the systematic shorter Cu-O distances obtained by B3LYP with respect to M06-2X (Table S2).

In the following we discuss some of the specific factors, mainly related to the coordination of Cu(II) to water or other oxygen ligands, that result in different B3LYP/M06-2X reaction energies.

Step 2. Since complexes **2** and **3** have two and three coordinated water molecules, respectively, B3LYP results in larger exothermicity.

Step 3b. The Cu-O_2 bond in complex $\mathbf{3}^-$ is stronger with M06-2X. On the other hand, M06-2X suggests that one water molecule coordinates to **4**, while B3LYP optimized geometry exhibits a pentacoordinated cooper atom. These two effects cancel to each other, resulting in a small difference between the two methods.

Step 4a. Complex **1** coordinates two water molecules. As a result, M06-2X predicts a less endothermic reaction.

Step 4c. The similarities in the computed energies for this reaction seem to come from a compensation of different effects. M06-2X shows stronger Cu-OOH interaction than B3LYP. In complex **5** M06-2X geometry presents a coordinated water molecule, while only H_2O_2 coordinates copper with B3LYP.

Steps 5a and 5c. M06-2X exhibits stronger stabilization of **1** with respect to **5** and $\mathbf{5}^{-}$ than B3LYP due to the coordination of two water molecules in **1**.

Table S2: Geometrical parameters for the ground and excited state copper porphyrin. The O atoms correspond to the water molecules.

			B3LYP			
complex	R_{Cu-O1}	R_{Cu-O2}	R_{Cu-N1}	R_{Cu-N2}	R_{Cu-N3}	R_{Cu-N4}
1	2.56	2.53	2.05	2.05	2.05	2.05
2	2.44	2.47	2.06	2.07	2.07	2.07
			M062X			
complex	R_{Cu-O1}	R_{Cu-O2}	R_{Cu-N1}	R_{Cu-N2}	R_{Cu-N3}	R_{Cu-N4}
1	2.36	2.36	2.05	2.05	2.05	2.06
2	2.31	2.32	2.06	2.07	2.06	2.08

Table S3: Copper porphyrin affinities to molecular oxygen. Relative enthalpy (kcal/mol), Gibbs free energy (kcal/mol) and entropy ($cal/(mol \cdot K)$).

	B3LYP			M062X		
reaction	$\triangle H$	$\triangle G$	$\triangle S$	$\triangle H$	$\triangle G$	$\triangle S$
${}^{2}[PorCu]^{3+} + O_2 \rightarrow {}^{4}[PorCuO_2]^{3+}$	-20.6	-19.6	-3.6	4.8	4.3	1.4

Table S4: Lowdin-Davidson spin densities for the studied copper porphyrin complexes. O1 indicates the O atom bound to Cu atom in the axial ligand, either from a water molecule or molecular oxygen derivatives. O2 indicates the O atom bound to O1 for the cases where the axial ligand is not a water molecule.

	B3LYP			M062X		
complex	ρ^S_{Cu}	ρ^S_{O1}	ρ^S_{O2}	ρ^S_{Cu}	ρ^S_{O1}	ρ^S_{O2}
1	0.67	0.00	-	0.81	0.00	-
2	0.68	0.01	-	0.81	0.00	-
3	0.64	1.02	0.97	0.78	0.98	1.00
$\mathbf{3}^{-}$	0.65	0.47	0.54	0.79	0.46	0.55
4	0.63	0.63	0.37	0.80	0.63	0.37
$\mathbf{4}^{-}$	0.67	0.00	0.00	0.80	0.00	0.00
5	0.63	0.00	0.00	0.79	0.00	0.00
$\mathbf{5}^{-}$	0.62	0.00	0.00	0.79	0.00	0.00

Bond analysis

Table S5: Natural bond orbital (NBO) analysis for complex $\mathbf{3}^{-}$. E^2 (in kcal/mol) is the second-order perturbative estimate of donor-acceptor interaction in the NBO basis

	E^2
$n_O \rightarrow \mathrm{Cu}(s)$	14.21
$n_O \rightarrow \mathrm{Cu}(p)$	19.08

Computation of reduction potentials

All reduction potentials are calculated with respect to O_2 reduction. The computation of ΔG following Eq. (1) has been designed to cancel out the errors in the computation of the reduction potentials, in particular for the oxygen species, since we expect similar errors for $X \rightarrow X^-$ of these species than in the $O_2 \rightarrow O_2^-$ semi reaction. Therefore, first we compute the Gibbs free energy of Eq. (1) and we obtain $E^0_{SHE}(X/X^-)$ inserting ΔG^0 and the experimental $E^0_{SHE}(O_2/O_2^-)$ reduction potential in Eq. (2).

$$X + O_2^- \rightarrow X^- + O_2 \tag{1}$$

$$E^0_{SHE}(X/X^-) = \frac{-\Delta G^0}{nF} + E^0_{SHE}(O_2/O_2^-) \tag{2}$$

The inclusion of explicit water molecules is taken into consideration as shown in Table S6.

Table S6: Dependence of the computed ΔG and E^0_{SHE} for the reduction of $^{\bullet}$OH with the number of explicit water molecules (N_w).

N_w	ΔG	E^0_{SHE}
0	-20.3	0.55
2	-43.7	1.57
25	-50.0	1.84

From the obtained values 25 explicit water molecules are required for an adequate description of the reduction potential.

Table S7: Reduction potential for the excited copper porphyrin $^4[\text{PorCu}]^{3+}$.

	E^0_{SHE}(V)	
reduction	B3LYP	M062X
$^4[\text{PorCu}]^{3+} + \frac{1}{2}\text{H}_2 \rightarrow {}^3[\text{PorCu}]^{2+} + \text{H}^+$	0.58	1.33

Computation of protonation energies

Concerning the protonation states of some complexes we have estimated their relative *p*Ka values, in order to justify the selected protonation state throught the discussion. Therefore, we have evaluated the following reactions (recall that all non complex charged or radical molecules were treated with 25 explicit water molecules):

$$\mathbf{3}^- + {}^\bullet\text{OOH} \rightarrow \mathbf{4} + {}^-\text{O}_2 \tag{3}$$

$$\mathbf{4}^- + \text{H}_2\text{O}_2 \rightarrow \mathbf{5} + {}^-\text{OOH} \tag{4}$$

where $p\text{Ka}({}^\bullet\text{OOH}/\text{O}_2^-) = 4.88$ and $p\text{Ka}(\text{H}_2\text{O}_2/{}^-\text{OOH}) = 11.75$ have been taken as reference values.

Table S8: Estimated *p*Ka values and the reference values are shown.

complex	*p*Ka
4	7.71
5	26.38

Computation of excitation energies

Table S9: Computed vertical transition wavelengths (λ in nm) and oscillator strengths for the lowest Soret (*S*) and *Q*-bands for the ground state copper porphyrin (**1**), computed with the M06-2X and CAM-B3LYP functionals and the Def2-SVP basis set in water solution.

	M06-2X		CAM-B3LYP	
charac.	λ, nm	strength	λ, nm	strength
Q	550	0.0381	588	0.0500
Q	545	0.0221	577	0.0197
S	402	1.4812	440	0.5860
S	399	1.5197	426	0.3983

Dissociation models

The dissociation energy profiles corresponding to **steps 4a** and **5c** of the reaction cycle shown in Figures 5 and 7 of the main manuscript have been computed at the M06-2X/Def2-SVP level with 6 explicit water molecules (3 above and 3 below the porphyrinic plane) embedded in a polarizable continuum model (IEF-PCM) with $\varepsilon = 79.4$. The computational model for the modeling of the energy profile of **step 5a** (Figure 6) was simplified by replacing the cyanophenyl and pyridine side groups of the porphyrin by hydrogen atoms. In this model we considered two explicit water molecules, 1 above and 1 below the porphyrinic plane. Convergence criteria for the transition states obtained along the three dissociation paths were considered converged at convergence criteria indicated in Table S10.

Table S10: Force and displacement (Displ.) convergence criteria used for the transition states along the dissociation paths, i.e. steps 4a, 5a and 5c, respectively shown in Figures 5, 6 and 7 of the main manuscript. All values in atomic unities.

Step	structure	Max Force	RMS Force	Max Displ.	RMS Displ.
step 4a	TS	0.043596	0.003528	0.041845	0.004756
step 5a	TS	0.002994	0.000532	0.015296	0.001969
step 5c	TS1	0.000803	0.000075	0.250468	0.028712
step 5c	TS2	0.000108	0.000013	0.039495	0.004978

Optimized molecular structures

Complex **1**
nuclear repulsion energy 9904.3531050587 a.u.
C 1.529053 -5.330654 1.177111
C 0.893082 -4.715991 0.094123
C 0.461706 -5.511282 -0.975778
C 0.672296 -6.874639 -0.931308
N 1.284709 -7.444508 0.126671
C 1.710828 -6.702033 1.164903
C 0.678248 -3.245316 0.072869
C 1.816061 -2.441848 -0.057599
N 1.829495 -1.082567 -0.100425
C 3.123932 -0.696841 -0.190795
C 3.988657 -1.866377 -0.216851
C 3.173671 -2.951008 -0.148056
Cu 0.190791 0.141093 0.058141
N -1.050203 -1.503037 0.123362
C -2.407038 -1.498844 0.098863
C -2.905588 -2.860993 0.124835
C -1.811580 -3.670229 0.191279
C -0.653128 -2.797169 0.155052
C -3.224463 -0.352030 0.093208
C -4.699824 -0.551551 -0.021635
C -5.351480 -0.176018 -1.204403
C -6.723308 -0.357084 -1.338325
C -7.453763 -0.915492 -0.280292
C -6.812076 -1.289687 0.907765
C -5.439082 -1.106742 1.029814
C -8.876943 -1.103351 -0.414181
N -10.017245 -1.253188 -0.522267
C 3.584358 0.636585 -0.189567
C 5.053070 0.844872 -0.294645
C 5.761144 0.424849 -1.430887
C 7.123945 0.628801 -1.505613
N 7.790962 1.225642 -0.497951
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C 5.777729 1.457912 0.735197
C 9.242685 1.438215 -0.636333
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N -1.451719 1.364426 0.201178
C -1.447346 2.718219 0.230445
C -2.811551 3.219899 0.230898
C -3.624017 2.130516 0.201918
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C 1.024870 3.084714 0.070627
N 1.416349 1.784171 0.003275

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O -0.222334 0.023162 -2.261042
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C -0.136307 5.838243 -0.825028
C -0.354899 7.201272 -0.748789
N -0.933260 7.747712 0.335579
C -1.314061 6.977417 1.374402
C -1.120097 5.611344 1.352137
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O 0.445719 -0.176096 2.383756
O -2.143443 -1.072237 3.124580
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O -0.863045 -2.752590 -2.763635
O 2.161990 -2.445557 2.853062
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H -2.237790 9.384594 0.513775
H -0.794243 9.662076 -0.512007
H -3.114329 4.263467 0.241878
H -4.710399 2.112627 0.200165
H -4.935979 -1.391379 1.955897
H -7.387438 -1.717505 1.728755
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H -7.232082 -0.069992 -2.258785
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H -0.023767 -5.052681 -1.839172
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H 1.869004 -4.732774 2.025038
H 1.998576 -9.197843 -0.782156
H 2.057669 -9.185858 1.008689
H 0.486304 -9.387130 0.170164
H 5.073673 -1.865374 -0.273461
H 9.715734 0.486076 -0.897156
H 9.417132 2.177356 -1.426095
H 9.639512 1.804134 0.313881
H 5.250070 -0.052038 -2.266910
H 7.717079 0.330793 -2.369978
H 7.746716 2.099758 1.385804
H 5.285600 1.788490 1.649510
H 4.312676 3.451257 -0.158287

H 3.469476 -3.996812 -0.156219
H 2.190290 5.038401 0.089445
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H -0.415791 -0.518518 2.687386
H -1.068481 0.486507 -2.411076
H -0.433708 -0.917333 -2.410875
H -2.781769 1.678674 -3.682516
H -2.925007 2.061405 -2.208189
H -1.084266 -2.909956 -3.690972
H -1.674057 -2.978505 -2.285366
H 2.982753 -2.382564 2.343265
H 2.454513 -2.467404 3.773940
H -2.665638 -0.448390 2.602030
H -2.287195 -1.921895 2.685106

Complex **2**
nuclear repulsion energy 9913.0205839039 a.u.
C -5.465290 -0.866675 1.105234
C -4.693768 -0.442870 0.018825
C -5.297477 -0.193559 -1.219089
C -6.666483 -0.373267 -1.373340
C -7.436435 -0.798706 -0.282628
C -6.837004 -1.043423 0.960396
C -3.223199 -0.255740 0.153948
C -2.751324 1.046260 0.143334
N -1.417302 1.425283 0.198426
C -1.396727 2.750720 0.117020
C -2.729581 3.283870 -0.009451
C -3.575057 2.211442 0.034025
Cu 0.183369 0.133788 -0.007447
O -0.340573 -0.078990 -2.214790
C -0.194791 3.570512 0.108922
C 1.114289 3.059723 0.005843
N 1.443518 1.748375 -0.172545
C 2.794272 1.682742 -0.163960
C 3.363947 2.979546 0.044687
C 2.315169 3.843587 0.163529
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C 6.986559 1.493860 -1.491272
N 7.772783 1.022457 -0.503186
C 7.244164 0.386178 0.555696
C 5.877251 0.195128 0.657132
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O -1.105586 -2.809973 -2.517004
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H -0.093467 -7.614572 -1.530341

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H 9.434162 2.307316 -0.538730
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H 7.490088 1.996206 -2.316845
H 7.940690 0.038722 1.317500
H 5.473139 -0.313441 1.531933
H 4.421443 3.213045 0.134194
H 3.334973 -4.095631 -0.345965
H 2.370267 4.905730 0.381094
H 1.147986 -0.742525 2.436943
H -0.290963 -0.178319 2.585850
H -1.139134 0.444845 -2.423034
H -0.618009 -1.006202 -2.344432
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H -2.946758 2.062937 -2.334278
H -1.324576 -3.101076 -3.411507
H -1.882484 -3.046353 -1.989019
H 3.052213 -2.302293 2.170550
H 2.505645 -2.492202 3.583060
H -2.586945 0.026026 2.626180
H -2.249615 -1.427419 2.949413

Complex **3**
nuclear repulsion energy 10227.0356263077 a.u.
C 5.605753 0.273327 1.265868
C 4.932632 0.700339 0.113756
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C 7.029803 1.493657 -0.807980
C 7.691430 1.066457 0.351097
C 6.978545 0.454477 1.390751
C 3.458190 0.496941 -0.004197
C 2.998062 -0.823319 -0.131801
N 1.691899 -1.225516 -0.188132
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C 3.073086 -3.039362 -0.528755
C 3.871755 -1.957868 -0.329235
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N 1.276942 1.634719 -0.113972
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C -0.756751 -2.936303 -0.417709
N -1.144935 -1.637958 -0.280094
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C -2.985888 -3.013016 -0.107434
C -1.908197 -3.811629 -0.319924
C -3.312591 -0.523805 0.058874
C -2.873387 0.804566 0.017245
N -1.575419 1.200372 -0.098586
C -1.582016 2.560651 -0.105775
C -2.940551 3.051457 0.022144
C -3.740750 1.960008 0.114105
C -1.472633 8.985626 -0.730657
C 9.115271 1.256679 0.474146
N 10.256098 1.408649 0.572897
C 0.774545 -4.842167 -0.764714
C 1.478684 -5.635534 0.152522
C 1.641344 -6.984931 -0.089801
N 1.133688 -7.554721 -1.200127
C 0.453587 -6.821718 -2.099739
C 0.257522 -5.466922 -1.906663
C 1.308575 -9.004359 -1.401469
O 0.078674 0.337657 -2.589950
C -4.755043 -0.761496 0.341289
C -5.746693 -0.493909 -0.610431
C -7.066897 -0.746553 -0.291058
N -7.407927 -1.236750 0.917510
C -6.473094 -1.484584 1.853731
C -5.134220 -1.255259 1.594184
C -8.827704 -1.520625 1.192816
O 1.602743 0.398235 2.758894
H 1.893518 -5.210447 1.066137
H 2.171748 -7.645306 0.595994
H 0.077396 -7.348268 -2.976076
H -0.289027 -4.900106 -2.659864
H 0.646761 -9.539166 -0.710829
H 2.353134 -9.263886 -1.203339
H 1.052201 -9.250845 -2.434861

H 3.386964 -4.056465 -0.746007
H 4.957519 -1.922530 -0.346924
H 5.044480 -0.200216 2.073303
H 7.499957 0.127259 2.290441
H 5.137063 1.633593 -1.823125
H 7.590786 1.964406 -1.615428
H 4.169271 3.291078 0.131441
H 2.034630 4.891955 -0.072253
H -1.657330 4.632905 -2.217779
H -2.089608 7.114944 -2.423124
H -0.311321 7.861962 1.252009
H 0.183353 5.435864 1.608904
H -2.139923 9.300812 0.078737
H -0.522571 9.526470 -0.670530
H -1.945487 9.167305 -1.698776
H -4.820005 1.938669 0.237236
H -9.423470 -0.642832 0.923561
H -9.136216 -2.386089 0.595656
H -8.945010 -1.737776 2.257308
H -5.471466 -0.091615 -1.588827
H -7.884838 -0.571205 -0.989612
H -6.828852 -1.866830 2.809804
H -4.378590 -1.431305 2.362883
H -4.021159 -3.319415 0.017209
H -3.240723 4.094864 0.064616
H -1.894149 -4.896351 -0.380576
H -0.235283 -0.400844 -3.132597
H 0.970608 0.529536 -2.916255
O 0.460884 0.620717 2.541591
O 0.163855 -2.203636 2.526567
H 0.018895 -3.156120 2.443657
H 0.798070 -1.986378 1.825814
O -0.138580 -0.761157 5.001176
H 0.248667 -1.369717 4.355739
H -0.966749 -0.527303 4.554327
O -2.173025 -0.684798 2.966601
H -1.444473 -1.244631 2.635788
H -2.118359 0.113748 2.424117
O -3.891098 0.569232 -2.925179
H -3.342013 -0.213999 -2.796138
H -3.245273 1.301832 -2.896421
O -1.795050 2.451249 -3.041128
H -1.089050 1.819926 -2.802299
H -1.669226 2.596945 -3.988096

Complex **3**$^{-}$
nuclear repulsion energy 10291.8632995078 a.u.

C -5.491464 -1.384612 1.047611
C -4.655550 -1.649455 -0.046424
C -5.112211 -2.495587 -1.066863
C -6.379115 -3.064070 -1.002875
C -7.204452 -2.789763 0.096057
C -6.759316 -1.948696 1.124573
C -3.294013 -1.046334 -0.119036
C -3.189647 0.351413 -0.131977
N -2.032566 1.076826 -0.085478
C -2.392503 2.386911 -0.087575
C -3.837144 2.508229 -0.164677
C -4.330114 1.245054 -0.196587
Cu -0.125082 0.343631 -0.105764
N -0.892430 -1.565324 -0.318430
C -0.153973 -2.709206 -0.217126
C -1.019018 -3.836500 0.044708
C -2.289761 -3.349853 0.082699
C -2.193599 -1.923833 -0.136492
C 1.238607 -2.791785 -0.351436
C 1.861231 -4.138800 -0.219093
C 2.671099 -4.431863 0.884395
C 3.236702 -5.690466 0.986999
N 3.022754 -6.627782 0.045636
C 2.238919 -6.369087 -1.020240
C 1.639095 -5.134953 -1.179816
C -1.512452 3.485265 -0.067440
C -0.113054 3.398081 -0.147175
N 0.598772 2.250088 -0.295043
C 1.914423 2.605052 -0.329926
C 2.045268 4.041586 -0.161933
C 0.786767 4.534717 -0.055301
C 2.991904 1.725473 -0.483854
C 2.889994 0.329330 -0.622319
N 1.747841 -0.390032 -0.515094
C 2.102588 -1.703596 -0.546966
C 3.533234 -1.824920 -0.750223
C 4.023694 -0.555600 -0.804354
C 3.648994 -7.955759 0.162269
C -8.518560 -3.377734 0.170928
N -9.571476 -3.848853 0.232651
C -2.117367 4.838611 0.033364
C -2.916453 5.188136 1.133102
C -3.477013 6.446739 1.203446
N -3.272700 7.350886 0.224651
C -2.510435 7.048721 -0.841671
C -1.920173 5.803909 -0.961960
C -3.902076 8.677973 0.341916

O -0.270531 -1.295255 -3.156296
C 4.363105 2.290442 -0.376628
C 4.886736 3.185389 -1.318245
C 6.163364 3.683567 -1.146063
N 6.910519 3.321612 -0.084606
C 6.433251 2.463313 0.836106
C 5.162947 1.931286 0.716121
C 8.265956 3.883285 0.053330
O -0.451988 -0.848674 2.585551
H -3.093298 4.481852 1.943793
H -4.097576 6.767823 2.039955
H -2.394177 7.825108 -1.596773
H -1.322367 5.585955 -1.846558
H -3.533868 9.165034 1.250929
H -4.988508 8.550467 0.393417
H -3.636134 9.272771 -0.535137
H -4.399950 3.435919 -0.221451
H -5.369432 0.940485 -0.280341
H -5.137630 -0.736187 1.850634
H -7.403425 -1.743528 1.979731
H -4.468652 -2.702842 -1.923693
H -6.732425 -3.716310 -1.801529
H -3.206531 -3.900459 0.274456
H -0.699811 -4.864965 0.192670
H 0.989412 -4.939623 -2.039064
H 2.113215 -7.181290 -1.736186
H 3.866250 -5.976295 1.829074
H 2.844939 -3.714731 1.696189
H 4.407834 -8.060807 -0.621079
H 4.113448 -8.041602 1.147781
H 2.876919 -8.722703 0.044662
H 5.055884 -0.252774 -0.960588
H 8.866161 3.577402 -0.810340
H 8.193280 4.974957 0.096840
H 8.712808 3.501465 0.974414
H 4.309477 3.488134 -2.191458
H 6.622204 4.378345 -1.849508
H 7.092588 2.223831 1.669477
H 4.777937 1.250454 1.479268
H 2.975651 4.601025 -0.118188
H 4.087522 -2.754396 -0.853218
H 0.497504 5.570880 0.096580
H -0.894795 -0.840664 -3.738596
H -0.632638 -1.190461 -2.258291
O 0.422964 -0.093782 1.996303
O 0.931762 -1.909616 4.544028
H 1.258979 -1.131807 5.011506

H 0.365727 -1.528904 3.812380
O 3.292671 -2.890705 3.574073
H 2.402196 -2.721633 3.949984
H 3.503369 -1.996467 3.256006
O 3.148033 -0.334783 2.386164
H 2.162613 -0.273492 2.335527
H 3.394631 -0.755964 1.552632
O 2.395301 -0.411474 -3.611527
H 1.493068 -0.694718 -3.384865
H 2.953273 -1.027668 -3.123530
O -0.590732 -4.097317 -3.162758
H -0.435122 -3.139303 -3.256135
H -1.308513 -4.146777 -2.518603

Complex **4**
nuclear repulsion energy 10592.5731008222 a.u.
C 5.505210 -1.247712 0.883363
C 5.037235 -0.420819 -0.148295
C 5.979213 0.156209 -1.011654
C 7.323112 -0.099064 -0.824887
N 7.743977 -0.894365 0.178124
C 6.863111 -1.463601 1.022728
C 3.577404 -0.190789 -0.289231
C 2.775357 -1.338209 -0.447766
N 1.424365 -1.375002 -0.363797
C 1.049489 -2.676532 -0.527490
C 2.219592 -3.491015 -0.811272
C 3.292377 -2.664608 -0.735262
Cu 0.175431 0.256499 -0.300033
O 0.653566 -0.003632 2.099922
O -0.250166 -0.000257 3.021833
C -0.258190 -3.155885 -0.377512
C -0.513688 -4.603371 -0.581016
C 0.180793 -5.597028 0.120033
C -0.098499 -6.930137 -0.120958
N -1.031467 -7.288881 -1.019957
C -1.725216 -6.355906 -1.703659
C -1.491604 -5.011450 -1.503951
C -1.314932 -8.711635 -1.278097
C 9.186800 -1.155752 0.322487
N -1.070228 1.861954 -0.071019
C -2.429540 1.822710 0.031254
C -2.972257 3.158131 -0.127289
C -1.911149 3.990289 -0.296616
C -0.721689 3.161310 -0.232504
C -3.200376 0.670624 0.262538
C -2.689261 -0.641743 0.281275

N -1.424809 -1.005318 -0.066843
C -1.379862 -2.358105 -0.043507
C -2.649355 -2.890099 0.412403
C -3.462158 -1.815845 0.624085
C 0.603231 3.649960 -0.295645
C 0.791826 5.122478 -0.352685
C 0.274213 5.963838 0.644371
C 0.480315 7.325938 0.569129
N 1.172035 7.866208 -0.453997
C 1.679884 7.088623 -1.426454
C 1.506479 5.716937 -1.400563
C 1.362732 9.326845 -0.486931
C -4.671491 0.834348 0.431183
C -5.197700 1.619205 1.466272
C -6.571494 1.777566 1.605345
C -7.435230 1.149508 0.697830
C -6.922863 0.360968 -0.340950
C -5.547650 0.205709 -0.466638
C -8.860949 1.314447 0.834695
N -10.003317 1.446166 0.944016
N 1.797668 1.500308 -0.312457
C 1.761729 2.857863 -0.260795
C 3.110483 3.380541 -0.097540
C 3.938299 2.308514 -0.051599
C 3.100015 1.129682 -0.217721
O 0.271945 -3.697227 2.757070
O 2.682643 -2.053078 2.525840
O 0.853772 -1.655520 4.538073
O -2.687478 0.383093 -2.918070
O -3.565137 -2.193926 -2.508103
O -0.028330 0.243616 -2.565233
H -0.274971 5.557974 1.493398
H 0.107572 8.019399 1.322821
H 2.220472 7.594558 -2.225459
H 1.920966 5.116529 -2.209881
H 1.906451 9.632145 0.413397
H 0.380611 9.810162 -0.519730
H 1.938356 9.587513 -1.378305
H -1.939510 5.062910 -0.467159
H -4.026421 3.421254 -0.127462
H -4.521482 2.099959 2.174797
H -6.977826 2.383273 2.415357
H -5.141566 -0.409433 -1.272821
H -7.599815 -0.121955 -1.045554
H -4.484414 -1.820314 0.993448
H -2.884669 -3.939141 0.578286
H -2.063731 -4.275647 -2.072500

H -2.462822 -6.725591 -2.415502
H 0.412147 -7.736861 0.403319
H 0.923710 -5.337107 0.873191
H -1.098474 -8.928377 -2.329730
H -0.679731 -9.321545 -0.631353
H -2.370466 -8.906909 -1.061061
H 4.335499 -2.923826 -0.894506
H 9.511586 -1.811839 -0.492888
H 9.724543 -0.203563 0.278801
H 9.363011 -1.639415 1.286447
H 5.671485 0.789832 -1.842860
H 8.095017 0.314732 -1.473485
H 7.278360 -2.088586 1.812403
H 4.799655 -1.701857 1.584644
H 5.014001 2.318150 0.099251
H 2.227685 -4.550904 -1.048470
H 3.383319 4.426786 0.010481
H -3.150031 1.002060 -2.340282
H -3.032833 -0.505379 -2.692816
H -0.031793 -4.555309 3.085034
H -0.472194 -3.352659 2.240662
H 0.485658 -2.491964 4.190828
H 1.750198 -1.677804 4.144893
H 2.142536 -1.336292 2.147330
H 2.153630 -2.845081 2.332910
H -0.998421 0.335383 -2.726885
H 0.183238 -0.646151 -2.876026
H -4.262658 -2.490265 -3.108190
H -3.823012 -2.526592 -1.636553
H 0.133067 -0.640386 3.756571

Complex **4**$^{-}$
nuclear repulsion energy 10619.8693781889 a.u.
C 5.337873 1.125494 1.086824
C 4.669898 1.611333 -0.045389
C 5.373359 2.432640 -0.935714
C 6.696093 2.734664 -0.679024
N 7.314789 2.255622 0.418094
C 6.661117 1.467976 1.293093
C 3.249888 1.227675 -0.249103
C 2.994575 -0.145168 -0.417671
N 1.780753 -0.739941 -0.377852
C 1.982646 -2.068939 -0.587720
C 3.392017 -2.322106 -0.825780
C 4.024324 -1.125278 -0.699063
Cu 0.026183 0.214585 0.094012
O 0.445301 0.289376 2.159533

O -0.193704 -0.858821 2.750479
C 0.989773 -3.057981 -0.541478
C 1.426504 -4.471097 -0.680503
C 2.330958 -5.029938 0.231677
C 2.728582 -6.346031 0.084174
N 2.258428 -7.099384 -0.926085
C 1.381500 -6.591908 -1.815514
C 0.946199 -5.285927 -1.715737
C 2.700873 -8.495703 -1.086900
C 8.723224 2.620078 0.653200
N -1.805109 1.164260 -0.048806
C -3.029360 0.561226 0.024976
C -4.076191 1.557010 -0.072467
C -3.458354 2.760317 -0.199823
C -2.031824 2.501582 -0.157025
C -3.273271 -0.815048 0.133529
C -2.287330 -1.811658 0.035461
N -0.961461 -1.594664 -0.204338
C -0.377071 -2.822611 -0.307623
C -1.363160 -3.859123 -0.095969
C -2.549145 -3.228697 0.126097
C -1.036944 3.498972 -0.229289
C -1.481988 4.914180 -0.277957
C -2.291532 5.462655 0.729437
C -2.684815 6.782942 0.654090
N -2.302802 7.562106 -0.377619
C -1.524604 7.069199 -1.357728
C -1.100723 5.753910 -1.333183
C -2.765530 8.960155 -0.422362
C -4.688763 -1.255928 0.306355
C -5.372689 -0.980643 1.497677
C -6.688486 -1.395973 1.668709
C -7.332445 -2.089720 0.635146
C -6.660694 -2.361345 -0.564538
C -5.343812 -1.944513 -0.724336
C -8.696448 -2.523970 0.806069
N -9.789220 -2.872604 0.942942
N 0.934929 2.032538 -0.273660
C 0.348079 3.256427 -0.240455
C 1.365285 4.291840 -0.141707
C 2.562749 3.656066 -0.106744
C 2.279095 2.235522 -0.213021
O 1.423294 -3.007162 2.511872
O 2.853778 -0.432164 2.592323
O 1.563421 -1.340600 4.824800
O -0.707107 -0.058215 -2.740529
O -3.467868 -0.816150 -3.072878

O 2.120010 -0.164648 -3.404173
H -2.602545 4.866087 1.586470
H -3.306170 7.254685 1.415234
H -1.258796 7.752862 -2.163033
H -0.482347 5.384315 -2.150593
H -2.503462 9.450294 0.520886
H -3.851839 8.968282 -0.563871
H -2.273779 9.468354 -1.255470
H -3.932210 3.728920 -0.332315
H -5.144093 1.354226 -0.069849
H -4.863555 -0.444212 2.300219
H -7.217438 -1.188118 2.598875
H -4.811334 -2.125321 -1.660029
H -7.172877 -2.892325 -1.367205
H -3.514091 -3.683032 0.333585
H -1.176487 -4.929855 -0.094836
H 0.244862 -4.901603 -2.455934
H 1.050228 -7.263903 -2.607088
H 3.425395 -6.826404 0.770048
H 2.701430 -4.438939 1.069876
H 3.246052 -8.585811 -2.032739
H 3.354626 -8.756928 -0.251351
H 1.821444 -9.148029 -1.092624
H 5.084975 -0.921719 -0.821530
H 9.315277 2.332199 -0.221759
H 8.787358 3.701663 0.814576
H 9.081554 2.087387 1.537382
H 4.903791 2.823590 -1.838016
H 7.297305 3.357625 -1.341016
H 7.228218 1.129344 2.159344
H 4.797229 0.502277 1.805743
H 3.545228 4.109822 -0.008925
H 3.841759 -3.280251 -1.071445
H 1.189299 5.361699 -0.072721
H -0.921262 0.794027 -2.330543
H -0.877180 -0.704392 -2.030769
H 0.860918 -3.786571 2.419452
H 0.799488 -2.249250 2.392502
H 1.537369 -2.234494 4.447500
H 2.179060 -0.907622 4.192172
H 1.921551 -0.075064 2.335196
H 2.878970 -1.303677 2.170898
H 1.190769 -0.149251 -3.119984
H 2.477836 -0.946019 -2.966778
H -2.554294 -0.537920 -3.243142
H -3.841651 -0.070801 -2.585810
H 0.178370 -0.862891 3.656780

Complex **5**
nuclear repulsion energy 10668.2406695530 a.u.
C 2.803877 1.603633 -0.259754
N 1.448203 1.725699 -0.320829
C 1.170675 3.058535 -0.318358
C 2.404614 3.820662 -0.240901
C 3.416120 2.918367 -0.187850
Cu 0.088210 0.197293 -0.262568
N -1.272827 -1.313385 -0.082562
C -2.604355 -1.196045 0.168358
C -3.199507 -2.510733 0.305804
C -2.202011 -3.409499 0.098338
C -0.999270 -2.638331 -0.147671
C -3.321344 0.009746 0.241899
C -4.800845 -0.073295 0.419281
C -5.410445 0.446627 1.568843
C -6.788570 0.370307 1.734852
C -7.572404 -0.228304 0.739268
C -6.975644 -0.745766 -0.418288
C -5.596163 -0.666364 -0.571493
C 0.267349 -3.206151 -0.379826
C 0.316340 -4.681211 -0.549472
C 0.995289 -5.498189 0.363300
C 1.008016 -6.865431 0.166152
N 0.379766 -7.417577 -0.890557
C -0.282985 -6.653161 -1.779916
C -0.335798 -5.279739 -1.635352
C 0.452870 -8.875169 -1.090114
C -9.002031 -0.310776 0.905662
N -10.147648 -0.377428 1.037966
C -0.111012 3.631713 -0.308875
C -0.195112 5.111928 -0.401799
C -0.793837 5.874383 0.612754
C -0.860110 7.247437 0.492857
N -0.358962 7.872625 -0.590660
C 0.226560 7.172225 -1.578635
C 0.324699 5.794985 -1.509037
C -0.439846 9.342048 -0.665105
C 3.516732 0.394458 -0.263455
C 2.940427 -0.887286 -0.340540
N 1.612982 -1.157361 -0.297097
C 1.477165 -2.505113 -0.440029
C 2.781394 -3.115596 -0.617304
C 3.692818 -2.112918 -0.534541
C 4.996294 0.457600 -0.137819
C 5.617785 -0.110478 0.982187

C 6.993854 -0.053158 1.101750
N 7.745145 0.539063 0.155127
C 7.174767 1.094560 -0.932188
C 5.805024 1.070863 -1.104519
C 9.209807 0.607149 0.299875
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O -0.321059 -0.863063 2.845868
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Complex **5**$^{-}$
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