The structure of Chlorophyll a - water complexes: insights from quantum chemistry calculations

By A. Ben Fredj, Z. Ben Lakhdar and M. F. Ruiz-López

Supplementary information

Table S1. Cartesian coordinates (in Å) and total energies (in Hartree) for Chl.a-46 and Chl.a-73 models and their monohydrated (1w) and dihydrated (2w and 2w') complexes for optimized geometries at the B3LYP/6-31G* level in gas phase.

Chl.a-46

N	-0.000056	0.000000	0.000045
C	-0.000039	0.000000	1.382464
C	1.301110	0.000000	-0.411981
C	-1.144575	0.000000	2.172163
C	-2.492559	0.000000	1.748842
N	-2.898196	0.000000	0.443889
C	-4.277686	0.000000	0.445745
C	-5.090526	0.000000	-0.701015
C	-4.650119	0.000000	-2.028288
N	-3.295144	0.000000	-2.353281
C	-3.239239	0.000000	-3.689079
H	-6.164449	0.000000	-0.534251
C	-5.439541	0.000000	-3.236323
H	-6.521394	0.000000	-3.277630
C	-4.749724	0.000000	1.807687
H	-5.790736	0.000000	2.106532
C	-4.533154	0.000000	-4.284821
C	-2.172694	0.000000	-4.616398
C	-0.838268	0.000000	-4.271161
N	-0.403494	0.000000	-2.966074
C	0.953867	0.000000	-2.910741
C	1.382406	0.000000	1.861869
C	-2.811081	0.000000	-6.000635
C	1.727787	0.000000	-1.758355
C	1.562120	0.000000	-4.309008
C	2.169782	0.000000	0.732253
H	3.251555	0.000000	0.684688
H	-0.998703	0.000000	3.247916
H	2.804133	0.000000	-1.908218
C	1.788696	0.000000	3.261584
C	-4.359636	0.000000	-5.747636
C	0.331021	0.000000	-5.240191
H	0.298463	0.878561	-5.895084
H	0.298463	-0.878561	-5.895084
C	-3.644220	0.000000	2.616147
H	0.984549	0.000000	3.994846
H	-2.551423	0.879581	-6.604889

Mg	-1.636802	0.000000	-1.200041
C	3.050042	0.000000	3.717538
H	2.199331	-0.879296	-4.455996
H	2.199331	0.879296	-4.455996
O	-5.196170	0.000000	-6.630524
H	-2.551423	-0.879581	-6.604889
H	3.909717	0.000000	3.052445
H	3.261302	0.000000	4.782312
H	-3.612392	0.000000	3.698694

ENERGY=-1418.636710 Hartree

Ch.a-46 1w

N	-0.004613	-0.015316	0.000814
C	-0.002946	-0.055700	-1.378197
C	1.292916	-0.013788	0.415314
C	-1.145745	-0.106534	-2.170634
C	-2.495654	-0.164994	-1.753087
N	-2.910132	-0.141236	-0.454738
C	-4.281644	-0.268155	-0.461339
C	-5.095033	-0.335619	0.682691
C	-4.660603	-0.305425	2.014432
N	-3.317499	-0.141155	2.345389
C	-3.254526	-0.240075	3.677539
H	-6.161663	-0.458286	0.512848
C	-5.440901	-0.481272	3.214977
H	-6.512069	-0.635207	3.250239
C	-4.744529	-0.359411	-1.826350
H	-5.778785	-0.469868	-2.128739
C	-4.536919	-0.441020	4.266526
C	-2.185840	-0.230242	4.606703
C	-0.850276	-0.161115	4.268358
N	-0.412498	-0.046478	2.971019
C	0.943247	-0.055609	2.916643
C	1.381717	-0.062875	-1.857765
C	-2.817879	-0.407893	5.983010
C	1.718305	-0.013881	1.764010
C	1.550832	-0.136254	4.314642
C	2.166895	-0.038369	-0.727681
H	3.248557	-0.055572	-0.678595
H	-0.994999	-0.134033	-3.245606
H	2.794776	-0.022694	1.914687
C	1.789759	-0.102113	-3.256382
C	-4.359060	-0.546081	5.723343
C	0.317835	-0.238103	5.238624
H	0.275352	0.569570	5.978768
H	0.295380	-1.177838	5.803184
C	-3.637701	-0.294563	-2.628367
H	0.989729	-0.213164	-3.985905
H	-2.648116	0.438827	6.662136
H	-3.596448	-0.342451	-3.709642
Mg	-1.660810	0.198693	1.187759
C	3.046583	-0.012602	-3.716413

H	2.215665	-1.002360	4.403702
H	2.160277	0.750380	4.526276
O	-5.187360	-0.704080	6.600940
H	-2.467428	-1.303629	6.513430
H	3.901201	0.107798	-3.055596
H	3.258920	-0.055660	-4.780185
O	-1.804232	2.329374	1.395608
H	-2.588014	2.481859	1.949991
H	-1.058162	2.734636	1.865703

ENERGY=-1495.073097 Hartree

Ch.a-46 2w (5-coordinated)

C	2.939747	-1.413905	0.145583
C	2.763790	-0.012898	0.228819
C	3.977302	0.712870	0.420447
C	5.089437	-0.251608	0.440703
C	4.439059	-1.665820	0.255417
C	3.615154	2.045966	0.530361
C	2.175879	2.074820	0.403951
N	1.692619	0.786338	0.202018
C	1.318478	3.181641	0.498125
C	-0.089123	3.148797	0.459042
N	-0.852301	2.013173	0.285776
C	-2.159549	2.389789	0.381794
C	-2.244686	3.816661	0.596576
C	-0.961112	4.287413	0.642911
C	-3.261422	1.506048	0.323076
C	-3.240719	0.118097	0.216142
N	-2.098110	-0.642506	0.091588
C	-2.476657	-1.951736	0.060018
C	-3.911713	-2.043919	0.145920
C	-4.410465	-0.765807	0.241944
Mg	-0.185555	0.065362	-0.215240
O	-0.193907	0.196117	-2.305039
C	-1.598707	-3.054658	-0.014944
C	-0.207193	-3.058550	-0.018222
N	0.592702	-1.967522	0.009138
C	1.912669	-2.332113	0.057151
C	2.070214	-3.843434	0.032325
C	0.611563	-4.345940	-0.030488
C	-5.796234	-0.329832	0.362607
C	-6.882219	-1.103125	0.215482
O	6.284300	-0.058356	0.566489
H	1.777561	4.153437	0.662959
H	4.248518	2.907152	0.703355
H	-0.632478	5.306437	0.807565
H	-4.472392	-2.970347	0.161070
H	-4.235965	1.976578	0.412220
H	-2.075915	-4.031108	-0.035177
H	2.664054	-4.163623	-0.831736
H	2.599101	-4.199430	0.924318
H	-5.949817	0.723066	0.592299
H	4.872965	-2.141185	-0.634829
H	0.349769	-4.984620	0.820479
H	0.407678	-4.927811	-0.936754

H	4.716628	-2.298055	1.109661
H	-6.814196	-2.160414	-0.027626
H	-7.881622	-0.695392	0.331761
H	-3.162911	4.379205	0.713229
H	0.207590	1.059456	-2.599515
H	-1.079323	0.149709	-2.696799
O	0.988293	2.577150	-2.761949
H	1.935031	2.399432	-2.639642
H	0.737564	3.034967	-1.938050

ENERGY=-1571.509875 Hartree

Chl.a-46 2w'(6-coordinated)

C	0.752737	4.452789	0.000000
C	-0.079670	3.272289	0.000000
N	0.713948	2.157660	0.000000
C	2.026621	2.579715	0.000000
C	2.054849	4.023438	0.000000
Mg	0.002293	0.158385	0.000000
N	-0.645800	-1.886304	0.000000
C	-1.949747	-2.240253	0.000000
C	-2.100162	-3.759931	0.000000
C	-0.638665	-4.266287	0.000000
C	0.173541	-2.980375	0.000000
C	3.155074	1.730041	0.000000
C	3.145044	0.327775	0.000000
N	1.959760	-0.389177	0.000000
C	2.296497	-1.678408	0.000000
C	3.714477	-1.861274	0.000000
C	4.266645	-0.591649	0.000000
C	3.984834	-3.309353	0.000000
C	2.582989	-4.013320	0.000000
C	1.555373	-2.886050	0.000000
C	-1.497005	3.259079	0.000000
C	-2.361402	2.160107	0.000000
N	-1.946825	0.844351	0.000000
C	-3.055620	0.047852	0.000000
C	-4.232614	0.876351	0.000000
C	-3.826242	2.194653	0.000000
C	-3.039914	-1.368512	0.000000
C	-4.639975	3.404053	0.000000
C	-5.980325	3.458391	0.000000
O	5.046972	-3.902753	0.000000
H	2.951524	4.631442	0.000000
H	5.312013	-0.309412	0.000000
H	-0.406893	-4.879309	0.878884
H	4.125576	2.219827	0.000000
H	-0.406893	-4.879309	-0.878884
H	-5.250349	0.505681	0.000000
H	-1.962158	4.240659	0.000000
H	-4.018899	-1.841430	0.000000
H	-4.094952	4.346501	0.000000
H	2.517259	-4.668473	0.879342
H	-2.659812	-4.097695	-0.879635

H	-2.659812	-4.097695	0.879635
H	2.517259	-4.668473	-0.879342
H	-6.599038	2.564708	0.000000
H	-6.503309	4.409706	0.000000
H	0.392978	5.474713	0.000000
O	-0.079670	0.301060	2.222897
O	-0.079670	0.301060	-2.222897
H	-0.953574	0.717993	2.313633
H	-0.953574	0.717993	-2.313633
H	0.556228	1.022285	-2.366270
H	0.556228	1.022285	2.366270

ENERGY=-1571.504143 Hartree

Chl.a-73

N	-0.648482	1.362157	-0.260604
C	-1.953721	1.089543	-0.338849
C	-2.739832	2.271835	-0.383685
C	-1.863123	3.350821	-0.332012
C	-0.544624	2.752351	-0.256117
C	-4.146332	1.900350	-0.474716
C	-4.162597	0.298643	-0.523069
C	-2.696486	-0.110717	-0.403699
C	-2.141558	-1.374152	-0.360790
N	-0.786287	-1.576936	-0.227357
C	-0.518853	-2.902920	-0.105414
C	-1.805383	-3.720052	-0.031038
C	-2.883399	-2.697699	-0.474415
C	0.740607	-3.484886	-0.014980
C	2.003825	-2.858018	0.002799
N	2.196773	-1.508872	-0.042030
C	3.555445	-1.279651	0.017749
C	4.255006	-2.559947	0.086788
C	3.282008	-3.542191	0.087255
C	4.151551	-0.022620	0.008336
C	3.524262	1.241101	-0.036710
N	2.174023	1.429845	-0.101832
C	1.956999	2.791095	-0.119510
C	3.229562	3.489001	-0.063031
C	4.207937	2.519676	-0.013593
Mg	0.755841	-0.082420	-0.156350
C	5.695108	2.702570	0.062125
C	3.404123	4.982174	-0.021794
C	3.250642	5.576743	1.392003
C	0.693803	3.399655	-0.190830
C	3.463088	-5.024827	0.203498
C	5.705000	-2.695315	0.179983
C	6.449487	-3.722564	-0.257630
C	-3.388260	-2.952636	-1.907283
C	-2.044977	-4.265224	1.388822
O	-5.145097	2.590953	-0.517850
C	-5.068007	-0.231989	0.575664
O	-6.357877	-0.182141	0.188932
C	-7.317240	-0.555472	1.190745

C	-2.196970	4.810277	-0.349034
O	-4.703883	-0.628799	1.663133
H	-4.614528	0.032135	-1.486113
H	-1.758008	-4.566453	-0.727896
H	-1.230692	-4.926737	1.703652
H	-2.116537	-3.445758	2.112786
H	-2.981340	-4.834021	1.427890
H	-3.736329	-2.711207	0.212833
H	-3.279043	4.948607	-0.415305
H	-1.843335	5.315603	0.558849
H	-1.733800	5.321414	-1.202809
H	0.677073	4.485700	-0.199526
H	4.393370	5.246586	-0.414319
H	2.680279	5.461086	-0.693873
H	3.379526	6.665210	1.374155
H	2.260848	5.356712	1.806594
H	3.995980	5.155696	2.075535
H	6.215118	2.122551	-0.710538
H	5.977198	3.751260	-0.071417
H	6.096930	2.379003	1.031678
H	5.236138	-0.006321	0.043381
H	6.225450	-1.862240	0.651943
H	7.527369	-3.724635	-0.123751
H	6.024374	-4.573251	-0.780582
H	4.389446	-5.262209	0.736513
H	2.633560	-5.489027	0.747635
H	3.519053	-5.514643	-0.778730
H	0.747266	-4.568623	0.050481
H	-8.292597	-0.440162	0.717495
H	-7.161380	-1.590868	1.506377
H	-7.233575	0.098719	2.062333
H	-4.112122	-2.194268	-2.222880
H	-2.557308	-2.942627	-2.622369
H	-3.878334	-3.931375	-1.970197

ENERGY= -1921.725176 Hartree

Ch.a-73 1w

N	-0.669574	1.365826	-0.229776
C	-1.967322	1.083236	-0.367540
C	-2.754967	2.259366	-0.500042
C	-1.881731	3.343659	-0.460981
C	-0.567711	2.753665	-0.296611
C	-4.154097	1.878092	-0.634494
C	-4.165557	0.275502	-0.602003
C	-2.700947	-0.123849	-0.450274
C	-2.144822	-1.388446	-0.420017
N	-0.799852	-1.592804	-0.231629
C	-0.524794	-2.920638	-0.179049
C	-1.807800	-3.749773	-0.199830
C	-2.876106	-2.708823	-0.627714
C	0.738946	-3.495699	-0.086648
C	1.999731	-2.859135	-0.047503
N	2.183433	-1.510787	-0.028277
C	3.538916	-1.273988	-0.000275
C	4.250951	-2.551773	-0.003852

C	3.284607	-3.539691	-0.024847
C	4.129032	-0.012610	-0.000641
C	3.499650	1.251555	-0.039465
N	2.151633	1.441809	-0.063807
C	1.935260	2.799052	-0.139788
C	3.211758	3.498553	-0.146484
C	4.188557	2.530371	-0.085459
Mg	0.728979	-0.077784	0.144599
O	0.285130	-0.089263	2.250122
C	5.677914	2.710037	-0.069627
C	3.388267	4.991633	-0.180376
C	3.258038	5.654558	1.204914
C	0.672195	3.404623	-0.236579
C	3.477820	-5.024995	0.010354
C	5.703645	-2.679055	0.042158
C	6.444794	-3.684243	-0.449738
C	-3.325196	-2.895675	-2.089316
C	-2.098532	-4.381385	1.173325
O	-5.155006	2.558772	-0.747602
C	-5.050975	-0.190420	0.541545
O	-6.344285	-0.214430	0.165970
C	-7.284257	-0.533033	1.204284
C	-2.215551	4.798766	-0.579999
O	-4.666761	-0.480723	1.656780
H	-4.626131	-0.048072	-1.542232
H	-1.728872	-4.554169	-0.941906
H	-1.289791	-5.052218	1.482987
H	-2.211981	-3.608155	1.942688
H	-3.028767	-4.960778	1.142455
H	-3.756027	-2.763150	0.024534
H	-3.297004	4.932266	-0.665294
H	-1.867898	5.367611	0.291877
H	-1.746573	5.249225	-1.464454
H	0.656066	4.488996	-0.300389
H	4.371239	5.235896	-0.600821
H	2.653975	5.438763	-0.863083
H	3.389626	6.740585	1.132814
H	2.274027	5.458609	1.644864
H	4.012616	5.264215	1.896563
H	6.166649	2.115528	-0.851833
H	5.957588	3.755461	-0.231011
H	6.115546	2.400488	0.888955
H	5.214305	0.006589	0.002670
H	6.231060	-1.857918	0.527339
H	7.525955	-3.680221	-0.345034
H	6.013617	-4.521093	-0.989708
H	4.411419	-5.283095	0.521002
H	2.657556	-5.525157	0.536633
H	3.528159	-5.461851	-0.996926
H	0.755347	-4.581540	-0.076821
H	-8.265431	-0.496886	0.730394
H	-7.087842	-1.529614	1.609424
H	-7.222048	0.199084	2.013572
H	-4.043624	-2.128460	-2.394665
H	-2.467256	-2.842052	-2.769445
H	-3.802487	-3.874073	-2.220264
H	-0.441640	0.551677	2.335202
H	-0.089529	-0.942870	2.522432

ENERGY=-1998.162800 Hartree

Ch.a-73 2w(5-coordinated)

N	-0.610940	1.303045	-0.508463
C	-1.903330	1.007935	-0.639010
C	-2.708138	2.175857	-0.758161
C	-1.843785	3.272331	-0.705426
C	-0.527793	2.692695	-0.540174
C	-4.102501	1.781810	-0.864609
C	-4.103593	0.179518	-0.763458
C	-2.630223	-0.207258	-0.672816
C	-2.069014	-1.466607	-0.594921
N	-0.725896	-1.649840	-0.391635
C	-0.437677	-2.967641	-0.295284
C	-1.707761	-3.816749	-0.312285
C	-2.788511	-2.799418	-0.764719
C	0.832221	-3.523132	-0.159732
C	2.078211	-2.868013	-0.081788
N	2.247287	-1.517920	-0.059591
C	3.597146	-1.270276	0.016993
C	4.324307	-2.542171	0.040589
C	3.370491	-3.537878	-0.012848
C	4.176959	-0.005242	0.037620
C	3.533251	1.250596	-0.038787
N	2.186038	1.422610	-0.109315
C	1.959585	2.776251	-0.236821
C	3.228882	3.491155	-0.213175
C	4.211850	2.536451	-0.093204
Mg	0.746237	-0.110811	0.115726
O	0.273272	-0.098194	2.148073
C	5.698407	2.730359	-0.036530
C	3.390118	4.984702	-0.283393
C	3.190952	5.684514	1.075401
C	0.699743	3.363099	-0.411934
C	3.575789	-5.021091	0.030741
C	5.775914	-2.653418	0.136874
C	6.544876	-3.647118	-0.335179
C	-3.240410	-3.025303	-2.219809
C	-1.993842	-4.428592	1.070692
O	-5.118573	2.442150	-0.974777
C	-4.887366	-0.186323	0.481615
O	-6.136364	-0.572424	0.195451
C	-6.992659	-0.828918	1.325084
C	-2.193974	4.725064	-0.813486
O	-4.466007	-0.111324	1.627203
O	-2.077461	1.098016	2.606675
H	-4.634762	-0.209315	-1.637430
H	-1.613277	-4.631772	-1.041187
H	-1.183788	-5.095080	1.385391
H	-2.096483	-3.644572	1.829770
H	-2.924030	-5.009155	1.050540
H	-3.669885	-2.852029	-0.112409
H	-3.279509	4.854105	-0.812947
H	-1.776613	5.310125	0.015481
H	-1.805093	5.163186	-1.742315
H	0.671318	4.446984	-0.479784
H	4.387802	5.229593	-0.666972
H	2.681507	5.402612	-1.010194
H	3.309678	6.770036	0.978093

H	2.191831	5.485554	1.478491
H	3.920869	5.325906	1.809538
H	6.214175	2.134741	-0.800407
H	5.973285	3.777151	-0.197426
H	6.112300	2.431110	0.935840
H	5.261109	0.025504	0.078912
H	6.276946	-1.829461	0.644878
H	7.621637	-3.632501	-0.192688
H	6.141534	-4.484710	-0.895235
H	4.502048	-5.269248	0.559161
H	2.750199	-5.526258	0.543709
H	3.647888	-5.460253	-0.974220
H	0.864155	-4.608252	-0.131646
H	-7.955821	-1.109066	0.899059
H	-6.587579	-1.640266	1.934986
H	-7.088133	0.069959	1.938590
H	-3.967418	-2.272183	-2.540190
H	-2.384808	-2.977752	-2.903105
H	-3.707441	-4.011527	-2.326745
H	0.914414	0.283037	2.765631
H	-0.614977	0.316591	2.362902
H	-2.075085	1.871200	2.019775
H	-2.855958	0.581563	2.299094

ENERGY=-2074.608093 Hartree

Chl.a-73 2w'(6-coordinated)

N	2.120561	1.446616	-0.075966
C	3.472414	1.253857	-0.023503
C	4.153467	2.536806	-0.003749
C	3.172632	3.505964	-0.047699
C	1.897421	2.807311	-0.095103
C	4.102539	-0.014457	0.012765
C	3.516816	-1.283545	0.007484
N	2.167943	-1.520682	-0.095590
C	1.964159	-2.864120	-0.016994
C	3.244037	-3.547650	0.113644
C	4.217793	-2.565035	0.117962
C	0.695072	-3.486513	-0.038787
C	-0.577557	-2.914757	-0.124321
N	-0.858824	-1.597309	-0.228083
C	-2.205412	-1.387875	-0.357041
C	-2.950422	-2.712299	-0.472555
C	-1.860639	-3.742747	-0.064560
C	-2.753726	-0.114727	-0.394660
C	-2.018354	1.094342	-0.324110
C	-2.811778	2.274406	-0.395786
C	-4.214205	1.891748	-0.500937
C	-4.221626	0.289875	-0.519215
C	-1.941895	3.359329	-0.341917
C	-0.618044	2.766558	-0.234568
N	-0.720568	1.381313	-0.217634
Mg	0.675787	-0.105980	-0.150253
O	0.578089	0.016974	2.072554

C	-2.283684	4.816580	-0.388904
C	0.626722	3.412868	-0.168823
C	-5.113624	-0.212482	0.603497
O	-4.740926	-0.524522	1.715563
O	-5.218207	2.573963	-0.566427
C	-2.088102	-4.333206	1.338548
C	-3.486841	-2.952864	-1.896037
C	5.664367	-2.696962	0.252836
C	6.422841	-3.735405	-0.132289
C	3.423234	-5.026835	0.270518
C	5.641050	2.724306	0.061510
C	3.347688	4.999558	-0.009843
C	3.193611	5.598476	1.402012
O	0.969386	-0.124638	-2.365569
O	-6.402793	-0.240442	0.210114
C	-7.350932	-0.592143	1.229974
H	-4.681021	-0.001447	-1.470955
H	-1.815547	-4.567022	-0.787909
H	-1.271259	-5.004454	1.625044
H	-2.150272	-3.537313	2.089161
H	-3.024096	-4.903448	1.368820
H	-3.788423	-2.737203	0.233681
H	-3.366705	4.948404	-0.454295
H	-1.928303	5.345162	0.505104
H	-1.827177	5.311432	-1.256048
H	0.611101	4.499192	-0.187964
H	4.336854	5.264289	-0.402556
H	2.623102	5.477013	-0.682358
H	3.323041	6.686860	1.382016
H	2.202715	5.380811	1.815536
H	3.938305	5.178994	2.087415
H	6.157891	2.144198	-0.713302
H	5.920456	3.773457	-0.074884
H	6.051133	2.402370	1.028292
H	5.186849	0.008491	0.063100
H	6.171419	-1.848169	0.711617
H	7.496739	-3.730246	0.030705
H	6.013661	-4.604069	-0.638118
H	4.332188	-5.250958	0.838467
H	2.576351	-5.478315	0.798204
H	3.511100	-5.540246	-0.697401
H	0.705026	-4.570682	0.027556
H	-8.327299	-0.553921	0.746260
H	-7.149491	-1.596120	1.613855
H	-7.304372	0.120922	2.057133
H	-4.223723	-2.196789	-2.185528
H	-2.671997	-2.925703	-2.628735
H	-3.970857	-3.934608	-1.960759
H	1.341711	0.605761	2.201431
H	-0.197538	0.593976	2.177694
H	1.348818	0.762275	-2.485911
H	1.737830	-0.721537	-2.336389

ENERGY=-2074.592243 Hartree

Table S2. Selected bond distances (in Å) for Chl.a-46 and Chl.a-73 models and their monohydrated (1w) and dihydrated (2w and 2w') complexes as computed at the B3LYP/6-31G* level in gas phase.

Bond distances	**Model Ch.a-46**				**Model Ch.a-73**			
	Chl.a	1w	2w	2w'	Chl.a	1w	2w	2w'
Mg-N	2.069	2.095	2.106	2.092	2.068	2.081	2.107	2.090
O···Mg	–	2.146	2.094	2.229	–	2.152	2.087	2.231
Mg-$N_{A,B,C}$ plane	0.000	0.277	0.361	0.000	0.004	0.275	0.406	0.000
Mg-$N_{A,C,D}$ plane	0.000	0.277	0.361	0.000	0.004	0.275	0.405	0.000
Mg-$N_{B,C,D}$ plane	0.000	0.293	0.365	0.000	0.005	0.289	0.360	0.009
Mg-$N_{A,B,D}$ plane	0.000	0.292	0.365	0.000	0.004	0.288	0.362	0.008

Table S3. Solvation energies at the B3LYP/6-31G* level for different species in cyclohexane using the Polarizable Continuum Model (PCM).

H_2O

```
Variational PCM results
 ======================
 <psi(f)|   H    |psi(f)>                    (a.u.) =     -76.408761
 <psi(f)|H+V(f)/2|psi(f)>                   (a.u.) =     -76.413574
 Total free energy in solution:
  with all non electrostatic terms          (a.u.) =     -76.411952
 ---------------------------------------------------------------------
 (Polarized solute)-Solvent              (kcal/mol) =      -3.02
 ---------------------------------------------------------------------
 Cavitation energy                       (kcal/mol) =       4.21
 Dispersion energy                       (kcal/mol) =      -3.60
 Repulsion energy                        (kcal/mol) =       0.41
 Total non electrostatic                 (kcal/mol) =       1.02
-----------------------------------------------------------------------
```

Ch.a-73

```
 Variational PCM results
 ======================
 <psi(f)|   H    |psi(f)>                    (a.u.) =   -1921.724766
 <psi(f)|H+V(f)/2|psi(f)>                   (a.u.) =   -1921.734572
 Total free energy in solution:
  with all non electrostatic terms          (a.u.) =   -1921.703710
 ---------------------------------------------------------------------
 (Polarized solute)-Solvent              (kcal/mol) =      -6.15
```

```
-------------------------------------------------------------------
Cavitation energy                       (kcal/mol) =      52.82
Dispersion energy                       (kcal/mol) =     -34.72
Repulsion energy                        (kcal/mol) =       1.27
Total non electrostatic                 (kcal/mol) =      19.37
-------------------------------------------------------------------
```

Chl.a-73 1w

```
Variational PCM results
=======================
<psi(f)|   H    |psi(f)>                    (a.u.) =   -1998.162435
<psi(f)|H+V(f)/2|psi(f)>                   (a.u.) =   -1998.171226
Total free energy in solution:
 with all non electrostatic terms          (a.u.) =   -1998.136568
-------------------------------------------------------------------
(Polarized solute)-Solvent              (kcal/mol) =      -5.52
-------------------------------------------------------------------
Cavitation energy                       (kcal/mol) =      54.91
Dispersion energy                       (kcal/mol) =     -34.44
Repulsion energy                        (kcal/mol) =       1.27
Total non electrostatic                 (kcal/mol) =      21.75
-------------------------------------------------------------------
```

Chl.a-73 2w (5-coordinated)

```
Variational PCM results
=======================
<psi(f)|   H    |psi(f)>                    (a.u.) =   -2074.607761
<psi(f)|H+V(f)/2|psi(f)>                   (a.u.) =   -2074.615496
Total free energy in solution:
 with all non electrostatic terms          (a.u.) =   -2074.578976
-------------------------------------------------------------------
(Polarized solute)-Solvent              (kcal/mol) =      -4.85
-------------------------------------------------------------------
Cavitation energy                       (kcal/mol) =      56.31
Dispersion energy                       (kcal/mol) =     -34.68
Repulsion energy                        (kcal/mol) =       1.28
Total non electrostatic                 (kcal/mol) =      22.92
-------------------------------------------------------------------
```

Chl.a-73 2w’ (6-coordinated)

```
Variational PCM results
=======================
<psi(f)|   H    |psi(f)>                    (a.u.) =   -2074.591863
<psi(f)|H+V(f)/2|psi(f)>                   (a.u.) =   -2074.600853
Total free energy in solution:
 with all non electrostatic terms          (a.u.) =   -2074.563890
-------------------------------------------------------------------
(Polarized solute)-Solvent              (kcal/mol) =      -5.64
-------------------------------------------------------------------
Cavitation energy                       (kcal/mol) =      56.22
Dispersion energy                       (kcal/mol) =     -34.30
Repulsion energy                        (kcal/mol) =       1.28
Total non electrostatic                 (kcal/mol) =      23.19
-------------------------------------------------------------------
```