Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Predictive power of long-range corrected functionals on the spectroscopic properties of tetrapyrrole derivatives for photodynamic therapy

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Supporting Information

S1: Red-most absorption wavelengths of chlorin obtained with two different basis sets used in excited state calculations.

S2: Selected bond lengths of the optimized chlorin, porphyrin, protoporphyrin IX and phytoporphyrin geometries obtained using the B3LYP, ωB97XD and M06 functionals.

S3: Cartesian coordinates of the optimized geometries of chlorin, porphyrin, protoporphyrin IX and phytoporphyrin in THF using the B3LYP, ωB97XD and M06 functionals.

S4: CI descriptions for the two peaks in the Q-band.

S5: Dihedral angles for the ground singlet state and the first excited triplet state geometries optimized with various functionals.

Table S1: Red-most absorption wavelengths (in nm) of chlorin obtained with two different basis sets used in excited state calculations.

		Wavelength	
Opt	TD-DFT	6-311G(2d,2p)	6-311+G(2d,2p)
B3LYP	ωB97X	636	639
ωB97XD	ωB97X	615	618
M06	ωB97X	625	627
Exp		626	

S2: Selected bond lengths of the optimized chlorin, porphyrin, protoporphyrin IX and phytoporphyrin geometries obtained using the B3LYP, ωB97XD and M06 functionals.

S2-1: Selected bond lengths of chlorin
(the geometry displayed below is optimized with B3LYP)

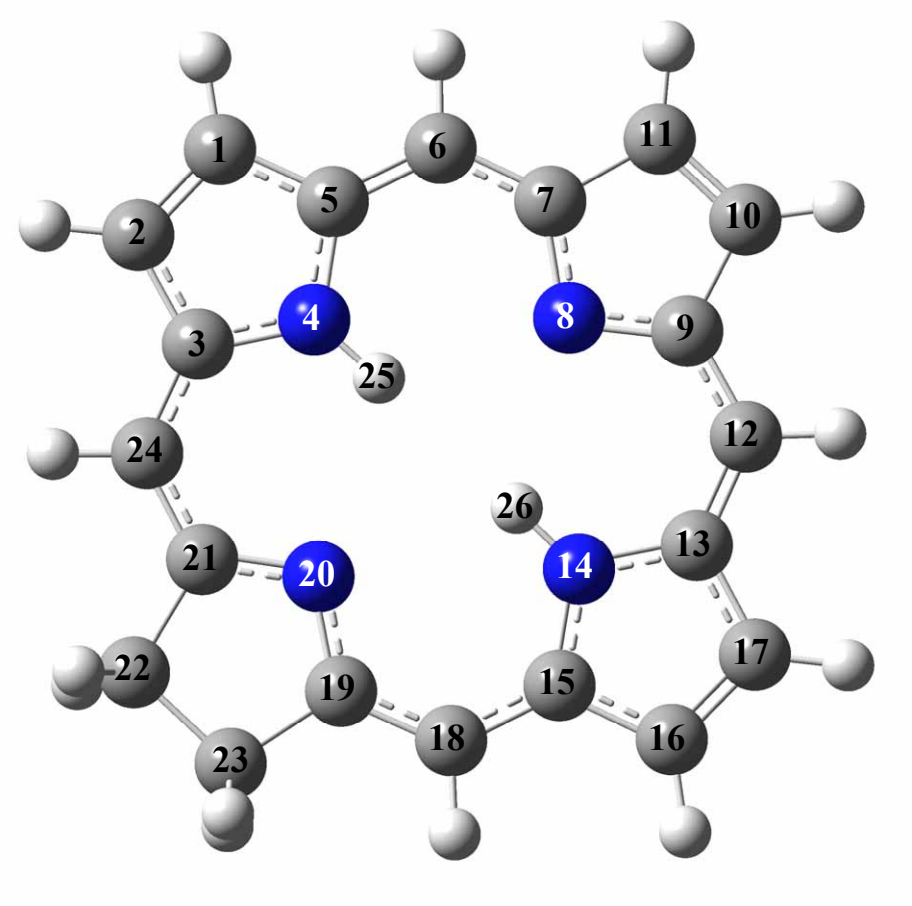

Table S2-1: Selected bond lengths of chlorin.

Atoms	Distance (Å)		
	B3LYP	ωB97XD	M06
1 – 2	1.369	1.361	1.364
2 – 3	1.433	1.433	1.426
3 – 4	1.364	1.352	1.358
4 – 5	1.380	1.378	1.377
1 – 5	1.430	1.429	1.423
5 – 6	1.384	1.373	1.376
6 – 7	1.403	1.403	1.398
7 – 8	1.363	1.356	1.358
8 – 9	1.363	1.356	1.358
9 – 10	1.449	1.440	1.440
10 – 11	1.359	1.358	1.355
7 – 11	1.449	1.440	1.440
9 – 12	1.403	1.403	1.398
12 – 13	1.384	1.373	1.376
13 – 14	1.380	1.378	1.377
14 – 15	1.364	1.352	1.358
15 – 16	1.433	1.433	1.426
16 – 17	1.369	1.361	1.364
13 – 17	1.430	1.429	1.423
15 – 18	1.399	1.396	1.393
18 – 19	1.387	1.380	1.381
19 – 20	1.349	1.346	1.345
20 – 21	1.349	1.346	1.345
21 – 22	1.521	1.515	1.508
22 – 23	1.535	1.527	1.522
19 – 23	1.521	1.515	1.508
21 – 24	1.387	1.380	1.381
3 – 24	1.399	1.396	1.393
(25 -- 26)	2.186	2.159	2.145
(8 -- 20)	4.166	4.132	4.117

S2-2: Selected bond lengths of porphyrin
(the geometry displayed below is optimized with B3LYP)

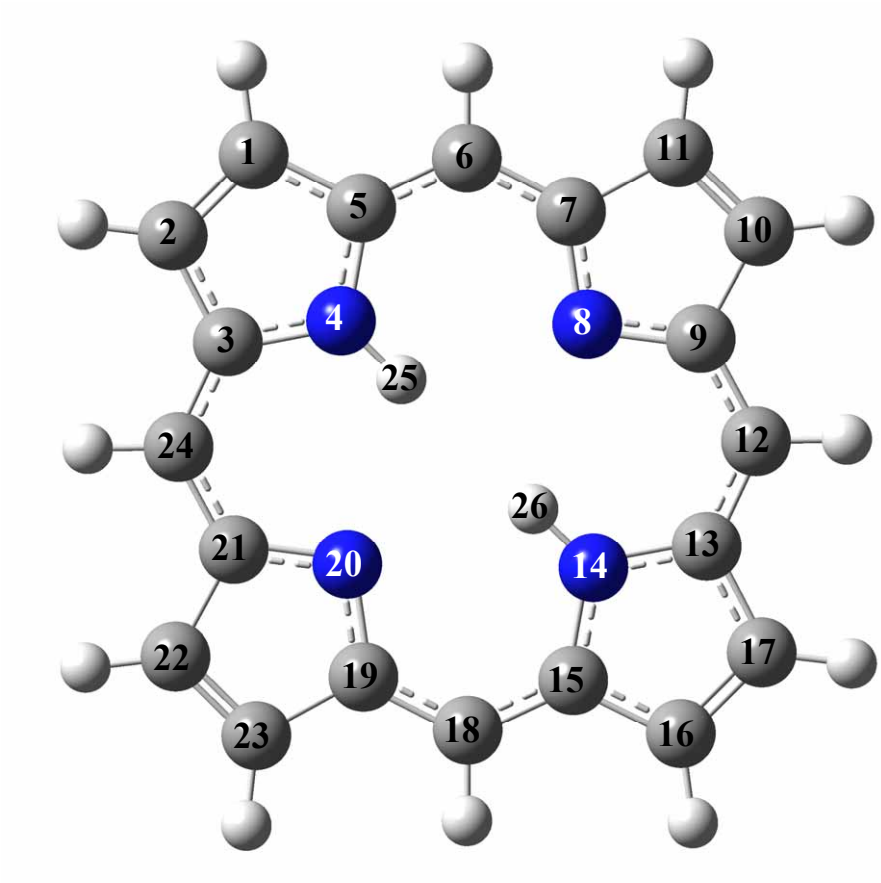

Table S2-2: Selected bond lengths of porphyrin.

Atoms	Distance (Å)		
	B3LYP	WB97XD	M06
1 – 2	1.368	1.362	1.363
2 – 3	1.433	1.430	1.425
3 – 4	1.370	1.363	1.365
4 – 5	1.370	1.363	1.365
1 – 5	1.433	1.430	1.425
5 – 6	1.390	1.385	1.384
6 – 7	1.397	1.392	1.392
7 – 8	1.362	1.356	1.357
8 – 9	1.362	1.356	1.357
9 – 10	1.457	1.454	1.448
10 – 11	1.353	1.348	1.349
7 – 11	1.457	1.454	1.448
9 – 12	1.397	1.392	1.392
12 – 13	1.390	1.385	1.384
13 – 14	1.370	1.363	1.365
14 – 15	1.370	1.363	1.365
15 – 16	1.433	1.430	1.425
16 – 17	1.368	1.362	1.363
13 – 17	1.433	1.430	1.425
15 – 18	1.390	1.385	1.384
18 – 19	1.397	1.392	1.392
19 – 20	1.362	1.356	1.357
20 – 21	1.362	1.356	1.357
21 – 22	1.457	1.454	1.448
22 – 23	1.353	1.348	1.349
19 – 23	1.457	1.454	1.448
21 – 24	1.397	1.392	1.392
3 – 24	1.390	1.385	1.384
(25 -- 26)	2.207	2.183	2.167
(8 -- 20)	4.056	4.024	4.011

S2-3: Selected bond lengths of protoporphyrin IX
(the geometry displayed below is optimized with B3LYP)

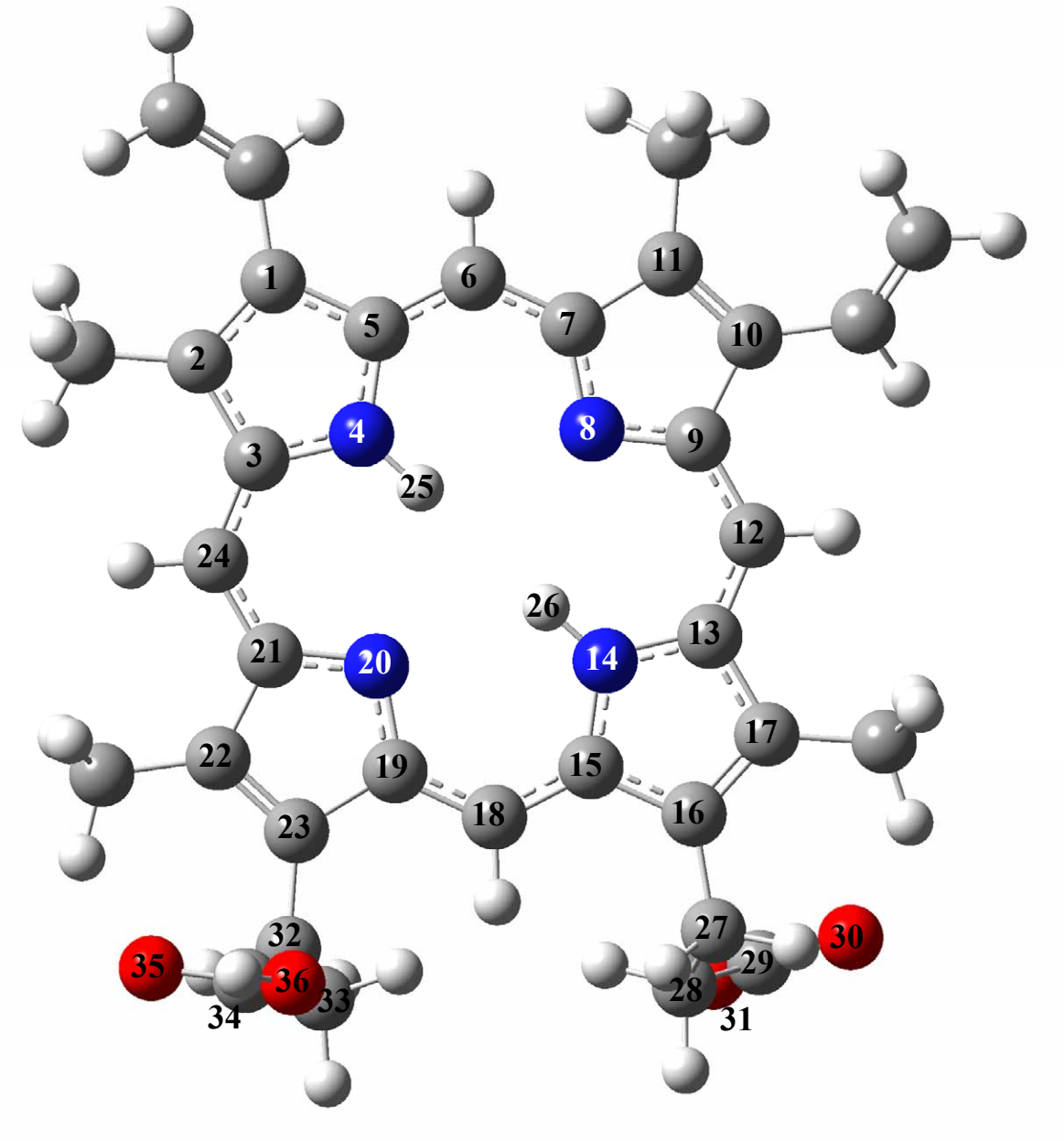

Table S2-3: Selected bond lengths of protoporphyrin IX.

Atoms	Distance (Å)		
	B3LYP	WB97XD	M06
1 – 2	1.388	1.382	1.383
2 – 3	1.435	1.428	1.427
3 – 4	1.370	1.362	1.365
4 – 5	1.366	1.359	1.362
1 – 5	1.446	1.434	1.436
5 – 6	1.390	1.390	1.385
6 – 7	1.397	1.385	1.391
7 – 8	1.364	1.363	1.360
8 – 9	1.355	1.345	1.350
9 – 10	1.470	1.464	1.459
10 – 11	1.371	1.361	1.365
7 – 11	1.461	1.458	1.452
9 – 12	1.400	1.400	1.395
12 – 13	1.386	1.376	1.379
13 – 14	1.368	1.363	1.364
14 – 15	1.367	1.361	1.363
15 – 16	1.445	1.445	1.437
16 – 17	1.377	1.365	1.371
13 – 17	1.444	1.444	1.436
15 – 18	1.389	1.378	1.382
18 – 19	1.399	1.399	1.395
19 – 20	1.358	1.347	1.353
20 – 21	1.363	1.362	1.359
21 – 22	1.467	1.463	1.457
22 – 23	1.361	1.353	1.356
19 – 23	1.469	1.464	1.459
21 – 24	1.393	1.382	1.388
3 – 24	1.393	1.393	1.387
16 – 27	1.503	1.498	1.491
27 – 28	1.538	1.530	1.524

Atoms	Distance (Å)		
	B3LYP	WB97XD	M06
28 – 29	1.509	1.505	1.498
29 – 30	1.209	1.206	1.203
29 – 31	1.347	1.338	1.338
23 – 32	1.502	1.498	1.491
32 – 33	1.539	1.532	1.524
33 – 34	1.509	1.506	1.498
34 – 35	1.209	1.206	1.203
34 – 36	1.347	1.337	1.337
(25 -- 26)	2.213	2.180	2.174
(8 -- 20)	4.069	4.035	4.023
(27 -- 32)	5.428	5.368	5.385
(28 -- 33)	5.574	5.520	5.598

S2-4: Selected bond lengths of phytoporphyrin
(the geometry displayed below is optimized with B3LYP)

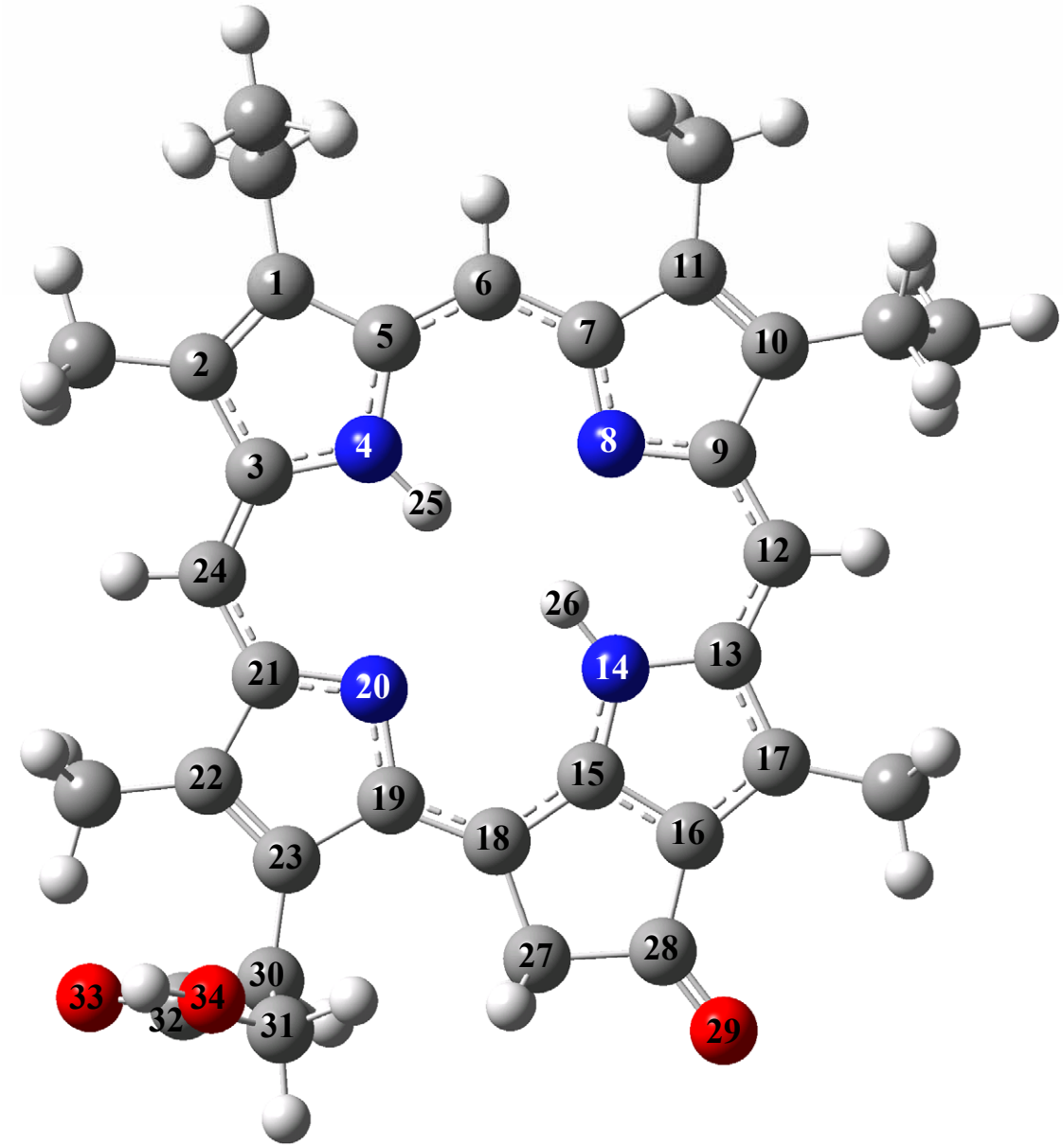

Table S2-4: Selected bond lengths of phytoporphyrin.

Atoms	Distance (Å)		
	B3LYP	WB97XD	M06
1 – 2	1.374	1.357	1.366
2 – 3	1.445	1.453	1.437
3 – 4	1.371	1.367	1.368
4 – 5	1.371	1.366	1.367
1 – 5	1.448	1.456	1.440
5 – 6	1.386	1.369	1.379
6 – 7	1.404	1.413	1.400
7 – 8	1.352	1.332	1.346
8 – 9	1.371	1.380	1.368
9 – 10	1.466	1.463	1.456
10 – 11	1.362	1.353	1.356
7 – 11	1.468	1.413	1.457
9 – 12	1.391	1.371	1.385
12 – 13	1.399	1.409	1.394
13 – 14	1.386	1.378	1.380
14 – 15	1.345	1.337	1.340
15 – 16	1.414	1.400	1.407
16 – 17	1.391	1.394	1.386
13 – 17	1.432	1.414	1.424
15 – 18	1.403	1.412	1.398
18 – 27	1.525	1.519	1.513
27 – 28	1.548	1.542	1.536
28 – 29	1.218	2.212	1.211
16 – 28	1.460	1.458	1.456
18 – 19	1.392	1.370	1.385
19 – 20	1.372	1.380	1.368
20 – 21	1.347	1.329	1.342
21 – 22	1.468	1.466	1.459
22 – 23	1.363	1.354	1.357
19 – 23	1.472	1.467	1.460

Atoms	Distance (Å)		
	B3LYP	WB97XD	M06
23 – 30	1.503	1.498	1.491
30 – 31	1.540	1.532	1.524
31 – 32	1.510	1.506	1.499
21 – 24	1.405	1.414	1.401
32 – 33	1.209	1.206	1.203
32 – 33	1.347	1.337	1.338
3 – 24	1.385	1.368	1.378
(25 -- 26)	2.090	2.065	2.059
(8 -- 20)	4.189	4.154	4.145
(27 -- 30)	3.283	3.246	3.221
(27 -- 31)	3.553	3.520	3.454

S3: Cartesian coordinates of the optimized geometries of chlorin, porphyrin, protoporphyrin IX and phytoporphyrin in THF using the B3LYP, ωB97XD and M06 functionals.

S3-1: Chlorin optimized with B3LYP.
S3-2: Chlorin optimized with ωB97XD.
S3-3: Chlorin optimized with M06.
S3-4: Porphyrin optimized with B3LYP.
S3-5: Porphyrin optimized with ωB97XD.
S3-6: Porphyrin optimized with M06.
S3-7: Protoporphyrin IX optimized with B3LYP.
S3-8: Protoporphyrin IX optimized with ωB97XD.
S3-9: Protoporphyrin IX optimized with M06.
S3-10: Phytoporphyrin optimized with B3LYP.
S3-11: Phytoporphyrin optimized with ωB97XD.
S3-12: Phytoporphyrin optimized with M06.

S3-1: Chlorin optimized with B3LYP.

C	0.685608	-1.021683	4.141915
H	1.362077	-0.559626	4.841848
C	-0.458476	-1.719818	4.421836
H	-0.881895	-1.928991	5.390121
C	-1.034125	-2.149588	3.181985
N	-0.212683	-1.692906	2.193560
H	-0.351616	-1.836697	1.205810
C	0.854812	-0.996647	2.722613
C	1.870636	-0.404312	1.992449
C	2.017212	-0.392072	0.597672
N	1.161927	-0.975763	-0.288484
C	1.680648	-0.722523	-1.523102
C	1.119674	-1.141183	-2.738449
H	1.646968	-0.863930	-3.641464
C	-0.040764	-1.874335	-2.916702
C	2.904793	0.046642	-1.420285
H	3.507476	0.375174	-2.252545
C	3.115362	0.253122	-0.094071
H	3.925439	0.785032	0.379914
H	2.632510	0.103660	2.568520
N	-0.864671	-2.330203	-1.907950
H	-0.692345	-2.165964	-0.928686
C	-1.924827	-3.019403	-2.419206
C	-1.771815	-3.005205	-3.843876
H	-2.458169	-3.471856	-4.530729
C	-0.630158	-2.311332	-4.143615
H	-0.219196	-2.111077	-5.119331
C	-2.957769	-3.621256	-1.692903
H	-3.707296	-4.121296	-2.291462
C	-3.136508	-3.655245	-0.317990
N	-2.315405	-3.093616	0.593387
C	-2.793054	-3.323050	1.834131
C	-2.208018	-2.891823	3.015347
H	-2.715837	-3.157491	3.932759
C	-4.082463	-4.130307	1.821370
H	-3.959327	-5.061648	2.374502
H	-4.889758	-3.577205	2.301597
C	-4.324520	-4.356760	0.323029
H	-5.261946	-3.921343	-0.023608
H	-4.342501	-5.412475	0.052094

S3-2: Chlorin optimized with ωB97XD.

C	0.679530	-1.027248	4.127104
H	1.359257	-0.563678	4.823707
C	-0.458127	-1.720935	4.406044
H	-0.885750	-1.932706	5.372261
C	-1.031510	-2.149056	3.164497
N	-0.219657	-1.698504	2.181343
H	-0.362227	-1.844258	1.194545
C	0.846915	-1.003300	2.708587
C	1.856506	-0.414274	1.988583
C	2.004492	-0.400608	0.593171
N	1.150740	-0.982324	-0.285679
C	1.669834	-0.727979	-1.512674
C	1.106936	-1.147389	-2.727786
H	1.632640	-0.870873	-3.632721
C	-0.044599	-1.874744	-2.899704
C	2.886163	0.036164	-1.415434
H	3.486144	0.363403	-2.250538
C	3.097165	0.241753	-0.089664
H	3.906044	0.772678	0.388138
H	2.617804	0.093122	2.567123
N	-0.867914	-2.330698	-1.893162
H	-0.699044	-2.168796	-0.913054
C	-1.917145	-3.013718	-2.404328
C	-1.766940	-3.001126	-3.829380
H	-2.456344	-3.469763	-4.512305
C	-0.632048	-2.310586	-4.126784
H	-0.217347	-2.107557	-5.100941
C	-2.950817	-3.617247	-1.685536
H	-3.700801	-4.118158	-2.282822
C	-3.120426	-3.645996	-0.316078
N	-2.297878	-3.083003	0.588944
C	-2.779487	-3.314387	1.824711
C	-2.204416	-2.889553	3.005314
H	-2.713537	-3.155569	3.921922
C	-4.064393	-4.117112	1.812647
H	-3.938495	-5.044756	2.370256
H	-4.867686	-3.557363	2.290780
C	-4.302943	-4.346225	0.321754
H	-5.237794	-3.911325	-0.030692
H	-4.312840	-5.401300	0.049853

S3-3: Chlorin optimized with M06.

C	0.677800	-1.027678	4.120205
H	1.359893	-0.562409	4.815940
C	-0.461600	-1.723188	4.400168
H	-0.890315	-1.936011	5.367767
C	-1.033685	-2.150198	3.165652
N	-0.219629	-1.697923	2.176724
H	-0.360823	-1.842766	1.186752
C	0.844160	-1.003904	2.707465
C	1.856026	-0.413582	1.984706
C	1.998202	-0.403991	0.593884
N	1.142299	-0.987671	-0.283521
C	1.664404	-0.732097	-1.510380
C	1.108824	-1.147479	-2.724249
H	1.637693	-0.869552	-3.630288
C	-0.045745	-1.876627	-2.897588
C	2.880978	0.031930	-1.412433
H	3.480109	0.357599	-2.251221
C	3.090711	0.238350	-0.089639
H	3.899263	0.770037	0.392168
H	2.620182	0.096022	2.562825
N	-0.865761	-2.329960	-1.889093
H	-0.694403	-2.166686	-0.906780
C	-1.919414	-3.015185	-2.404358
C	-1.768186	-3.001658	-3.822315
H	-2.459442	-3.470958	-4.505879
C	-0.630656	-2.310375	-4.119804
H	-0.213275	-2.105992	-5.094377
C	-2.949589	-3.615539	-1.684582
H	-3.703786	-4.118290	-2.281400
C	-3.117861	-3.643248	-0.314058
N	-2.293829	-3.080452	0.587917
C	-2.776977	-3.313793	1.821386
C	-2.202923	-2.889390	3.003658
H	-2.715460	-3.158136	3.921723
C	-4.054982	-4.114134	1.808098
H	-3.929667	-5.044176	2.367620
H	-4.860387	-3.559684	2.295348
C	-4.295289	-4.338388	0.321919
H	-5.233031	-3.903155	-0.031577
H	-4.313824	-5.394659	0.043617

S3-4: Porphyrin optimized with B3LYP.

C	0.788258	-1.161316	4.319130
C	1.728671	-0.470950	5.191355
N	1.359427	-0.595517	6.496422
C	0.218736	-1.339695	6.487857
C	-0.152426	-1.702565	5.126855
C	2.850860	0.218945	4.725532
C	3.791723	0.900058	5.489525
N	3.779992	1.013938	6.854598
C	4.849731	1.749881	7.291153
C	5.588778	2.127341	6.123423
C	4.947164	1.611976	5.030848
C	5.136169	2.054528	8.617034
C	4.402618	1.676766	9.744629
N	3.261927	0.932593	9.736063
C	2.892682	0.808034	11.041123
C	3.833039	1.498484	11.913353
C	4.773746	2.039702	11.105627
C	1.770488	0.118130	11.506939
C	0.829654	-0.563024	10.742953
C	-0.325930	-1.274729	11.201607
C	-0.967545	-1.790099	10.109036
C	-0.228357	-1.412849	8.941328
N	0.841538	-0.677146	9.377900
C	-0.514822	-1.717460	7.615443
H	-0.609807	-1.367222	12.236689
H	-1.869447	-2.379006	10.091718
H	1.543705	-0.273703	8.775240
H	6.024289	2.648241	8.784972
H	5.636326	2.626252	11.379937
H	3.762954	1.548421	12.988492
H	1.608830	0.108087	12.576155
H	3.077525	0.610940	7.457207
H	5.230987	1.704551	3.995758
H	6.490626	2.716329	6.140732
H	3.012467	0.229071	3.656311
H	-1.402995	-2.311089	7.447497
H	-1.014966	-2.289191	4.852595
H	0.858448	-1.211334	3.244003

S3-5: Porphyrin optimized with ωB97XD.

C	0.795395	-1.155284	4.335952
C	1.732247	-0.467024	5.209105
N	1.366932	-0.589466	6.509223
C	0.231384	-1.330513	6.497796
C	-0.141618	-1.694339	5.140487
C	2.848799	0.218875	4.739664
C	3.784517	0.896674	5.503908
N	3.771168	1.008971	6.862133
C	4.836137	1.741334	7.294627
C	5.576089	2.119683	6.130969
C	4.937104	1.606450	5.042894
C	5.124473	2.046693	8.614727
C	4.389940	1.667631	9.734681
N	3.254405	0.926563	9.723255
C	2.889078	0.804141	11.023371
C	3.825936	1.492390	11.896525
C	4.762938	2.031463	11.091989
C	1.772524	0.118243	11.492812
C	0.836819	-0.559574	10.728570
C	-0.315799	-1.269305	11.189579
C	-0.954786	-1.782533	10.101504
C	-0.214803	-1.404233	8.937850
N	0.850214	-0.671945	9.370351
C	-0.503152	-1.709572	7.617749
H	-0.596594	-1.359765	12.226168
H	-1.856818	-2.371967	10.080243
H	1.552209	-0.268680	8.767879
H	6.012905	2.640571	8.782890
H	5.626977	2.618577	11.361834
H	3.751867	1.539780	12.971862
H	1.610972	0.108240	12.562430
H	3.069068	0.605866	7.464589
H	5.217890	1.696925	4.006304
H	6.478109	2.709134	6.152230
H	3.010333	0.228906	3.670044
H	-1.391606	-2.303416	7.449583
H	-1.005664	-2.281444	4.870645
H	0.869472	-1.202679	3.260616

S3-6: Porphyrin optimized with M06.

C	0.799468	-1.152060	4.341978
C	1.732386	-0.466670	5.212078
N	1.370014	-0.586990	6.514205
C	0.233868	-1.328800	6.498901
C	-0.138180	-1.691508	5.147148
C	2.848422	0.218761	4.741182
C	3.783312	0.895951	5.504508
N	3.767426	1.006851	6.865101
C	4.835029	1.740719	7.295713
C	5.571737	2.117215	6.135202
C	4.932440	1.603713	5.046371
C	5.122865	2.045634	8.614597
C	4.387458	1.665916	9.733576
N	3.251312	0.924104	9.718271
C	2.888940	0.803784	11.020399
C	3.821843	1.489198	11.890497
C	4.759497	2.028637	11.085327
C	1.772905	0.118351	11.491295
C	0.838023	-0.558851	10.727970
C	-0.311131	-1.266574	11.186104
C	-0.950426	-1.780078	10.097273
C	-0.213694	-1.403617	8.936764
N	0.853939	-0.669797	9.367381
C	-0.501538	-1.708520	7.617880
H	-0.590392	-1.355813	12.224983
H	-1.853736	-2.370570	10.073327
H	1.557959	-0.265398	8.763321
H	6.013575	2.641116	8.784303
H	5.625761	2.616980	11.352612
H	3.745127	1.535023	12.967539
H	1.611863	0.108968	12.564021
H	3.063352	0.602536	7.469154
H	5.211691	1.692969	4.007490
H	6.475037	2.707723	6.159146
H	3.009449	0.228168	3.668454
H	-1.392263	-2.303980	7.448172
H	-1.004447	-2.279846	4.879863
H	0.876175	-1.197872	3.264935

S3-7: Protoporphyrin IX optimized with B3LYP.

C	-4.367550	2.497791	0.360926
C	-5.851297	2.685245	0.346090
H	-6.278117	2.632406	1.351426
H	-6.114360	3.662414	-0.060005
H	-6.346491	1.925211	-0.256621
C	-3.390363	3.448139	0.519764
C	-3.513020	4.885025	0.725094
H	-2.666129	5.477578	0.395868
C	-4.540331	5.542636	1.274605
H	-4.517051	6.620499	1.362153
H	-5.412000	5.040267	1.668344
C	-2.112462	2.731746	0.401387
N	-2.312931	1.407687	0.194206
C	-3.666232	1.234259	0.160069
C	-4.314219	0.012908	-0.042122
C	-3.736461	-1.235097	-0.248037
N	-2.394375	-1.490934	-0.270086
H	-1.676512	-0.797998	-0.113950
C	-2.153107	-2.821101	-0.494211
C	-0.890457	-3.405163	-0.578206
H	-0.879060	-4.470917	-0.749909
C	0.350672	-2.783452	-0.461855
C	-3.426061	-3.467979	-0.625435
C	-3.613203	-4.921462	-0.921904
H	-4.453198	-5.072979	-1.600202
H	-2.725694	-5.351104	-1.382125
H	-3.824553	-5.495253	-0.016205
C	-4.406621	-2.496085	-0.468492
C	-5.856260	-2.623431	-0.537147
H	-6.389219	-1.707831	-0.767805
C	-6.587904	-3.725104	-0.341270
H	-7.665153	-3.685964	-0.428314
H	-6.155721	-4.677629	-0.073169
H	-5.393103	0.032729	-0.033668
N	0.547973	-1.452111	-0.243099
C	1.896520	-1.290064	-0.198738
C	2.599599	-2.567434	-0.393481
C	1.625447	-3.502574	-0.561559
C	2.551193	-0.067977	-0.010220
H	3.630116	-0.091475	-0.000258
C	4.091223	-2.744032	-0.400242
C	4.721856	-2.869810	1.001192
H	5.801386	-2.714035	0.907513
H	4.342253	-2.097627	1.669822
H	4.353323	-3.641956	-0.958413
H	4.547688	-1.901843	-0.925104
C	1.770973	-4.970327	-0.820214
C	1.974717	1.182105	0.169430
H	1.101315	-5.552952	-0.184715
H	2.786428	-5.298825	-0.612110
H	1.524765	-5.219823	-1.856150
N	0.629941	1.429955	0.194221
H	-0.080886	0.727383	0.055756
C	0.390862	2.759346	0.414702
C	-0.859813	3.350424	0.507052
H	-0.853085	4.414129	0.690065
C	1.675644	3.407306	0.536419
C	1.865073	4.867582	0.806895
H	1.748063	5.091685	1.870672
H	1.129802	5.466783	0.268938
H	2.854663	5.188338	0.489528
C	2.647172	2.443862	0.384287
C	4.139301	2.609398	0.428468
C	4.803007	2.735051	-0.957198
H	5.879004	2.575990	-0.835649
H	4.438702	1.963038	-1.634182
H	4.391875	3.502320	0.998010
H	4.572670	1.759621	0.959558
C	4.530549	-4.254068	1.670229
O	4.698841	-5.266041	0.937839
O	4.262008	-4.259338	2.896083
C	4.633032	4.119193	-1.632372
O	4.413514	4.123321	-2.867212
O	4.768781	5.131372	-0.892863

S3-8: Protoporphyrin IX optimized with ωB97XD.

C	-4.277130	2.561199	0.300322
C	-5.754855	2.769904	0.265147
H	-6.206890	2.600080	1.245077
H	-5.989856	3.793289	-0.027402
H	-6.236059	2.093057	-0.440454
C	-3.291647	3.485467	0.471170
C	-3.402466	4.926366	0.683341
H	-2.606386	5.533673	0.264159
C	-4.379051	5.545915	1.343001
H	-4.383360	6.623703	1.439901
H	-5.184958	5.004238	1.820772
C	-2.029493	2.751000	0.366667
N	-2.240692	1.439727	0.158010
C	-3.595477	1.287807	0.109946
C	-4.259689	0.088501	-0.086033
C	-3.698338	-1.170496	-0.272924
N	-2.366284	-1.444774	-0.286186
H	-1.636715	-0.762132	-0.140751
C	-2.151514	-2.773790	-0.492545
C	-0.898279	-3.380519	-0.575478
H	-0.902072	-4.448973	-0.740116
C	0.337201	-2.774293	-0.467462
C	-3.426594	-3.400143	-0.615934
C	-3.642155	-4.853280	-0.882976
H	-4.516709	-5.000923	-1.516958
H	-2.781933	-5.298829	-1.379420
H	-3.814336	-5.405443	0.043213
C	-4.384783	-2.411924	-0.474948
C	-5.839081	-2.528423	-0.544631
H	-6.366756	-1.644852	-0.888091
C	-6.558098	-3.601388	-0.223223
H	-7.635545	-3.588409	-0.320956
H	-6.108121	-4.506984	0.160075
H	-5.339963	0.125146	-0.088279
N	0.549872	-1.444830	-0.248993
C	1.888818	-1.304269	-0.210815
C	2.577051	-2.581518	-0.418974
C	1.600888	-3.504116	-0.575070
C	2.567345	-0.098599	-0.002182
H	3.647149	-0.138912	0.017463
C	4.062100	-2.770780	-0.426341
C	4.664917	-2.844090	0.983165
H	5.754791	-2.841205	0.895240
H	4.371372	-1.970309	1.565788
H	4.310458	-3.692444	-0.952241
H	4.530286	-1.953705	-0.980056
C	1.730912	-4.970588	-0.824904
C	2.004194	1.143746	0.187462
H	1.093522	-5.542437	-0.148420
H	2.755706	-5.296385	-0.661197
H	1.434263	-5.224694	-1.845264
N	0.669979	1.414859	0.191461
H	-0.052769	0.728705	0.037822
C	0.455520	2.742553	0.412510
C	-0.772273	3.358259	0.490867
H	-0.750821	4.422766	0.676533
C	1.751480	3.365436	0.558012
C	1.961683	4.819436	0.823603
H	1.752932	5.060699	1.868163
H	1.300073	5.428281	0.206430
H	2.986262	5.098686	0.587217
C	2.696402	2.390445	0.426344
C	4.186232	2.517848	0.495968
C	4.851357	2.543004	-0.884778
H	5.933505	2.460452	-0.749682
H	4.529295	1.688097	-1.479564
H	4.448282	3.434654	1.021772
H	4.587584	1.686803	1.079939
C	4.255532	-4.123432	1.742625
O	4.513443	-5.213726	1.176077
O	3.713090	-3.978311	2.859335
C	4.585593	3.839157	-1.680330
O	4.281374	3.710840	-2.885487
O	4.728322	4.920330	-1.059220

S3-9: Protoporphyrin IX optimized with M06.

C	-4.438467	2.210070	0.314249
C	-5.918759	2.304134	0.255828
H	-6.374897	2.215812	1.247562
H	-6.230528	3.268959	-0.151974
H	-6.349317	1.519594	-0.369177
C	-3.527727	3.215613	0.474758
C	-3.744416	4.639063	0.648241
H	-2.941210	5.286270	0.301334
C	-4.813405	5.221857	1.189115
H	-4.879148	6.300700	1.260418
H	-5.639447	4.654435	1.600998
C	-2.216989	2.580673	0.394501
N	-2.323513	1.247394	0.210021
C	-3.659653	0.996920	0.153208
C	-4.230842	-0.256575	-0.037618
C	-3.571424	-1.461373	-0.215751
N	-2.218660	-1.625008	-0.219127
H	-1.547265	-0.880981	-0.072976
C	-1.895027	-2.935667	-0.427010
C	-0.603101	-3.437847	-0.502624
H	-0.519764	-4.507132	-0.660346
C	0.585324	-2.730311	-0.398806
C	-3.114956	-3.661286	-0.561818
C	-3.207497	-5.114312	-0.848175
H	-4.009728	-5.316435	-1.562530
H	-2.277814	-5.501231	-1.266304
H	-3.429926	-5.694500	0.052882
C	-4.152647	-2.755847	-0.426570
C	-5.582465	-2.981306	-0.508930
H	-6.182967	-2.101553	-0.729363
C	-6.222378	-4.136578	-0.336596
H	-7.300333	-4.187116	-0.427161
H	-5.710416	-5.055907	-0.081689
H	-5.313183	-0.303949	-0.045697
N	0.689392	-1.390559	-0.190802
C	2.020827	-1.145538	-0.168432
C	2.800041	-2.362603	-0.377367
C	1.893560	-3.360341	-0.514525
C	2.600486	0.108432	0.022434
H	3.683452	0.157749	0.022086
C	4.287590	-2.442148	-0.400736
C	4.890803	-2.704610	0.981281
H	5.973913	-2.553614	0.928137
H	4.478838	-2.002454	1.712589
H	4.609371	-3.249588	-1.065336
H	4.699127	-1.517265	-0.816469
C	2.126232	-4.810267	-0.738009
C	1.940504	1.307091	0.211572
H	1.731138	-5.401217	0.094245
H	3.191238	-5.033228	-0.806888
H	1.631709	-5.162986	-1.648141
N	0.585324	1.457241	0.239859
H	-0.076722	0.703353	0.109841
C	0.262074	2.768122	0.435476
C	-1.015296	3.282958	0.507136
H	-1.077633	4.353384	0.665608
C	1.492054	3.500184	0.544845
C	1.566753	4.969698	0.744799
H	1.074266	5.275156	1.672339
H	1.070480	5.494033	-0.077200
H	2.600341	5.314595	0.760090
C	2.521147	2.606324	0.411035
C	3.985727	2.879472	0.413200
C	4.530162	3.176319	-0.987710
H	5.623015	3.206990	-0.939501
H	4.233032	2.381299	-1.678197
H	4.204877	3.737909	1.054760
H	4.516269	2.025321	0.844598
C	4.630851	-4.151068	1.432369
O	5.194314	-5.038171	0.751142
O	3.876684	-4.326124	2.410542
C	4.024805	4.535261	-1.497227
O	3.190451	4.529213	-2.424456
O	4.482064	5.537961	-0.902859

S3-10: Phytoporphyrin optimized with B3LYP.

C	2.348147	3.950431	-0.206387
C	3.521419	4.876560	-0.073426
H	4.399717	4.425731	-0.537902
C	3.850375	5.240310	1.384867
H	3.006437	5.740570	1.860589
H	4.710757	5.909336	1.428116
H	4.083251	4.349472	1.968500
C	1.028634	4.290116	-0.381443
C	0.434772	5.657773	-0.504337
H	-0.169411	5.748218	-1.408596
H	1.207469	6.422361	-0.538591
H	-0.218306	5.882317	0.341459
C	0.258235	3.068225	-0.416060
N	1.145038	2.034314	-0.255750
H	0.881645	1.062650	-0.294190
C	2.425504	2.506277	-0.128642
C	3.569390	1.741462	0.042149
C	3.679225	0.345661	0.145599
N	2.644031	-0.523091	0.108679
C	3.194933	-1.771231	0.244901
C	2.460756	-2.953086	0.266041
H	2.998373	-3.882817	0.382121
C	1.070830	-3.044569	0.137233
C	4.652618	-1.684890	0.371914
C	5.588341	-2.850821	0.502596
H	6.495375	-2.530341	1.017253
H	5.136171	-3.617343	1.135288
C	5.975767	-3.479475	-0.847655
H	6.650570	-4.323995	-0.700242
H	6.477543	-2.750705	-1.485085
C	4.955893	-0.358276	0.311604
C	6.299613	0.297007	0.387157
H	7.081656	-0.428760	0.603238
H	6.329097	1.061443	1.166354
H	6.558179	0.790650	-0.552716
H	4.492576	2.298379	0.105856
N	0.267705	-1.924744	-0.008427
H	0.651781	-0.990051	0.015573
C	-1.014995	-2.305141	-0.142408
C	-1.061151	-3.716950	-0.075503
C	0.230406	-4.203581	0.100570
C	-2.262244	-1.692798	-0.339802
C	0.675996	-5.624567	0.220481
C	-2.454154	-0.320338	-0.463018
H	1.168026	-5.805914	1.178013
H	1.390698	-5.883951	-0.562792
H	-0.175674	-6.295838	0.142293
N	-1.376700	0.528373	-0.402046
C	-1.877010	1.768820	-0.567843
C	-1.112517	2.947921	-0.570149
C	-4.198315	2.941977	-0.970148
H	-1.651159	3.875561	-0.696610
C	-3.334447	1.740028	-0.744457
C	-3.702143	0.429732	-0.679057
H	-3.925674	3.754860	-0.294758
H	-5.244653	2.705268	-0.792174
H	-4.090536	3.325078	-1.988929
C	-2.453692	-4.129008	-0.229214
C	-5.086930	-0.139387	-0.809379
C	-3.275026	-2.830716	-0.405417
O	-2.925277	-5.252508	-0.229398
H	-4.033363	-2.775376	0.376474
H	-3.804473	-2.876268	-1.358535
C	-5.787737	-0.435962	0.530977
H	-6.639763	-1.094665	0.335449
H	-5.123889	-0.963494	1.214698
H	-5.714740	0.564389	-1.353758
H	-5.048791	-1.049694	-1.408335
H	3.320133	5.791084	-0.632153
H	5.095145	-3.838509	-1.380845
C	-6.349898	0.812971	1.256490
O	-6.194210	0.859357	2.500739
O	-6.950297	1.661843	0.544702

S3-11: Phytoporphyrin optimized with ωB97XD.

C	2.250422	3.954009	-0.252374
C	3.418481	4.878770	-0.116771
H	4.285333	4.451685	-0.623722
C	3.769129	5.162337	1.347596
H	2.925936	5.628066	1.858954
H	4.625532	5.833487	1.415960
H	4.013784	4.239206	1.874238
C	0.943352	4.275168	-0.424733
C	0.325213	5.625901	-0.560597
H	-0.189771	5.724443	-1.517699
H	1.074078	6.411891	-0.493489
H	-0.414117	5.793773	0.224179
C	0.179374	3.039520	-0.447839
N	1.074599	2.019020	-0.279915
H	0.815978	1.046638	-0.293198
C	2.345051	2.503925	-0.156796
C	3.490655	1.774875	0.024073
C	3.608894	0.371462	0.137785
N	2.595922	-0.493068	0.099498
C	3.164514	-1.741335	0.252218
C	2.460143	-2.917839	0.272249
H	3.007433	-3.842039	0.402661
C	1.063358	-3.032135	0.126624
C	4.616057	-1.628569	0.390286
C	5.563439	-2.779109	0.522331
H	6.494449	-2.430553	0.970831
H	5.150938	-3.521017	1.209473
C	5.866444	-3.445735	-0.823812
H	6.574434	-4.265863	-0.700156
H	6.296134	-2.724492	-1.520307
C	4.895720	-0.306572	0.316874
C	6.220692	0.379699	0.382696
H	7.024038	-0.331542	0.567209
H	6.240766	1.127446	1.177831
H	6.440821	0.897997	-0.552951
H	4.408465	2.342082	0.090553
N	0.257049	-1.927274	-0.040801
H	0.627544	-0.987889	-0.034053
C	-1.011006	-2.325678	-0.174896
C	-1.047300	-3.722011	-0.089509
C	0.253120	-4.190362	0.101710
C	-2.270694	-1.719342	-0.378588
C	0.719867	-5.600379	0.248809
C	-2.469939	-0.370575	-0.499953
H	1.199226	-5.755159	1.216654
H	1.448790	-5.856450	-0.521446
H	-0.119359	-6.287484	0.169434
N	-1.397531	0.499546	-0.445094
C	-1.917912	1.712935	-0.593623
C	-1.173775	2.916752	-0.597463
C	-4.243284	2.873949	-0.918332
H	-1.726503	3.837693	-0.720676
C	-3.374625	1.671298	-0.750331
C	-3.723355	0.364894	-0.697474
H	-4.043866	3.603807	-0.131548
H	-5.296354	2.610580	-0.852964
H	-4.056057	3.367071	-1.875025
C	-2.434986	-4.147264	-0.237649
C	-5.101510	-0.215765	-0.767145
C	-3.265572	-2.864809	-0.439404
O	-2.896133	-5.268592	-0.217698
H	-4.033795	-2.805840	0.331678
H	-3.775523	-2.927284	-1.401662
C	-5.714907	-0.460075	0.620549
H	-6.659547	-0.993565	0.494012
H	-5.048711	-1.073890	1.226983
H	-5.754697	0.467829	-1.309801
H	-5.087104	-1.147108	-1.332836
H	3.197673	5.817001	-0.625638
H	4.956840	-3.844442	-1.274403
C	-5.996341	0.863941	1.358821
O	-5.325531	1.102082	2.386515
O	-6.874007	1.603391	0.851572

S3-12: Phytoporphyrin optimized with M06.

C	2.262251	3.925789	-0.269240
C	3.417596	4.857463	-0.145535
H	4.307958	4.413749	-0.600758
C	3.706699	5.218056	1.307360
H	2.837653	5.699986	1.763272
H	4.555296	5.900372	1.385860
H	3.933598	4.322698	1.891529
C	0.944799	4.254043	-0.422098
C	0.342591	5.605798	-0.539021
H	-0.165274	5.734547	-1.499199
H	1.097965	6.386916	-0.449677
H	-0.405689	5.772561	0.240595
C	0.187624	3.032413	-0.442176
N	1.078764	2.006266	-0.289492
H	0.816581	1.031330	-0.310754
C	2.351983	2.491422	-0.177597
C	3.500384	1.749578	0.003117
C	3.614286	0.359547	0.129282
N	2.585444	-0.507020	0.092465
C	3.144519	-1.744509	0.256740
C	2.430166	-2.931492	0.276484
H	2.980271	-3.856099	0.414485
C	1.048125	-3.038313	0.124736
C	4.588930	-1.647321	0.407716
C	5.529532	-2.792952	0.555249
H	6.395577	-2.482649	1.147972
H	5.054271	-3.601388	1.119568
C	6.004199	-3.321458	-0.794154
H	6.689419	-4.163338	-0.674861
H	6.522389	-2.537005	-1.352402
C	4.885162	-0.326050	0.322446
C	6.215677	0.331018	0.393803
H	7.009607	-0.397228	0.567750
H	6.258440	1.071193	1.198440
H	6.451057	0.860563	-0.534661
H	4.421427	2.319599	0.061746
N	0.242402	-1.930773	-0.046326
H	0.614066	-0.989861	-0.031660
C	-1.029257	-2.326417	-0.183560
C	-1.066901	-3.729434	-0.098286
C	0.223802	-4.198845	0.096547
C	-2.276236	-1.727746	-0.385902
C	0.685337	-5.600410	0.245823
C	-2.467779	-0.362706	-0.503748
H	1.168688	-5.757469	1.214079
H	1.417648	-5.862249	-0.522611
H	-0.152971	-6.291985	0.168501
N	-1.397211	0.489150	-0.447347
C	-1.919240	1.718648	-0.578954
C	-1.176906	2.907394	-0.578561
C	-4.242429	2.874404	-0.856277
H	-1.727676	3.835174	-0.688275
C	-3.370421	1.679540	-0.724678
C	-3.717081	0.368776	-0.687740
H	-4.121271	3.537123	0.006317
H	-5.296216	2.597874	-0.895964
H	-3.995458	3.459424	-1.747701
C	-2.453555	-4.147540	-0.250282
C	-5.087508	-0.212982	-0.755238
C	-3.273152	-2.863831	-0.445704
O	-2.919468	-5.265598	-0.236556
H	-4.044688	-2.807039	0.328188
H	-3.796194	-2.926628	-1.404901
C	-5.694672	-0.449491	0.630227
H	-6.640866	-0.988065	0.515857
H	-5.018723	-1.056085	1.240283
H	-5.748368	0.468028	-1.299191
H	-5.073094	-1.147618	-1.322315
H	3.210827	5.768105	-0.714744
H	5.158361	-3.654285	-1.401367
C	-5.965855	0.884859	1.342674
O	-5.246441	1.165536	2.322709
O	-6.876142	1.589172	0.851445

S4: CI descriptions for the two peaks in the Q-band.

Chlorin: MO 82→ 83 = HOMO→LUMO

Chlorin B3LYP geometry

wB97XD

Excited State 1: Singlet-A 2.0795 eV 596.22 nm f=0.1538 <S**2>=0.000
81 -> 84 0.33839
82 -> 83 0.62222
81 <- 84 0.10104
Excited State 2: Singlet-A 2.5318 eV 489.71 nm f=0.0029 <S**2>=0.000
81 -> 83 0.53587
82 -> 84 -0.45629

wB97X

Excited State 1: Singlet-A 1.9504 eV 635.69 nm f=0.1470 <S**2>=0.000
81 -> 84 -0.34799
82 -> 83 0.62201
81 <- 84 -0.12499
Excited State 2: Singlet-A 2.5623 eV 483.89 nm f=0.0002 <S**2>=0.000
81 -> 83 0.51941
82 -> 84 0.47545

wB97

Excited State 1: Singlet-A 1.8703 eV 662.92 nm f=0.1435 <S**2>=0.000
81 -> 84 -0.35375
82 -> 83 0.62307
81 <- 84 -0.13829
82 <- 83 0.10720
Excited State 2: Singlet-A 2.5943 eV 477.90 nm f=0.0003 <S**2>=0.000
81 -> 83 0.50583
82 -> 84 0.48994

Chlorin wB97XD geometry

wB97XD

Excited State 1: Singlet-A 2.1297 eV 582.17 nm f=0.1460 <S**2>=0.000
81 -> 84 -0.34103
82 -> 83 0.61991
Excited State 2: Singlet-A 2.5963 eV 477.53 nm f=0.0001 <S**2>=0.000
81 -> 83 0.52041
82 -> 84 0.47326

wB97X

Excited State 1: Singlet-A 2.0156 eV 615.13 nm f=0.1386 <S**2>=0.000
81 -> 84 -0.35022
82 -> 83 0.61878
81 <- 84 -0.11858
Excited State 2: Singlet-A 2.6483 eV 468.17 nm f=0.0013 <S**2>=0.000
81 -> 83 0.49983
82 -> 84 0.49471

wB97

Excited State 1: Singlet-A 1.9463 eV 637.01 nm f=0.1346 <S**2>=0.000

81 -> 84 -0.35555
82 -> 83 0.61905
81 <- 84 -0.13033
82 <- 83 0.10050
Excited State 2: Singlet-A 2.6931 eV 460.37 nm f=0.0057 <S**2>=0.000
81 -> 83 0.48259
82 -> 84 0.51112

Chlorin M06 geometry

wB97XD
Excited State 1: Singlet-A 2.1081 eV 588.12 nm f=0.1551 <S**2>=0.000
81 -> 84 -0.33519
82 -> 83 0.62358
Excited State 2: Singlet-A 2.5688 eV 482.65 nm f=0.0020 <S**2>=0.000
81 -> 83 0.53246
82 -> 84 0.45989

wB97X
Excited State 1: Singlet-A 1.9853 eV 624.51 nm f=0.1477 <S**2>=0.000
81 -> 84 -0.34499
82 -> 83 0.62277
81 <- 84 -0.12187
Excited State 2: Singlet-A 2.6070 eV 475.58 nm f=0.0000 <S**2>=0.000
81 -> 83 0.51526
82 -> 84 0.47930

wB97
Excited State 1: Singlet-A 1.9093 eV 649.37 nm f=0.1438 <S**2>=0.000
81 -> 84 -0.35077
82 -> 83 0.62338
81 <- 84 -0.13448
82 <- 83 0.10307
Excited State 2: Singlet-A 2.6435 eV 469.02 nm f=0.0008 <S**2>=0.000
81 -> 83 0.50090
82 -> 84 0.49418

Porphyrin: MO 81→ 82 = HOMO→LUMO

Porphyrin B3LYP geometry

wB97XD

Excited State 1: Singlet-A 2.1213 eV 584.46 nm f=0.0009 <S**2>=0.000
80 -> 83 -0.48412
81 -> 82 0.51929

Excited State 2: Singlet-A 2.3217 eV 534.02 nm f=0.0032 <S**2>=0.000
80 -> 82 0.50731
81 -> 83 0.49347

wB97X

Excited State 1: Singlet-A 1.9638 eV 631.34 nm f=0.0036 <S**2>=0.000
80 -> 82 0.51028
81 -> 83 0.50605
80 <- 82 0.12545
81 <- 83 0.13196

Excited State 2: Singlet-A 2.2067 eV 561.84 nm f=0.0061 <S**2>=0.000
80 -> 83 -0.48409
81 -> 82 0.52245
81 <- 82 0.10183

wB97

Excited State 1: Singlet-A 1.8565 eV 667.83 nm f=0.0062 <S**2>=0.000
80 -> 82 0.50659
81 -> 83 0.52042
80 <- 82 0.14946
81 <- 83 0.15428

Excited State 2: Singlet-A 2.1322 eV 581.47 nm f=0.0086 <S**2>=0.000
80 -> 83 -0.47892
81 -> 82 0.53222
80 <- 83 -0.11613
81 <- 82 0.11808

Porphyrin wB97XD geometry

wB97XD

Excited State 1: Singlet-A 2.1526 eV 575.97 nm f=0.0017 <S**2>=0.000
80 -> 83 0.48864
81 -> 82 0.51394

Excited State 2: Singlet-A 2.3473 eV 528.20 nm f=0.0039 <S**2>=0.000
80 -> 82 0.50963
81 -> 83 -0.49004

wB97X

Excited State 1: Singlet-A 1.9969 eV 620.89 nm f=0.0048 <S**2>=0.000
80 -> 82 -0.50555
81 -> 83 0.51004
80 <- 82 -0.12422
81 <- 83 0.12908

Excited State 2: Singlet-A 2.2330 eV 555.23 nm f=0.0071 <S**2>=0.000
80 -> 83 0.48122
81 -> 82 0.52485
81 <- 82 0.10023

wB97
Excited State 1: Singlet-A 1.8908 eV 655.72 nm f=0.0076 <S**2>=0.000
80 -> 83 0.50186
81 -> 82 0.52378
80 <- 83 0.14759
81 <- 82 0.15097

Excited State 2: Singlet-A 2.1588 eV 574.32 nm f=0.0096 <S**2>=0.000
80 -> 82 -0.47610
81 -> 83 0.53437
80 <- 82 -0.11551
81 <- 83 0.11633

Porphyrin M06 geometry

wB97XD
Excited State 1: Singlet-A 2.1527 eV 575.94 nm f=0.0007 <S**2>=0.000
80 -> 83 -0.48337
81 -> 82 0.51963

Excited State 2: Singlet-A 2.3477 eV 528.12 nm f=0.0030 <S**2>=0.000
80 -> 82 0.50722
81 -> 83 0.49344

wB97X
Excited State 1: Singlet-A 1.9980 eV 620.53 nm f=0.0031 <S**2>=0.000
80 -> 82 0.51056
81 -> 83 0.50481
80 <- 82 0.12303
81 <- 83 0.12982

Excited State 2: Singlet-A 2.2334 eV 555.14 nm f=0.0059 <S**2>=0.000
80 -> 83 -0.48403
81 -> 82 0.52220
81 <- 82 0.10076

wB97
Excited State 1: Singlet-A 1.8926 eV 655.09 nm f=0.0054 <S**2>=0.000
80 -> 82 0.50671
81 -> 83 0.51884
80 <- 82 0.14650
81 <- 83 0.15156

Excited State 2: Singlet-A 2.1591 eV 574.23 nm f=0.0082 <S**2>=0.000
80 -> 83 -0.47884
81 -> 82 0.53185
80 <- 83 -0.11498
81 <- 82 0.11684

Protoporphyrin IX: MO 149→ 150 = HOMO→LUMO

Protopophyrin B3LYP geometry

wB97XD

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.0687 eV	Excited State 1: Singlet-A 2.0738 eV
599.34 nm f=0.0224 <S**2>=0.000	597.86 nm f=0.0222 <S**2>=0.000
148 -> 150 0.37690	148 -> 150 0.37355
148 -> 151 0.29341	148 -> 151 0.29921
149 -> 150 -0.34206	149 -> 150 -0.34890
149 -> 151 0.39437	149 -> 151 0.38552
Excited State 2: Singlet-A 2.2417 eV	Excited State 2: Singlet-A 2.2416 eV
553.08 nm f=0.0408 <S**2>=0.000	553.11 nm f=0.0405 <S**2>=0.000
148 -> 150 0.28844	148 -> 150 0.29828
148 -> 151 -0.33418	148 -> 151 -0.32815
149 -> 150 0.42956	149 -> 150 0.42354
149 -> 151 0.34455	149 -> 151 0.34786

wB97X

Protonated	**Deprotonated**
Excited State 1: Singlet-A 1.9279 eV	Excited State 1: Singlet-A 1.9382 eV
643.12 nm f=0.0291 <S**2>=0.000	639.67 nm f=0.0289 <S**2>=0.000
148 -> 150 0.35486	148 -> 150 -0.34852
148 -> 151 0.30888	148 -> 151 -0.31656
149 -> 150 -0.37330	149 -> 150 0.38298
149 -> 151 0.38885	149 -> 151 -0.37685
Excited State 2: Singlet-A 2.1341 eV	Excited State 2: Singlet-A 2.1374 eV
580.97 nm f=0.0438 <S**2>=0.000	580.07 nm f=0.0426 <S**2>=0.000
148 -> 150 0.30284	148 -> 150 0.31486
148 -> 151 -0.31529	148 -> 151 -0.30719
149 -> 150 0.41645	149 -> 150 0.40665
149 -> 151 0.37358	149 -> 151 0.37976

wB97

Protonated	**Deprotonated**
Excited State 1: Singlet-A 1.8387 eV	Excited State 1: Singlet-A 1.8541 eV
674.31 nm f=0.0341 <S**2>=0.000	668.71 nm f=0.0341 <S**2>=0.000
148 -> 150 -0.34103	148 -> 150 -0.33181
148 -> 151 -0.32007	148 -> 151 -0.32935
149 -> 150 0.39465	149 -> 150 0.40691
149 -> 151 -0.38314	149 -> 151 -0.36759
148 <- 150 -0.10650	148 <- 150 -0.10142
148 <- 151 -0.10540	148 <- 151 -0.10694
149 <- 151 -0.10457	149 <- 150 0.10023
	149 <- 151 -0.10044
Excited State 2: Singlet-A 2.0669 eV	
599.85 nm f=0.0464 <S**2>=0.000	Excited State 2: Singlet-A 2.0735 eV
148 -> 150 0.31283	597.94 nm f=0.0444 <S**2>=0.000
148 -> 151 -0.30217	148 -> 150 0.32701
149 -> 150 0.40654	148 -> 151 -0.29156
149 -> 151 0.39308	149 -> 150 0.39306
	149 -> 151 0.40166

Protopophyrin wB97XD geometry

wB97XD

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.1306 eV	Excited State 1: Singlet-A 2.1448 eV
581.92 nm f=0.0274 <S**2>=0.000	578.08 nm f=0.0274 <S**2>=0.000
148 -> 150 -0.34431	148 -> 150 0.33768
148 -> 151 -0.31939	148 -> 151 0.32788
149 -> 150 0.38032	149 -> 150 0.39280
149 -> 151 -0.36775	149 -> 151 -0.35095
Excited State 2: Singlet-A 2.2819 eV	Excited State 2: Singlet-A 2.2864 eV
543.33 nm f=0.0403 <S**2>=0.000	542.27 nm f=0.0373 <S**2>=0.000
148 -> 150 0.31651	148 -> 150 -0.33387
148 -> 151 -0.30443	148 -> 151 0.29281
149 -> 150 0.40011	149 -> 150 0.38831
149 -> 151 0.38087	149 -> 151 0.38573

wB97X

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.0241 eV	Excited State 1: Singlet-A 2.0531 eV
612.54 nm f=0.0358 <S**2>=0.000	603.89 nm f=0.0375 <S**2>=0.000
148 -> 150 -0.31341	148 -> 150 0.29286
148 -> 151 -0.33724	148 -> 151 0.35344
149 -> 150 0.41797	149 -> 150 0.44211
149 -> 151 -0.34981	149 -> 151 -0.31726
Excited State 2: Singlet-A 2.1841 eV	Excited State 2: Singlet-A 2.1973 eV
567.67 nm f=0.0425 <S**2>=0.000	564.25 nm f=0.0368 <S**2>=0.000
148 -> 150 0.33506	148 -> 150 -0.36227
148 -> 151 -0.27784	148 -> 151 0.25405
149 -> 150 0.37510	149 -> 150 0.34617
149 -> 151 0.41572	149 -> 151 0.43108

wB97

Protonated	**Deprotonated**
Excited State 1: Singlet-A 1.9697 eV	Excited State 1: Singlet-A 2.0108 eV
629.47 nm f=0.0428 <S**2>=0.000	616.58 nm f=0.0466 <S**2>=0.000
148 -> 150 -0.28829	148 -> 150 0.25000
148 -> 151 -0.35170	148 -> 151 0.37494
149 -> 150 0.44696	149 -> 150 0.48237
149 -> 151 -0.32955	149 -> 151 -0.27592
148 <- 151 -0.10950	148 <- 151 0.11298
149 <- 150 0.10013	149 <- 150 0.10230
Excited State 2: Singlet-A 2.1272 eV	Excited State 2: Singlet-A 2.1498 eV
582.84 nm f=0.0441 <S**2>=0.000	576.73 nm f=0.0357 <S**2>=0.000
148 -> 150 0.35046	148 -> 150 -0.38706
148 -> 151 -0.25494	148 -> 151 0.21502
149 -> 150 0.35095	149 -> 150 0.29977
149 -> 151 0.44241	149 -> 151 0.46778

Protopophyrin M06 geometry

wB97XD

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.0978 eV	Excited State 1: Singlet-A 2.1036 eV
591.02 nm f=0.0230 <S**2>=0.000	589.38 nm f=0.0220 <S**2>=0.000
148 -> 150 0.36441	148 -> 150 0.37710
148 -> 151 0.30600	148 -> 151 0.29279
149 -> 150 -0.35868	149 -> 150 -0.34051
149 -> 151 0.38115	149 -> 151 0.39389
Excited State 2: Singlet-A 2.2650 eV	Excited State 2: Singlet-A 2.2639 eV
547.38 nm f=0.0392 <S**2>=0.000	547.65 nm f=0.0402 <S**2>=0.000
148 -> 150 0.30257	148 -> 150 0.28917
148 -> 151 -0.32222	148 -> 151 -0.33437
149 -> 150 0.41602	149 -> 150 0.42956
149 -> 151 0.35985	149 -> 151 0.34199

wB97X

Protonated	**Deprotonated**
Excited State 1: Singlet-A 1.9624 eV	Excited State 1: Singlet-A 1.9744 eV
631.79 nm f=0.0296 <S**2>=0.000	627.95 nm f=0.0287 <S**2>=0.000
148 -> 150 -0.34168	148 -> 150 0.35214
148 -> 151 -0.32053	148 -> 151 0.31062
149 -> 150 0.38934	149 -> 150 -0.37492
149 -> 151 -0.37390	149 -> 151 0.38495
Excited State 2: Singlet-A 2.1592 eV	Excited State 2: Singlet-A 2.1610 eV
574.22 nm f=0.0418 <S**2>=0.000	573.72 nm f=0.0422 <S**2>=0.000
148 -> 150 0.31624	148 -> 150 0.30667
148 -> 151 -0.30284	148 -> 151 -0.31347
149 -> 150 0.40146	149 -> 150 0.41282
149 -> 151 0.38836	149 -> 151 0.37408

wB97

Protonated	**Deprotonated**
Excited State 1: Singlet-A 1.8779 eV	Excited State 1: Singlet-A 1.8958 eV
660.24 nm f=0.0346 <S**2>=0.000	654.00 nm f=0.0339 <S**2>=0.000
148 -> 150 -0.32677	148 -> 150 -0.33451
148 -> 151 -0.33139	148 -> 151 -0.32440
149 -> 150 0.41070	149 -> 150 0.40009
149 -> 151 -0.36646	149 -> 151 -0.37444
148 <- 150 -0.10002	148 <- 150 -0.10077
148 <- 151 -0.10738	148 <- 151 -0.10290
149 <- 150 0.10035	
	Excited State 2: Singlet-A 2.0981 eV
Excited State 2: Singlet-A 2.0933 eV	590.93 nm f=0.0438 <S**2>=0.000
592.28 nm f=0.0441 <S**2>=0.000	148 -> 150 0.32028
148 -> 150 0.32615	148 -> 151 -0.29707
148 -> 151 -0.28892	149 -> 150 0.39822
149 -> 150 0.38999	149 -> 151 0.39713
149 -> 151 0.40792	

Phytoporphyrin: MO 142→ 143 = HOMO→LUMO

Phytoporphyrin B3LYP geometry

wB97XD

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.1121 eV	Excited State 1: Singlet-A 2.1189 eV
587.00 nm f=0.0316 <S**2>=0.000	585.13 nm f=0.0381 <S**2>=0.000
141 -> 143 -0.28892	141 -> 143 -0.29787
141 -> 144 0.36332	141 -> 144 0.35833
142 -> 143 0.45149	142 -> 143 0.45082
142 -> 144 0.28235	142 -> 144 0.27992
Excited State 2: Singlet-A 2.2522 eV	Excited State 2: Singlet-A 2.2554 eV
550.51 nm f=0.0029 <S**2>=0.000	549.72 nm f=0.0053 <S**2>=0.000
141 -> 143 0.42706	141 -> 143 0.43144
141 -> 144 0.24183	141 -> 144 0.23878
142 -> 143 0.32243	142 -> 143 0.33087
142 -> 144 -0.39004	142 -> 144 -0.37979

wB97X

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.0703 eV	Excited State 1: Singlet-A 2.0790 eV
598.86 nm f=0.0392 <S**2>=0.000	596.35 nm f=0.0468 <S**2>=0.000
141 -> 143 -0.16722	141 -> 143 -0.15703
141 -> 144 -0.41863	141 -> 144 0.41758
142 -> 143 0.52303	142 -> 143 0.53147
142 -> 144 -0.16641	142 -> 144 0.15011
141 <- 144 -0.10912	141 <- 144 0.10974
Excited State 2: Singlet-A 2.1897 eV	Excited State 2: Singlet-A 2.1972 eV
566.22 nm f=0.0005 <S**2>=0.000	564.29 nm f=0.0013 <S**2>=0.000
141 -> 143 0.48191	141 -> 143 0.49338
141 -> 144 -0.14226	141 -> 144 0.12605
142 -> 143 0.18634	142 -> 143 0.17525
142 -> 144 0.46146	142 -> 144 -0.45827

wB97

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.0720 eV	Excited State 1: Singlet-A 2.0801 eV
598.38 nm f=0.0463 <S**2>=0.000	596.04 nm f=0.0542 <S**2>=0.000
141 -> 144 -0.43325	141 -> 144 0.43158
142 -> 143 0.55191	142 -> 143 0.56168
141 <- 144 -0.12410	141 <- 144 0.12448
142 <- 143 0.10998	142 <- 143 0.10852
Excited State 2: Singlet-A 2.1596 eV	Excited State 2: Singlet-A 2.1721 eV
574.10 nm f=0.0001 <S**2>=0.000	570.81 nm f=0.0006 <S**2>=0.000
141 -> 143 0.49753	141 -> 143 0.50954
142 -> 144 0.49009	142 -> 144 -0.48775
142 <- 144 0.10510	142 <- 144 -0.10699

Phytoporphyrin wB97XD geometry

wB97XD

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.3527 eV	Excited State 1: Singlet-A 2.3572 eV
526.99 nm f=0.0304 <S**2>=0.000	525.99 nm f=0.0361 <S**2>=0.000
141 -> 144 -0.42094	141 -> 143 0.11984
142 -> 143 0.55500	141 -> 144 0.40478
	142 -> 143 0.55311
Excited State 2: Singlet-A 2.3775 eV	
521.48 nm f=0.0134 <S**2>=0.000	Excited State 2: Singlet-A 2.3951 eV
141 -> 143 0.51157	517.67 nm f=0.0213 <S**2>=0.000
142 -> 144 0.47259	141 -> 143 0.51225
	141 -> 144 -0.10174
	142 -> 143 -0.11731
	142 -> 144 -0.45499

wB97X

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.3458 eV	Excited State 1: Singlet-A 2.3512 eV
528.54 nm f=0.0074 <S**2>=0.000	527.32 nm f=0.0167 <S**2>=0.000
141 -> 143 0.42419	141 -> 143 0.38931
141 -> 144 -0.23661	141 -> 144 -0.27158
142 -> 143 0.31757	142 -> 143 -0.37919
142 -> 144 0.39533	142 -> 144 -0.35185
Excited State 2: Singlet-A 2.4743 eV	Excited State 2: Singlet-A 2.5008 eV
501.08 nm f=0.0512 <S**2>=0.000	495.78 nm f=0.0570 <S**2>=0.000
141 -> 143 -0.28746	141 -> 143 0.34659
141 -> 144 -0.34741	141 -> 144 0.30964
142 -> 143 0.46437	142 -> 143 0.42358
142 -> 144 -0.27229	142 -> 144 -0.31141

wB97

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.3478 eV	Excited State 1: Singlet-A 2.3552 eV
528.09 nm f=0.0055 <S**2>=0.000	526.43 nm f=0.0141 <S**2>=0.000
141 -> 143 0.45480	141 -> 143 0.42652
141 -> 144 -0.18440	141 -> 144 -0.22572
142 -> 143 -0.25251	142 -> 143 -0.32172
142 -> 144 -0.43340	142 -> 144 -0.39475
Excited State 2: Singlet-A 2.5685 eV	Excited State 2: Singlet-A 2.5981 eV
482.72 nm f=0.0699 <S**2>=0.000	477.20 nm f=0.0784 <S**2>=0.000
141 -> 143 0.22646	141 -> 143 0.29165
141 -> 144 0.36443	141 -> 144 0.32975
142 -> 143 0.51107	142 -> 143 0.47767
142 -> 144 -0.21515	142 -> 144 -0.26227

Phytoporphyrin M06 geometry

wB97XD

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.1525 eV	Excited State 1: Singlet-A 2.1631 eV
576.00 nm f=0.0310 <S**2>=0.000	573.17 nm f=0.0375 <S**2>=0.000
141 -> 143 -0.28876	141 -> 143 -0.30058
141 -> 144 0.36436	141 -> 144 0.35629
142 -> 143 0.45196	142 -> 143 0.44900
142 -> 144 0.27940	142 -> 144 0.28128
Excited State 2: Singlet-A 2.2801 eV	Excited State 2: Singlet-A 2.2837 eV
543.77 nm f=0.0030 <S**2>=0.000	542.92 nm f=0.0055 <S**2>=0.000
141 -> 143 0.42853	141 -> 143 0.42860
141 -> 144 0.24166	141 -> 144 0.24058
142 -> 143 0.31995	142 -> 143 0.33334
142 -> 144 -0.39022	142 -> 144 -0.37921

wB97X

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.1213 eV	Excited State 1: Singlet-A 2.1372 eV
584.46 nm f=0.0389 <S**2>=0.000	580.11 nm f=0.0468 <S**2>=0.000
141 -> 143 -0.14256	141 -> 143 -0.12993
141 -> 144 -0.42513	141 -> 144 0.42248
142 -> 143 0.53123	142 -> 143 0.54005
142 -> 144 -0.14072	142 -> 144 0.12341
141 <- 144 -0.10732	141 <- 144 0.10692
Excited State 2: Singlet-A 2.2221 eV	Excited State 2: Singlet-A 2.2322 eV
557.96 nm f=0.0004 <S**2>=0.000	555.44 nm f=0.0012 <S**2>=0.000
141 -> 143 0.49056	141 -> 143 0.50059
141 -> 144 -0.12086	141 -> 144 0.10274
142 -> 143 0.15811	142 -> 143 0.14544
142 -> 144 0.46829	142 -> 144 -0.46579

wB97

Protonated	**Deprotonated**
Excited State 1: Singlet-A 2.1275 eV	Excited State 1: Singlet-A 2.1427 eV
582.78 nm f=0.0449 <S**2>=0.000	578.64 nm f=0.0514 <S**2>=0.000
141 -> 144 -0.43821	141 -> 144 -0.42963
142 -> 143 0.55895	142 -> 143 0.56267
141 <- 144 -0.12120	141 <- 144 -0.11871
142 <- 143 0.10629	142 <- 143 0.10179
Excited State 2: Singlet-A 2.1970 eV	Excited State 2: Singlet-A 2.2163 eV
564.34 nm f=0.0011 <S**2>=0.000	559.42 nm f=0.0036 <S**2>=0.000
141 -> 143 0.50510	141 -> 143 0.51021
142 -> 144 0.49577	142 -> 144 0.48787
142 <- 144 0.10473	142 <- 144 0.10494

Table S5: Dihedral angles (in degrees) for the ground singlet state and the first excited triplet state geometries optimized with various functionals.
Numbers refer to the numbering scheme in Fig. 1.

Compound	Functional / Multiplicity	Dihedral angle			
		$C_1N_{21}N_{23}C_{14}$	$C_1N_{21}N_{23}C_{11}$	$C_6N_{22}N_{24}C_{19}$	$C_6N_{22}N_{24}C_{16}$
Chlorin	B3LYP / singlet	-0.092	179.904	0.030	-179.948
	B3LYP / triplet	-0.084	179.916	0.019	-179.952
	M06 / singlet	-0.108	179.893	0.053	-179.933
	M06 / triplet	-0.102	179.897	0.021	-179.937
	PBE0 / singlet	-0.089	179.913	-0.009	-179.946
	PBE0 / triplet	-0.094	179.906	0.025	-179.944
	wB97 / singlet	-0.223	179.776	-2.097	-179.952
	wB97 / triplet	-0.077	179.923	-0.002	-179.957
	wB97X / singlet	-0.064	179.945	-0.131	-179.968
	wB97X / triplet	-0.073	179.928	-0.006	-179.961
	wB97XD / singlet	-0.042	179.967	-0.037	-179.982
	wB97XD / triplet	0.003	179.996	-0.024	-179.998
Porphyrin	B3LYP / singlet	-0.001	180.000	-0.029	179.985
	B3LYP / triplet	0.002	-179.997	-0.020	179.997
	M06 / singlet	0.001	-180.000	-0.029	179.997
	M06 / triplet	0.003	-179.996	-0.024	179.999
	PBE0 / singlet	0.001	-180.000	-0.026	179.993
	PBE0 / triplet	0.003	-179.996	-0.022	179.998
	wB97 / singlet	-0.002	179.998	-0.037	179.996
	wB97 / triplet	0.013	-179.988	-0.054	179.974
	wB97X / singlet	-0.001	179.998	-0.034	179.996
	wB97X / triplet	-0.001	-179.983	-0.004	179.931
	wB97XD / singlet	-0.001	179.999	-0.026	179.995
	wB97XD / triplet	-0.002	179.989	-0.009	-179.980
Protoporphyrin IX	B3LYP / singlet	1.005	-178.398	-1.685	179.645
	B3LYP / triplet	1.042	-178.758	-0.738	-179.975
	M06 / singlet	0.777	-179.153	-0.610	-179.866
	M06 / triplet	0.470	-178.789	2.969	-179.595
	PBE0 / singlet	1.000	-178.397	-1.448	179.620
	PBE0 / triplet	0.991	-178.808	-0.606	-179.855
	wB97 / singlet	0.626	-179.577	-1.137	-179.559
	wB97 / triplet	0.952	-179.089	-0.495	179.986

	wB97X / singlet	0.489	-179.565	-0.906	-179.357
	wB97X / triplet	0.730	-178.928	-0.486	-179.840
	wB97XD / singlet	-0.235	179.756	-0.039	-178.721
	wB97XD / triplet	0.822	-179.031	-0.611	-179.816
Phytoporphyrin	B3LYP / singlet	1.651	-179.646	2.385	177.185
	B3LYP / triplet	1.364	-179.420	3.021	177.511
	M06 / singlet	1.350	179.896	3.328	176.980
	M06 / triplet	1.266	-179.572	3.397	176.919
	PBE0 / singlet	1.680	-179.585	2.125	177.229
	PBE0 / triplet	1.394	-179.206	2.682	177.497
	wB97 / singlet	0.414	179.352	2.595	176.006
	wB97 / triplet	0.722	-179.895	4.065	177.879
	wB97X / singlet	0.624	179.308	2.629	176.189
	wB97X / triplet	0.761	179.969	3.850	177.613
	wB97XD / singlet	1.087	179.155	2.738	176.899
	wB97XD / triplet	0.753	179.510	4.388	178.684
Foscan	B3LYP / singlet	0.160	-179.377	4.754	179.976
	B3LYP / triplet	14.168	-177.239	-9.758	-177.411
	M06 / singlet	0.356	-179.557	5.577	179.565
	M06 / triplet	9.112	179.387	-7.118	-176.159
	PBE0 / singlet	0.864	-179.158	5.730	179.404
	PBE0 / triplet	13.966	-178.345	-4.857	-175.604
	wB97 / singlet	-0.544	179.656	5.705	-179.698
	wB97 / triplet	-2.873	177.866	8.672	-178.973
	wB97X / singlet	0.098	-178.941	4.748	178.862
	wB97X / triplet	-1.982	178.296	7.858	-178.952
	wB97XD / singlet	-0.050	-179.245	4.545	178.735
	wB97XD / triplet	-3.659	178.180	6.024	-179.623
Chlorin e6	B3LYP / singlet	8.821	-165.789	4.533	174.012
	B3LYP / triplet	22.242	-150.655	7.716	152.644
	M06 / singlet	7.264	-166.923	3.468	175.943
	M06 / triplet	17.823	-154.296	3.989	159.811
	PBE0 / singlet	7.008	-167.908	4.186	176.226
	PBE0 / triplet	21.765	-151.250	7.128	153.275
	wB97 / singlet	13.635	-162.286	11.952	167.079
	wB97 / triplet	17.781	-154.663	5.450	157.167
	wB97X / singlet	12.776	-163.059	10.878	168.523
	wB97X / triplet	23.347	-149.734	6.753	149.478

	wB97XD / singlet	8.585	-167.215	7.555	173.528
	wB97XD / triplet	23.339	-149.100	5.845	150.586
Chlorin p6	B3LYP / singlet	9.040	-167.035	6.182	173.121
	B3LYP / triplet	24.488	-150.779	4.793	150.152
	M06 / singlet	9.805	-167.406	4.280	173.080
	M06 / triplet	22.890	-152.897	4.059	152.171
	PBE0 / singlet	8.733	-167.748	5.787	173.579
	PBE0 / triplet	23.574	-151.590	4.272	151.162
	wB97 / singlet	14.211	-163.898	12.153	165.150
	wB97 / triplet	22.445	-151.804	3.686	150.960
	wB97X / singlet	13.778	-164.105	10.966	165.728
	wB97X / triplet	22.659	-151.713	4.143	150.731
	wB97XD / singlet	11.543	-165.846	8.472	168.894
	wB97XD / triplet	23.839	-150.099	3.843	149.571