How can we predict accurate electrochromic shifts for biochromophores? A case study on the photosynthetic reaction center

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Supporting Information

Table S1. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using canonical CC2 in the gas phase. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	2.126	0.19	HOMO → LUMO	0.50
			HOMO−1 → LUMO	0.27
			HOMO−1 → LUMO+1	0.15
P_{D2}	2.131	0.16	HOMO → LUMO	0.44
			HOMO−1 → LUMO	0.32
			HOMO−1 → LUMO+1	0.13
Chl_{D1}	2.128	0.21	HOMO → LUMO	0.51
			HOMO−1 → LUMO	0.26
			HOMO−1 → LUMO+1	0.14
Chl_{D2}	2.117	0.21	HOMO → LUMO	0.53
			HOMO−1 → LUMO	0.24
			HOMO−1 → LUMO+1	0.15
$Pheo_{D1}$	2.089	0.17	HOMO → LUMO	0.69
			HOMO−1 → LUMO+1	0.25
$Pheo_{D2}$	2.084	0.17	HOMO → LUMO	0.69
			HOMO−1 → LUMO+1	0.25

Table S2. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using canonical CC2 in the protein electrostatic environment. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	2.137	0.25	HOMO → LUMO	0.60
			HOMO−1 → LUMO	0.18
			HOMO−1 → LUMO+1	0.15
P_{D2}	2.134	0.20	HOMO → LUMO	0.54
			HOMO−1 → LUMO	0.24
			HOMO−1 → LUMO+1	0.14
Chl_{D1}	2.098	0.27	HOMO → LUMO	0.56
			HOMO−1 → LUMO	0.23
			HOMO−1 → LUMO+1	0.14
Chl_{D2}	2.105	0.25	HOMO → LUMO	0.60
			HOMO−1 → LUMO	0.18
			HOMO−1 → LUMO+1	0.15
$Pheo_{D1}$	2.114	0.19	HOMO → LUMO	0.66
			HOMO−1 → LUMO+1	0.22
$Pheo_{D2}$	2.099	0.18	HOMO → LUMO	0.61
			HOMO−1 → LUMO+1	0.21

Table S3. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SOS-CC2 in the gas phase. Corresponding oscillator strengths (*f*) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	*f*	Frontier Molecular Orbitals	% Contribution
P_{D1}	2.022	0.21	HOMO → LUMO	0.72
			HOMO−1 → LUMO+1	0.19
P_{D2}	2.027	0.19	HOMO → LUMO	0.72
			HOMO−1 → LUMO+1	0.21
Chl_{D1}	2.027	0.23	HOMO → LUMO	0.73
			HOMO−1 → LUMO+1	0.19
Chl_{D2}	2.037	0.22	HOMO → LUMO	0.72
			HOMO−1 → LUMO+1	0.19
$Pheo_{D1}$	2.002	0.17	HOMO → LUMO	0.69
			HOMO−1 → LUMO+1	0.24
$Pheo_{D2}$	2.004	0.17	HOMO → LUMO	0.69
			HOMO−1 → LUMO+1	0.24

Table S4. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SOS-CC2 in the protein electrostatic environment. Corresponding oscillator strengths (*f*) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	*f*	Frontier Molecular Orbitals	% Contribution
P_{D1}	2.004	0.26	HOMO → LUMO	0.76
			HOMO−1 → LUMO+1	0.18
P_{D2}	2.012	0.24	HOMO → LUMO	0.76
			HOMO−1 → LUMO+1	0.19
Chl_{D1}	1.961	0.29	HOMO → LUMO	0.77
			HOMO−1 → LUMO+1	0.17
Chl_{D2}	2.010	0.25	HOMO → LUMO	0.75
			HOMO−1 → LUMO+1	0.18
$Pheo_{D1}$	2.154	0.14	HOMO → LUMO	0.68
			HOMO−1 → LUMO+1	0.23
$Pheo_{D2}$	2.171	0.14	HOMO → LUMO	0.67
			HOMO−1 → LUMO+1	0.24

Table S5. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SCS-CC2 in the gas phase. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	2.064	0.23	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.20
P_{D2}	2.071	0.20	HOMO → LUMO HOMO−1 → LUMO+1	0.74 0.21
Chl_{D1}	2.068	0.24	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.19
Chl_{D2}	2.071	0.24	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.20
$Pheo_{D1}$	2.023	0.17	HOMO → LUMO HOMO−1 → LUMO+1	0.71 0.25
$Pheo_{D2}$	2.023	0.17	HOMO → LUMO HOMO−1 → LUMO+1	0.71 0.25

Table S6. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SCS-CC2 in the protein electrostatic environment. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	2.051	0.27	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.18
P_{D2}	2.058	0.24	HOMO → LUMO HOMO−1 → LUMO+1	0.76 0.19
Chl_{D1}	2.011	0.30	HOMO → LUMO HOMO−1 → LUMO+1	0.78 0.17
Chl_{D2}	2.046	0.27	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.18
$Pheo_{D1}$	2.134	0.17	HOMO → LUMO HOMO−1 → LUMO+1	0.71 0.24
$Pheo_{D2}$	2.142	0.17	HOMO → LUMO HOMO−1 → LUMO+1	0.71 0.24

Table S7. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using ADC(2) in the gas phase. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.887	0.21	HOMO → LUMO	0.46
			HOMO−1 → LUMO	0.37
			HOMO−1 → LUMO+1	0.07
P_{D2}	1.898	0.18	HOMO → LUMO	0.45
			HOMO−1 → LUMO	0.36
			HOMO→ LUMO+1	0.07
Chl_{D1}	1.896	0.24	HOMO → LUMO	0.51
			HOMO−1 → LUMO	0.32
			HOMO−1 → LUMO+1	0.08
Chl_{D2}	1.883	0.25	HOMO → LUMO	0.57
			HOMO−1 → LUMO	0.26
			HOMO−1 → LUMO+1	0.09
$Pheo_{D1}$	1.873	0.23	HOMO → LUMO	0.74
			HOMO−1 → LUMO+1	0.17
$Pheo_{D2}$	1.863	0.23	HOMO → LUMO	0.74
			HOMO−1 → LUMO+1	0.16

Table S8. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using ADC(2) in the protein electrostatic environment. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.920	0.28	HOMO → LUMO	0.62
			HOMO−1 → LUMO	0.22
			HOMO−1 → LUMO+1	0.09
P_{D2}	1.918	0.25	HOMO → LUMO	0.59
			HOMO−1 → LUMO	0.24
			HOMO−1 → LUMO+1	0.08
Chl_{D1}	1.878	0.29	HOMO → LUMO	0.53
			HOMO−1 → LUMO	0.31
			HOMO−1 → LUMO+1	0.08
Chl_{D2}	1.874	0.29	HOMO → LUMO	0.65
			HOMO−1 → LUMO	0.19
			HOMO−1 → LUMO+1	0.09
$Pheo_{D1}$	1.916	0.23	HOMO → LUMO	0.72
			HOMO−1 → LUMO+1	0.14
$Pheo_{D2}$	1.897	0.22	HOMO → LUMO	0.67
			HOMO−1 → LUMO	0.14
			HOMO−1 → LUMO+1	0.13

Table S9. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SOS-ADC(2) in the gas phase. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.936	0.24	HOMO → LUMO HOMO−1 → LUMO+1	0.73 0.16
P_{D2}	1.940	0.21	HOMO → LUMO HOMO−1 → LUMO+1	0.73 0.18
Chl_{D1}	1.942	0.26	HOMO → LUMO HOMO−1 → LUMO+1	0.74 0.16
Chl_{D2}	1.952	0.24	HOMO → LUMO HOMO−1 → LUMO+1	0.73 0.16
$Pheo_{D1}$	1.937	0.19	HOMO → LUMO HOMO−1 → LUMO+1	0.72 0.21
$Pheo_{D2}$	1.939	0.19	HOMO → LUMO HOMO−1 → LUMO+1	0.72 0.21

Table S10. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SOS-ADC(2) in the protein electrostatic environment. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.924	0.29	HOMO → LUMO HOMO−1 → LUMO+1	0.78 0.15
P_{D2}	1.933	0.27	HOMO → LUMO HOMO−1 → LUMO+1	0.79 0.16
Chl_{D1}	1.879	0.33	HOMO → LUMO HOMO−1 → LUMO+1	0.79 0.14
Chl_{D2}	1.926	0.28	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.15
$Pheo_{D1}$	2.098	0.16	HOMO → LUMO HOMO−1 → LUMO+1	0.69 0.21
$Pheo_{D2}$	2.116	0.15	HOMO → LUMO HOMO−1 → LUMO+1	0.67 0.21

Table S11. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SCS-ADC(2) in the gas phase. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.946	0.26	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.16
P_{D2}	1.952	0.23	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.18
Chl_{D1}	1.952	0.28	HOMO → LUMO HOMO−1 → LUMO+1	0.78 0.16
Chl_{D2}	1.955	0.27	HOMO → LUMO HOMO−1 → LUMO+1	0.78 0.16
$Pheo_{D1}$	1.930	0.21	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.20
$Pheo_{D2}$	1.929	0.21	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.20

Table S12. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using SCS-ADC(2) in the protein electrostatic environment. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.940	0.31	HOMO → LUMO HOMO−1 → LUMO+1	0.81 0.14
P_{D2}	1.947	0.29	HOMO → LUMO HOMO−1 → LUMO+1	0.80 0.15
Chl_{D1}	1.898	0.35	HOMO → LUMO HOMO−1 → LUMO+1	0.81 0.14
Chl_{D2}	1.930	0.31	HOMO → LUMO HOMO−1 → LUMO+1	0.81 0.14
$Pheo_{D1}$	2.059	0.19	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.20
$Pheo_{D2}$	2.070	0.20	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.20

Table S13. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using DLPNO-STEOM-CCSD in the gas phase. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.633	0.22	HOMO → LUMO HOMO−1 → LUMO+1	0.69 0.18
P_{D2}	1.635	0.20	HOMO → LUMO HOMO−1 → LUMO+1	0.69 0.19
Chl_{D1}	1.642	0.23	HOMO → LUMO HOMO−1 → LUMO+1	0.69 0.17
Chl_{D2}	1.649	0.23	HOMO → LUMO HOMO−1 → LUMO+1	0.68 0.17
$Pheo_{D1}$	1.601	0.15	HOMO → LUMO HOMO−1 → LUMO+1	0.66 0.25
$Pheo_{D2}$	1.591	0.16	HOMO → LUMO HOMO−1 → LUMO+1	0.66 0.25

Table S14. The vertical excitation energies of the lowest excited state (i.e. Q_y) using the QM/MM optimized geometries of the RC chromophores computed using DLPNO-STEOM-CCSD in the protein electrostatic environment. Corresponding oscillator strengths (f) are also shown. The major contributions in the canonical basis associated with the Q_y state are described.

Chromophore	Energy (eV)	f	Frontier Molecular Orbitals	% Contribution
P_{D1}	1.613	0.27	HOMO → LUMO HOMO−1 → LUMO+1	0.73 0.17
P_{D2}	1.620	0.26	HOMO → LUMO HOMO−1 → LUMO+1	0.74 0.18
Chl_{D1}	1.575	0.30	HOMO → LUMO HOMO−1 → LUMO+1	0.74 0.16
Chl_{D2}	1.624	0.26	HOMO → LUMO HOMO−1 → LUMO+1	0.71 0.17
$Pheo_{D1}$	1.743	0.13	HOMO → LUMO HOMO−1 → LUMO+1	0.63 0.26
$Pheo_{D2}$	1.768	0.12	HOMO → LUMO HOMO−1 → LUMO+1	0.62 0.27

Table S15. The vertical excitation energies of the lowest excited state (i.e. Q_y) using gas-phase optimized geometry of the Chlorophyll *a* computed using DLPNO-STEOM-CCSD, CC2, ADC(2), SOS-CC2, SOS-ADC(2), SCS-CC2 and SCS-ADC(2) The geometry in this case is optimized at the PBE/Def2-TZVP level of theory. Corresponding oscillator strengths (*f*) are also shown. The major contributions in the canonical basis associated with the Q_y state are described. The coordinates for this geometry are provided at the end of this document.

Method	Energy (eV)	*f*	Frontier Molecular Orbitals	% Contribution
DLPNO-STEOM-CCSD	1.663	0.25	HOMO → LUMO HOMO−1 → LUMO+1	0.72 0.19
CC2	2.146	0.25	HOMO → LUMO HOMO−1 → LUMO+1	0.70 0.16
SOS-CC2	2.021	0.23	HOMO → LUMO HOMO−1 → LUMO+1	0.75 0.19
SCS-CC2	2.064	0.24	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.18
ADC(2)	1.925	0.29	HOMO → LUMO HOMO−1 → LUMO+1	0.74 0.11
SOS-ADC(2)	1.936	0.26	HOMO → LUMO HOMO−1 → LUMO+1	0.77 0.16
SCS-ADC(2)	1.947	0.28	HOMO → LUMO HOMO−1 → LUMO+1	0.79 0.15

1. P_{D1}

C	6.561183000	-1.337207000	-2.286065000
H	6.676942000	-2.364582000	-1.916161000
H	7.192958000	-0.675062000	-1.679021000
C	5.124996000	-0.930653000	-2.166373000
N	4.737416000	0.371020000	-1.917928000
H	5.334816000	1.193472000	-1.770921000
C	3.389192000	0.425031000	-1.875317000
H	2.827933000	1.336427000	-1.696338000
N	2.868858000	-0.780775000	-2.076528000
C	3.941222000	-1.634565000	-2.262778000
H	3.799038000	-2.696824000	-2.434626000
C	-0.885181000	-4.449801000	-5.625559000
C	-1.464510000	3.906245000	-2.693646000
C	-0.134366000	-0.520158000	3.781782000
C	1.345966000	-6.491047000	-1.663925000
N	0.590609000	-2.225264000	-3.815376000
C	-2.090227000	4.805988000	-3.480338000
C	-1.534225000	-0.497010000	4.415842000
C	1.289603000	-5.959793000	-3.192419000
N	-0.149696000	0.447149000	-2.755974000
O	1.368412000	-7.673442000	-1.372947000
C	2.533595000	-6.436934000	-3.879334000
N	0.892038000	-3.042951000	-0.990643000
C	3.468203000	-8.392990000	-4.846346000
C	1.092565000	-4.465090000	-3.066586000
C	0.031510000	-0.230275000	-5.115860000
C	-0.653484000	1.691347000	-0.701512000
C	0.679127000	-2.497829000	1.386841000
C	2.029951000	-2.208749000	-6.780757000
C	-0.911119000	2.707585000	-5.636723000
C	-0.986864000	2.165166000	2.377600000
C	1.404911000	-5.603695000	1.724024000
C	0.807684000	-3.553185000	-4.062310000
C	-0.250831000	0.705447000	-4.095788000
C	-0.333754000	0.732623000	0.276139000
C	0.943103000	-3.412265000	0.352918000
O	3.597154000	-5.842865000	-3.974717000
C	0.539856000	-3.875315000	-5.518624000
C	-0.728786000	2.052229000	-4.313443000
C	-0.501022000	0.923575000	1.706183000
C	1.211036000	-4.837415000	0.471160000
O	2.328239000	-7.696585000	-4.328013000
C	0.649650000	-2.482430000	-6.173726000
C	-0.948447000	2.605389000	-3.055143000
C	-0.119818000	-0.256414000	2.308782000
C	1.284979000	-5.297954000	-0.847445000
C	0.390746000	-1.563092000	-4.983081000
C	-0.569931000	1.577261000	-2.089473000
C	0.280533000	-1.158533000	1.231308000
C	1.102223000	-4.162249000	-1.687077000

N	0.150668000	-0.519906000	0.012120000
Mg	0.787417000	-1.199088000	-1.884403000
H	-1.593067000	-3.662074000	-5.329312000
H	-1.009769000	-5.279062000	-4.915586000
H	-1.364020000	4.164735000	-1.637540000
H	0.481549000	0.253682000	4.270959000
H	0.349765000	-1.477150000	4.005600000
H	-2.314936000	4.612484000	-4.527375000
H	-2.470206000	5.735033000	-3.056189000
H	-2.151667000	-1.339696000	4.080028000
H	-2.076345000	0.425138000	4.167933000
H	-1.458426000	-0.547081000	5.508421000
H	0.452681000	-6.481441000	-3.679642000
H	3.565982000	-8.201122000	-5.923682000
H	3.269699000	-9.454939000	-4.657145000
H	4.382943000	-8.076823000	-4.336094000
H	-0.092012000	0.128887000	-6.138455000
H	-1.073893000	2.620669000	-0.318842000
H	0.739744000	-2.869980000	2.411686000
H	2.240229000	-2.895762000	-7.615656000
H	2.814281000	-2.333108000	-6.019037000
H	2.079534000	-1.178781000	-7.157276000
H	-0.431221000	2.139405000	-6.445619000
H	-0.473863000	3.715851000	-5.626742000
H	-1.976911000	2.822468000	-5.892988000
H	-0.828425000	2.119285000	3.461476000
H	-2.060827000	2.330273000	2.203467000
H	-0.465049000	3.057866000	2.008495000
H	0.677545000	-6.422478000	1.828803000
H	1.325476000	-4.940843000	2.590446000
H	2.396366000	-6.079407000	1.745880000
H	1.267884000	-4.593403000	-5.927997000
H	-0.119998000	-2.338501000	-6.950339000
H	-1.140234000	-4.800848000	-6.625450000
H	6.946715000	-1.360860000	-3.305316000

2. P$_{D2}$

C	-11.022748000	3.671999000	-1.950795000
H	-11.272523000	4.612080000	-1.450057000
H	-11.465349000	2.864540000	-1.351235000
C	-9.535578000	3.487269000	-2.025157000
N	-8.934424000	2.340769000	-1.557392000
H	-9.428578000	1.509355000	-1.209747000
C	-7.607336000	2.413907000	-1.788479000
H	-6.900746000	1.638932000	-1.508996000
N	-7.303074000	3.564213000	-2.386263000
C	-8.498963000	4.240367000	-2.543647000
H	-8.534807000	5.228216000	-2.995544000
C	-4.552423000	7.622774000	-6.676039000
C	-3.182927000	-1.051278000	-3.785480000
C	-4.729078000	3.034200000	2.882779000
C	-6.010874000	9.287992000	-2.231040000
N	-5.332948000	5.114555000	-4.595771000
C	-3.606767000	-2.232829000	-4.259697000

C	-6.111074000	3.631075000	3.218910000
C	-6.126400000	8.796863000	-3.764532000
N	-4.518827000	2.400809000	-3.695798000
O	-6.173567000	10.442556000	-1.882883000
C	-7.529239000	9.021535000	-4.272106000
N	-5.167708000	5.877749000	-1.742130000
C	-8.980742000	10.557227000	-5.321535000
C	-5.744971000	7.328226000	-3.722727000
C	-4.871547000	3.160792000	-6.004542000
C	-4.009101000	1.041241000	-1.705535000
C	-4.840103000	5.231743000	0.592056000
C	-7.188371000	4.977407000	-7.362152000
C	-3.685786000	0.306774000	-6.681799000
C	-3.972711000	0.305653000	1.341257000
C	-5.297004000	8.370476000	1.081159000
C	-5.647128000	6.434967000	-4.770914000
C	-4.471495000	2.200238000	-5.041596000
C	-4.247544000	1.959766000	-0.666348000
C	-5.078061000	6.205177000	-0.391389000
O	-8.454255000	8.247123000	-4.122556000
C	-5.762120000	6.784214000	-6.239601000
C	-3.982579000	0.857750000	-5.326400000
C	-4.242757000	1.651284000	0.757478000
C	-5.351860000	7.622554000	-0.196750000
O	-7.644097000	10.214735000	-4.900952000
C	-5.786546000	5.391821000	-6.905417000
C	-3.743266000	0.259345000	-4.098519000
C	-4.509079000	2.837438000	1.414107000
C	-5.653369000	8.102934000	-1.475898000
C	-5.282352000	4.475324000	-5.791828000
C	-4.078694000	1.250889000	-3.084418000
C	-4.642391000	3.857610000	0.375782000
C	-5.511265000	7.003453000	-2.370470000
N	-4.516118000	3.282463000	-0.868261000
Mg	-5.227530000	4.061416000	-2.687135000
H	-3.641033000	7.021656000	-6.537374000
H	-4.446386000	8.503517000	-6.029872000
H	-2.349067000	-1.044879000	-3.074168000
H	-3.945633000	3.673515000	3.317391000
H	-4.621943000	2.059914000	3.380808000
H	-4.473229000	-2.305786000	-4.915839000
H	-3.144545000	-3.167290000	-3.941500000
H	-6.864736000	3.306015000	2.486646000
H	-6.076972000	4.727749000	3.227599000
H	-6.454153000	3.313990000	4.209018000
H	-5.444574000	9.438867000	-4.342644000
H	-9.234691000	10.000715000	-6.231307000
H	-8.977721000	11.635777000	-5.503222000
H	-9.708637000	10.302232000	-4.544132000
H	-4.862246000	2.825106000	-7.044997000
H	-3.712383000	0.040900000	-1.392921000
H	-4.830922000	5.565317000	1.630833000
H	-7.581870000	5.673471000	-8.119033000
H	-7.876253000	4.984060000	-6.503684000
H	-7.165620000	3.964338000	-7.784169000
H	-3.246953000	-0.695237000	-6.589897000

H	-2.966642000	0.944858000	-7.222555000
H	-4.585377000	0.230895000	-7.315392000
H	-4.553284000	-0.486424000	0.845558000
H	-4.208665000	0.271288000	2.411781000
H	-2.907292000	0.045441000	1.243720000
H	-5.949024000	9.250742000	1.072445000
H	-4.279839000	8.728888000	1.302026000
H	-5.579723000	7.722747000	1.913884000
H	-6.690109000	7.344443000	-6.445380000
H	-5.101600000	5.374212000	-7.766450000
H	-4.626722000	7.947537000	-7.713862000
H	-11.490202000	3.698130000	-2.935107000

3. Chl$_{D1}$

C	-10.810443000	-6.084505000	-7.523658000
C	-4.656624000	-12.511456000	-6.162534000
C	-2.086851000	-6.322250000	-1.919862000
C	-9.453513000	-3.174805000	-3.548861000
N	-8.959229000	-7.651019000	-5.258760000
C	-4.674525000	-13.639000000	-6.903597000
C	-1.784117000	-7.195385000	-0.692121000
C	-10.358640000	-4.171354000	-4.381471000
N	-6.705894000	-9.575810000	-5.245589000
O	-9.872844000	-2.086488000	-3.172643000
C	-11.527277000	-4.584377000	-3.515704000
N	-7.117667000	-5.803083000	-3.848199000
C	-13.878907000	-4.906592000	-3.428779000
C	-9.470323000	-5.381844000	-4.627178000
C	-8.969117000	-9.924217000	-6.150975000
C	-4.313763000	-9.804594000	-4.749128000
C	-4.964088000	-5.400834000	-2.794230000
C	-11.974033000	-8.964765000	-5.210545000
C	-7.760084000	-12.647446000	-7.092363000
C	-1.548951000	-9.020877000	-3.565779000
C	-6.300804000	-2.550577000	-2.097796000
C	-9.788603000	-6.564711000	-5.265661000
C	-7.638839000	-10.330944000	-5.900839000
C	-4.071383000	-8.588707000	-4.092731000
C	-6.256777000	-4.979111000	-3.127942000
O	-11.408013000	-5.018274000	-2.381801000
C	-10.985728000	-6.810167000	-6.165807000
C	-7.049995000	-11.573146000	-6.346732000
C	-2.800300000	-8.212284000	-3.502791000
C	-6.899212000	-3.715977000	-2.808069000
O	-12.707684000	-4.452534000	-4.150057000
C	-11.005647000	-8.354400000	-6.233663000
C	-5.710382000	-11.542247000	-5.963820000
C	-3.015336000	-7.014323000	-2.859525000
C	-8.184457000	-3.832327000	-3.356419000
C	-9.559060000	-8.696746000	-5.885178000
C	-5.520788000	-10.271669000	-5.272786000
C	-4.387033000	-6.628189000	-3.150955000
C	-8.248396000	-5.114500000	-3.978881000
N	-5.014366000	-7.622715000	-3.873103000
Mg	-7.088999000	-7.844699000	-4.151969000

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H    -10.851956000    -4.997637000    -7.357655000
H    -11.647910000    -6.331614000    -8.193115000
H     -3.725839000   -12.295603000    -5.628967000
H     -2.511774000    -5.364438000    -1.598022000
H     -1.161982000    -6.058677000    -2.444190000
H     -5.544262000   -13.958276000    -7.472008000
H     -3.796184000   -14.283376000    -6.943107000
H     -1.020703000    -6.732963000    -0.056581000
H     -1.412671000    -8.184536000    -0.982845000
H     -2.690464000    -7.348193000    -0.093887000
H    -10.722467000    -3.664398000    -5.287865000
H    -14.679699000    -4.201527000    -3.661185000
H    -13.683742000    -4.920643000    -2.353062000
H    -14.132024000    -5.912539000    -3.787760000
H     -9.605646000   -10.659797000    -6.641167000
H     -3.453379000   -10.469661000    -4.833147000
H     -4.350703000    -4.717995000    -2.206916000
H    -11.937117000   -10.062699000    -5.234122000
H    -13.007100000    -8.643927000    -5.412732000
H    -11.708532000    -8.647165000    -4.191936000
H     -8.848941000   -12.544246000    -7.013838000
H     -7.481301000   -13.637873000    -6.708431000
H     -7.502316000   -12.640261000    -8.164814000
H     -1.678385000    -9.985375000    -3.055882000
H     -0.708712000    -8.510230000    -3.082171000
H     -1.257318000    -9.238113000    -4.605067000
H     -5.829213000    -1.863354000    -2.818794000
H     -5.532068000    -2.860943000    -1.379226000
H     -7.065265000    -1.969544000    -1.564867000
H    -11.913759000    -6.427356000    -5.716163000
H    -11.276821000    -8.705484000    -7.240718000
O     -8.124328000    -8.400456000    -2.453477000
H     -8.595619000    -7.657014000    -1.962026000
H     -7.684303000    -8.903141000    -1.731645000
O     -9.268408000    -6.408855000    -1.095814000
H     -9.972141000    -5.841189000    -1.478310000
H     -9.361138000    -6.352022000    -0.121204000
H     -9.879590000    -6.291951000    -8.051433000
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4. Chl$_{D2}$

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C     6.415649000     7.974332000    -8.721952000
C     0.709841000    15.156722000    -7.053634000
C    -2.364416000     9.044716000    -3.025333000
C     4.975949000     5.601465000    -4.392073000
N     4.531634000     9.842713000    -6.614432000
C     0.708470000    16.264213000    -7.819837000
C    -2.517624000     9.688443000    -1.637451000
C     5.878677000     6.474945000    -5.364676000
N     2.461400000    11.956535000    -6.462500000
O     5.393793000     4.572361000    -3.877829000
C     7.061247000     6.985115000    -4.567327000
N     2.684596000     8.234903000    -4.926269000
C     9.410053000     7.040598000    -4.317648000
C     4.993508000     7.647371000    -5.749177000
C     4.627599000    12.055273000    -7.637674000
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C	0.202784000	12.477061000	-5.655440000
C	0.543865000	8.004084000	-3.779553000
C	7.612009000	11.086544000	-6.829793000
C	3.626527000	14.829991000	-8.533922000
C	-2.605898000	11.898438000	-4.389429000
C	1.820419000	5.232033000	-2.806917000
C	5.325354000	8.732010000	-6.535908000
C	3.377607000	12.590881000	-7.257290000
C	-0.136212000	11.271180000	-5.015737000
C	1.824087000	7.519203000	-4.094217000
O	6.955101000	7.689742000	-3.574372000
C	6.534605000	8.853739000	-7.451768000
C	2.883298000	13.892368000	-7.649385000
C	-1.424669000	10.986313000	-4.407385000
C	2.444340000	6.282615000	-3.658838000
O	8.247323000	6.597093000	-5.067641000
C	6.572574000	10.380195000	-7.710127000
C	1.632891000	14.041235000	-7.057488000
C	-1.324432000	9.728156000	-3.855443000
C	3.717139000	6.299122000	-4.257117000
C	5.155848000	10.806072000	-7.334855000
C	1.381978000	12.798589000	-6.329796000
C	0.016555000	9.246123000	-4.162820000
C	3.790893000	7.497314000	-5.025398000
N	0.710641000	10.209339000	-4.869171000
Mg	2.762272000	10.237263000	-5.358957000
H	6.467356000	6.910967000	-8.445783000
H	7.268890000	8.175040000	-9.387105000
H	-0.083945000	15.090306000	-6.303187000
H	-2.132541000	7.975097000	-2.920435000
H	-3.330448000	9.087694000	-3.552300000
H	1.441067000	16.447334000	-8.602465000
H	-0.046176000	17.032721000	-7.661465000
H	-2.780697000	10.751146000	-1.721058000
H	-1.586842000	9.618529000	-1.061404000
H	-3.304530000	9.195086000	-1.056281000
H	6.228025000	5.842588000	-6.194140000
H	9.265015000	6.863504000	-3.246999000
H	9.576502000	8.112525000	-4.490025000
H	10.243888000	6.436491000	-4.683844000
H	5.269342000	12.706428000	-8.233190000
H	-0.571776000	13.244845000	-5.640420000
H	-0.094176000	7.366678000	-3.166096000
H	7.549516000	12.178690000	-6.930059000
H	8.629885000	10.771263000	-7.102058000
H	7.452672000	10.836735000	-5.771035000
H	3.364155000	14.666438000	-9.590439000
H	4.711338000	14.683686000	-8.454353000
H	3.407329000	15.876366000	-8.294328000
H	-2.432628000	12.773722000	-3.742866000
H	-3.497990000	11.387377000	-4.004671000
H	-2.847053000	12.266772000	-5.398877000
H	1.685918000	4.292086000	-3.362744000
H	0.829027000	5.534548000	-2.450886000
H	2.446931000	4.984573000	-1.937269000
H	7.451887000	8.532292000	-6.933375000

H	6.787282000	10.607219000	-8.765825000
O	3.920034000	10.804230000	-3.762742000
H	4.208042000	11.696258000	-3.516107000
H	4.296514000	10.147331000	-3.079707000
O	4.847236000	8.982889000	-2.173282000
H	5.022543000	9.043072000	-1.209283000
H	5.577982000	8.459424000	-2.572351000
H	5.500383000	8.122249000	-9.295080000

5. Pheo_{D1}

C	-5.779036000	-14.313517000	-15.277842000
C	-4.907337000	-7.492629000	-9.022869000
C	0.209299000	-5.409055000	-14.730193000
C	-2.797078000	-12.001538000	-18.486612000
N	-5.257916000	-11.008703000	-14.473016000
C	-5.662823000	-7.415200000	-7.911420000
C	1.510787000	-6.227966000	-14.681531000
C	-4.001125000	-12.672822000	-17.693400000
N	-4.895731000	-8.985857000	-12.363174000
O	-2.303641000	-12.472652000	-19.505200000
C	-5.181422000	-12.911639000	-18.601436000
N	-2.862809000	-9.695975000	-15.846541000
C	-7.010419000	-11.912076000	-19.719031000
C	-4.235829000	-11.756494000	-16.502132000
C	-6.562341000	-10.793831000	-12.430886000
C	-3.507586000	-7.050514000	-11.751140000
C	-1.243064000	-7.884719000	-15.961042000
C	-8.556736000	-11.848560000	-14.740246000
C	-7.018706000	-9.869842000	-9.464056000
C	-1.395306000	-4.813619000	-11.980809000
C	-0.453504000	-9.411003000	-18.684038000
C	-5.222261000	-11.854905000	-15.536110000
C	-5.885278000	-9.749585000	-11.793682000
C	-2.673581000	-6.920389000	-12.879798000
C	-1.817318000	-9.041075000	-16.503887000
O	-5.459552000	-13.990434000	-19.106967000
C	-6.328609000	-12.895949000	-15.505877000
C	-6.099149000	-9.257547000	-10.457391000
C	-1.637838000	-5.887389000	-12.984425000
C	-1.513426000	-9.759819000	-17.697598000
O	-5.884880000	-11.787863000	-18.822222000
C	-7.191881000	-12.398905000	-14.319990000
C	-5.222133000	-8.192384000	-10.253510000
C	-0.977232000	-6.123641000	-14.163097000
C	-2.424971000	-10.831924000	-17.728571000
C	-6.305413000	-11.334271000	-13.691176000
C	-4.475852000	-8.006660000	-11.490155000
C	-1.634470000	-7.285642000	-14.762050000
C	-3.253940000	-10.754169000	-16.574788000
N	-2.663443000	-7.745453000	-13.961062000
H	-4.558754000	-9.106430000	-13.315700000
H	-3.205736000	-9.324859000	-14.948768000
H	-5.344063000	-14.331868000	-14.269382000
H	-4.959694000	-14.541861000	-15.975242000
H	-3.909515000	-7.044643000	-8.992562000

H	0.363024000	-4.473612000	-14.171267000
H	0.001972000	-5.111231000	-15.769769000
H	-6.666932000	-7.829200000	-7.844311000
H	-5.277216000	-6.920258000	-7.019610000
H	2.369031000	-5.618159000	-14.992000000
H	1.463381000	-7.111769000	-15.332849000
H	1.706068000	-6.578257000	-13.660074000
H	-3.644507000	-13.669761000	-17.393132000
H	-7.825242000	-12.449491000	-19.223171000
H	-6.717990000	-12.441020000	-20.634310000
H	-7.312983000	-10.885683000	-19.947701000
H	-7.374262000	-11.247514000	-11.863067000
H	-3.332766000	-6.336596000	-10.946110000
H	-0.410379000	-7.441405000	-16.504181000
H	-8.444292000	-11.009864000	-15.443057000
H	-9.118050000	-11.495769000	-13.866922000
H	-9.157462000	-12.629503000	-15.228328000
H	-7.911102000	-9.250669000	-9.291199000
H	-6.510069000	-9.962848000	-8.494975000
H	-7.355088000	-10.866362000	-9.775898000
H	-0.614426000	-4.126694000	-12.325943000
H	-1.065081000	-5.213135000	-11.011004000
H	-2.310000000	-4.227961000	-11.803491000
H	0.448447000	-9.042051000	-18.177002000
H	-0.788718000	-8.614154000	-19.364654000
H	-0.192257000	-10.284212000	-19.294948000
H	-6.904628000	-12.849476000	-16.446719000
H	-7.351812000	-13.208718000	-13.593782000
H	-6.531968000	-15.094958000	-15.380363000

6. Pheo$_{D2}$

C	1.286223000	15.625657000	-17.037650000
C	0.859739000	9.331298000	-10.315170000
C	-4.929460000	7.256077000	-15.423025000
C	-1.493314000	12.839529000	-20.223511000
N	0.760150000	12.554059000	-15.966991000
C	1.484424000	9.596059000	-9.151202000
C	-6.318892000	7.896633000	-15.582210000
C	-0.201586000	13.491147000	-19.554555000
N	0.331210000	10.918080000	-13.581624000
O	-1.868912000	13.100064000	-21.362053000
C	1.036964000	13.218693000	-20.386649000
N	-1.871157000	11.358117000	-17.058722000
C	2.896754000	11.778889000	-20.662797000
C	-0.181745000	12.946588000	-18.138267000
C	2.198267000	12.460921000	-14.007331000
C	-1.149931000	9.168329000	-12.689701000
C	-3.650400000	9.721273000	-16.826775000
C	4.009645000	12.927778000	-16.622598000
C	3.014077000	11.582731000	-11.117030000
C	-3.199944000	6.868045000	-12.714293000
C	-4.210751000	10.652380000	-19.884495000
C	0.770151000	13.194240000	-17.165694000
C	1.483125000	11.564049000	-13.209506000
C	-2.113536000	9.038890000	-13.714063000

C	-2.978344000	10.691322000	-17.587368000
O	1.446524000	13.923493000	-21.291498000
C	1.882655000	14.220284000	-17.267745000
C	1.841624000	11.097352000	-11.895673000
C	-3.118824000	7.965582000	-13.719788000
C	-3.143991000	11.105422000	-18.944743000
O	1.649792000	12.064006000	-20.008648000
C	2.816954000	13.755969000	-16.126133000
C	0.910616000	10.128591000	-11.525196000
C	-3.853234000	8.134345000	-14.865712000
C	-2.070763000	11.984315000	-19.206409000
C	1.877033000	12.894939000	-15.292618000
C	-0.055531000	10.017763000	-12.614347000
C	-3.270367000	9.288980000	-15.551978000
C	-1.294041000	12.100756000	-18.019282000
N	-2.227498000	9.824290000	-14.818271000
H	-0.116971000	11.044840000	-14.487128000
H	-1.572067000	11.153798000	-16.093642000
H	0.945818000	15.682767000	-15.992874000
H	0.389989000	15.773469000	-17.659902000
H	0.208087000	8.454367000	-10.345159000
H	-5.018959000	6.364726000	-14.785007000
H	-4.600206000	6.886424000	-16.407143000
H	2.097849000	10.478280000	-8.984419000
H	1.340113000	8.936606000	-8.296122000
H	-6.943606000	7.278408000	-16.241013000
H	-6.259590000	8.899479000	-16.026671000
H	-6.846652000	7.980818000	-14.624487000
H	-0.342427000	14.579811000	-19.583054000
H	2.742491000	11.527151000	-21.721742000
H	3.315884000	10.920461000	-20.127049000
H	3.576343000	12.639280000	-20.594941000
H	3.118546000	12.854169000	-13.574910000
H	-1.273969000	8.497527000	-11.839668000
H	-4.486802000	9.211970000	-17.304421000
H	4.622369000	12.568549000	-15.784156000
H	4.650324000	13.528568000	-17.283192000
H	3.661613000	12.050460000	-17.189029000
H	3.733955000	12.120120000	-11.747047000
H	3.533587000	10.743825000	-10.636349000
H	2.704844000	12.266079000	-10.310868000
H	-2.288221000	6.251237000	-12.746649000
H	-4.061322000	6.214462000	-12.903874000
H	-3.285528000	7.248213000	-11.688114000
H	-5.086310000	10.270547000	-19.341919000
H	-3.844674000	9.846431000	-20.541702000
H	-4.533665000	11.477588000	-20.535018000
H	2.391165000	14.164777000	-18.244859000
H	3.188517000	14.603300000	-15.530820000
H	1.977155000	16.441291000	-17.250773000

PBE/Def2-TZVP Gas-Phase Optimized Geometry of Chlorophyll *a*

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C   -6.96955532980476    35.83164086066760    8.03087168346602
C   -3.97831446364572    34.71442905049682   -0.71308596099324
C    2.45801151962580    37.09786154429551    3.41015181100734
C   -2.25026671626436    35.85967478018361    9.96992474855971
N   -4.58659058760425    34.88156724656598    5.84430804701611
H   -6.98958954258222    36.57850224351265    7.22343249572018
C   -4.89233224915220    34.72948689924828   -1.70223098938268
C    2.52385946996387    38.62831126608160    3.53936219159616
C   -3.74599807311062    35.42120662514685    9.57471435664959
N   -3.77223904702334    34.97699286375801    2.97409194529472
O   -1.87383718468599    36.02293371624963   11.11651349952769
C   -4.09203904321669    34.12740795346006   10.27977253109801
N   -1.85831276169031    35.81191110379756    6.44112915379949
C   -4.82281511907293    33.21105520941798   12.32358878357142
C   -3.73610606053716    35.33027716483542    8.05963353418130
C   -5.92528970775784    34.22783557201340    3.89514612776429
C   -1.92803971175853    35.53689316425194    1.44864988062107
C    0.36022880270147    36.45692962956236    5.65072406411389
C   -6.79236886599198    32.41253494646393    6.39593124954742
C   -6.64031937301997    33.80542421905502    0.87353634555162
C    0.94793893748929    36.46968974618806    0.63596432033778
C    0.94177079268199    36.75803224725851    8.78956480066019
C   -4.75622380891666    34.94904232325437    7.20743091331833
C   -5.05202006781342    34.50967153667435    2.82490358112479
C   -0.92991324334456    35.90740357907517    2.36906362609743
C   -0.54813174111192    36.22159822221447    6.68973612285199
O   -3.93119799304285    33.00906596236503    9.82885145666293
C   -6.17460823102262    34.59020996249630    7.60195831178209
C   -5.35849264033969    34.33542229852746    1.42029928321632
C    0.41389822242334    36.33553271306462    2.02406126481293
C   -0.32594555069147    36.35236474374192    8.11836227341463
O   -4.58073709434601    34.38187257126852   11.51799599260500
C   -6.72225844141453    33.94328099918019    6.30815144852252
C   -4.22033174139175    34.71372501976756    0.71606414645017
C    1.06386186242389    36.58964979459695    3.21533443017390
C   -1.54635156551351    36.00789345544521    8.70421046205845
C   -5.71068747576708    34.38347673631521    5.26017815683008
C   -3.22780166128736    35.10277567822087    1.71318573719710
C    0.10805657613462    36.32086507410688    4.27691472404557
C   -2.43920267987864    35.68994099652298    7.64205750443535
N   -1.09128831387975    35.90893933672996    3.73011409984025
Mg  -2.82908677152284    35.39254551907499    4.72337394089593
H   -6.52924865915722    36.30486166012889    8.91909448387902
H   -8.00731053865120    35.55832942094849    8.27203244496026
H   -2.92414538058384    34.70714595736468   -1.00899440381850
H    3.08680002802214    36.77746790380147    2.56459371405324
H    2.90197812048313    36.63588674622336    4.30667032059589
H   -5.96379662293370    34.78007986612220   -1.51332031097650
H   -4.57814101692053    34.71912524256556   -2.74608102450737
H    3.55867848830001    38.96942775066955    3.68827003164468
H    1.92097918095002    38.97661643942445    4.39010883661435
H    2.12915290783496    39.11245008606240    2.63474380195741
H   -4.40195652559290    36.21463927293521    9.96605403960215
H   -5.19709578144030    33.58757420563515   13.28076507620918
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H  -3.89182642716462    32.64683241500218   12.46618879623649
H  -5.56498856074647    32.55882189634930   11.84372442131859
H  -6.90395466887648    33.83114597727975    3.62011159735627
H  -1.64454379926567    35.59646372317199    0.39704499642482
H   1.36294784211267    36.78092893583597    5.93526832059795
H  -7.10269209982149    31.97218692157744    5.43796722506948
H  -7.51302112794546    32.10349047217936    7.16722942589882
H  -5.80946051293792    31.99653072793389    6.66114446142932
H  -6.45610328543132    33.16376714798754   -0.00100706944107
H  -7.31295218976082    34.61434054515752    0.54286687581539
H  -7.18576188492248    33.21368464240687    1.62087530442276
H   2.01964951049906    36.70858030111329    0.64196068664663
H   0.43520479229202    37.27068036564848    0.07955188329943
H   0.81647434269838    35.54170567440227    0.05803091212039
H   0.79472655720226    36.84120984694055    9.87300989840401
H   1.30604949455989    37.72643943992408    8.41269141892819
H   1.74220520217878    36.02263437339533    8.60959099626279
H  -6.16636801731903    33.86158602379247    8.42730063398050
H  -7.72274823890209    34.33636840986109    6.06599257797070
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