Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Modeling and Computations of the Intramolecular Electron Transfer process in the Two-Heme Protein Cytochrome c_4

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This supporting information includes 3 Figures and 7 Tables for the details: the potential energy surfaces of the cyt c_4 heme group vs. the rotation angle of methionine and histidine ligands; Optimized structure of cyt c_4 heme group (ox., low spin state) with four water molecules; Selected virtual orbitals of cyt c_4 (Red) as possible candidates for bridge-assisted ET; Table of Parameters of the Kihara potential; Tables of Cartesian coordinates (Å) and the atomic ChelpG charges describing the optimized cyt c_4 heme group structures; Table of calculated vibrational frequencies of selected calculated Raman bands.

S1

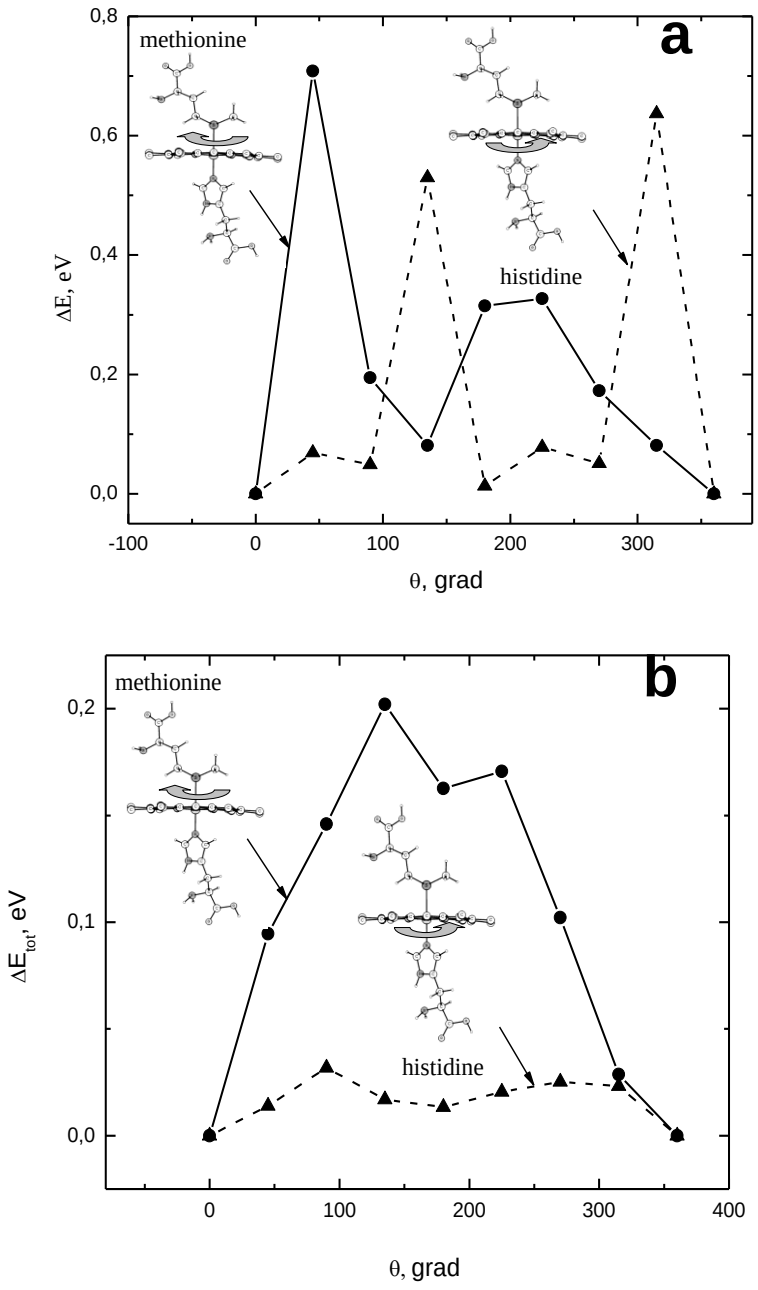

Figure S1. Potential energy surfaces of the cyt c_4 heme group vs. the rotation angle of methionine and histidine ligands relative to the heme ring calculated for a low spin oxidized (**a**) and singlet reduced (**b**) states. The total energies of fully optimized structures are taken as reference point.

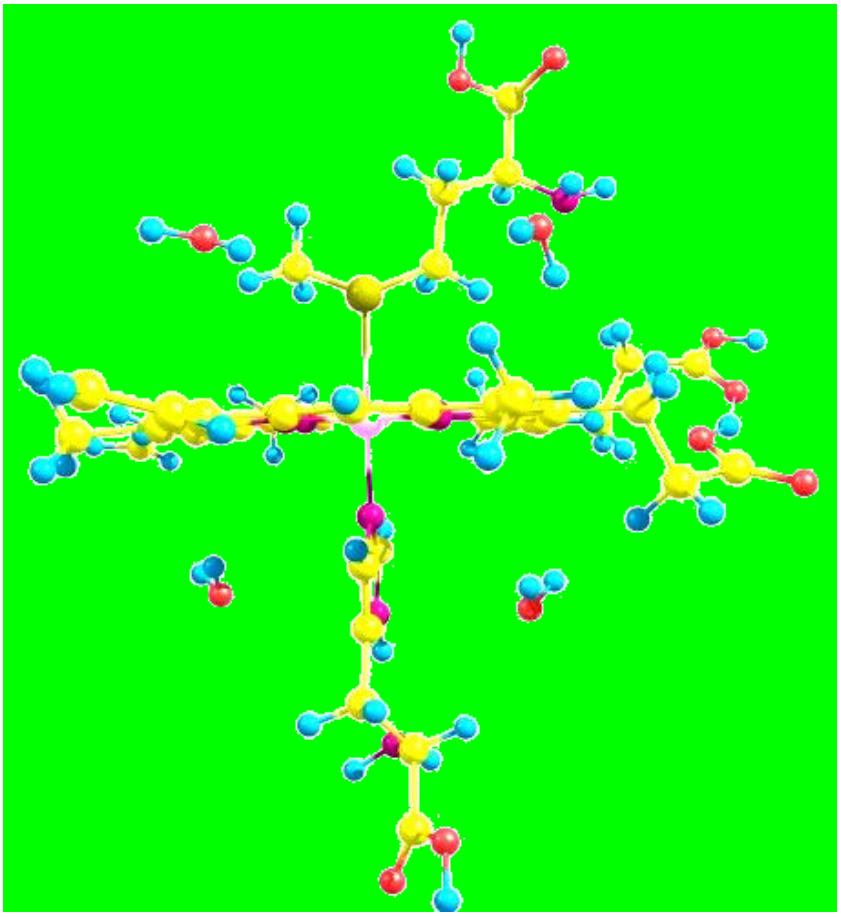

Figure S2. Optimized structure of cyt c_4 heme group in its oxidized and low spin state associating with four H_2O molecules.

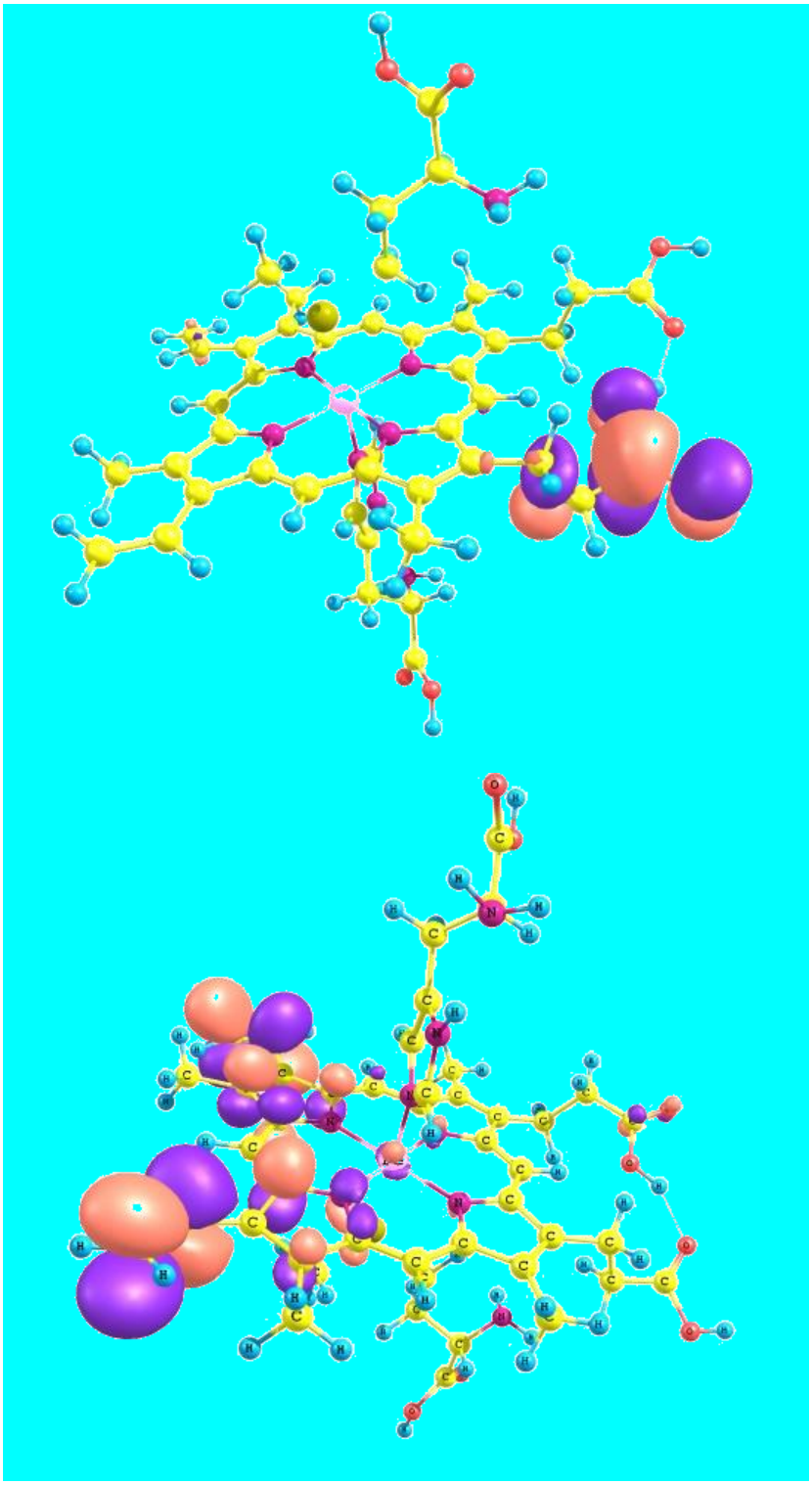

Figure 3. Selected virtual orbitals of cyt c_4 (reduced form) as possible candidates for bridge assisted ET.

Table S1. The parameters of the Kihara potential, eq.(14) calculated using the data at the website http://lrb.jinr.ru/kafedra/html/for_students/for_students.shtml (V. A. Osipov, *Workbook on biophysics*).

atom pair [&]	ε 100 (eV)	σ (Å)
HH	0.533	2.4
CC	0.521	3.4
NN	0.89	3.1
OO	1.01	3.04
SS	3.	3.6

[&]As the contribution of the Fe atoms to the non-Coulomb term is rather minor, we did not include them in the calculations.

Table S2. Cartesian coordinates (Å) and the atomic ChelpG charges describing the optimized structure of cyt c_4 heme group in the oxidized state (m_s = 2).

atom	*x*	*y*	*z*	*q*
c	-2.39749	1.08212	-2.19558	-0.184238
h	-1.81076	-0.10895	-5.25444	0.073140
c	-2.59422	-0.13918	-4.48534	-0.215450
c	-0.30186	-1.71893	-3.11164	-0.261418
c	-0.96693	-0.66598	-2.49012	0.205673
h	4.89632	-3.4925	5.06722	0.172190
c	4.09561	-5.28274	-3.80151	-0.361568
c	3.63952	-4.79538	-2.6206	-0.107028
c	2.43457	-3.00016	-1.2028	0.018988
c	3.09861	-2.42666	1.11484	0.042787
fe	0.73553	-0.8038	0.06773	0.948618
n	2.09272	-1.49757	1.38294	-0.044899
n	0.05674	0.45878	1.47443	-0.234181
n	-0.68616	-0.18032	-1.21152	-0.361196
n	1.33335	-2.15616	-1.30511	-0.235760
c	3.26787	-3.10446	-0.09109	-0.183508
h	4.10258	-3.79126	-0.15672	0.135758
c	2.58578	-3.79713	-2.42288	0.054492
h	4.10578	-5.18243	-1.71458	0.127353
h	4.87899	-6.03574	-3.82353	0.162101
h	3.73063	-4.93892	-4.76413	0.177847
c	1.53743	-3.43379	-3.26444	-0.058112
c	1.19461	-3.99116	-4.61896	-0.068976
h	0.1328	-3.86638	-4.8561	0.033094
h	1.42026	-5.06314	-4.66473	0.056718
h	1.76942	-3.50528	-5.42075	0.046243
c	0.78439	-2.40499	-2.5671	0.170954
c	2.27346	-1.11958	2.71112	-0.005443
c	3.93113	-2.6378	2.29151	-0.050596

c	5.13549	-3.53601	2.35183	-0.050467
h	5.59166	-3.67695	1.3662	0.026055
h	4.88319	-4.53228	2.74328	0.060382
h	5.90004	-3.11309	3.01395	0.043641
c	3.40483	-1.83602	3.30004	0.073459
c	3.85458	-1.652	4.68248	-0.108865
h	3.55949	-0.71663	5.15818	0.120224
c	4.5872	-2.51636	5.42744	-0.354895
h	4.87273	-2.26509	6.44556	0.160806
c	1.50056	-0.1733	3.38138	-0.204374
h	1.71667	0.01167	4.42668	0.148903
c	0.47714	0.56858	2.79978	0.121227
c	-0.94952	1.40841	1.32052	0.174479
c	-0.28808	1.59734	3.49824	0.010878
c	-1.17315	2.12521	2.57779	-0.113701
c	-0.10594	1.96043	4.94771	-0.245434
h	-0.27738	1.09797	5.60576	0.077601
h	-0.80245	2.74776	5.2516	0.107034
h	0.90949	2.32842	5.14889	0.091873
h	-0.62847	-1.99713	-4.10702	0.151056
c	-2.03559	0.10956	-3.10921	-0.013688
h	-3.07902	-1.12283	-4.55523	0.084235
h	-3.34339	0.6128	-4.75292	0.096108
c	-1.56006	0.88543	-1.01449	0.179938
c	-3.45126	2.15207	-2.33851	0.282860
c	-1.68164	1.63034	0.15709	-0.243257
h	-2.42297	2.42131	0.17781	0.184741
c	-2.23833	3.17414	2.78395	0.114278
h	-3.19423	2.77667	2.42338	-0.021620
h	-2.36626	3.36204	3.85491	0.037436
h	-3.56343	2.42434	-3.39523	-0.012638
h	-3.14703	3.05837	-1.80607	-0.079724
c	-4.842	1.6959	-1.79021	-0.226465
h	-5.23494	0.86294	-2.37847	0.085824
h	-4.72863	1.35517	-0.75295	0.043084
c	-1.96689	4.54282	2.0645	-0.211864
h	-1.17613	4.41725	1.31421	0.035564
h	-1.63267	5.30219	2.77594	0.084040
c	-3.193	5.08334	1.34325	0.798931
o	-3.70767	6.19711	1.50539	-0.594342
o	-3.66916	4.15392	0.43671	-0.660986
h	-4.48792	4.38514	-0.09039	0.521243
c	-5.84422	2.82944	-1.80758	0.915286
o	-5.71283	3.93618	-1.24229	-0.680616
o	-6.9712	2.54011	-2.5361	-0.750624
h	-7.61215	3.28993	-2.53407	0.521685
c	4.57159	4.35693	-1.44196	0.254901
h	3.58587	4.82447	-1.33341	0.044087
c	5.6274	5.40749	-1.07102	0.789166
c	4.65888	3.1598	-0.4449	-0.280020
h	5.65315	2.69776	-0.54421	0.107365
h	4.58221	3.54081	0.5775	0.131570

n	4.72388	3.89603	-2.84352	-0.775880
h	5.69916	3.6728	-3.05894	0.333497
h	4.39337	4.59158	-3.51457	0.328313
o	5.34095	6.00245	0.14104	-0.766228
h	6.01388	6.67651	0.39246	0.524656
o	6.62401	5.68602	-1.74952	-0.583262
c	3.58535	2.13464	-0.68204	0.210473
n	3.20009	1.77026	-1.97843	-0.197639
c	2.83226	1.34462	0.16724	-0.140869
c	2.24873	0.80344	-1.89965	0.198369
h	1.76455	0.3429	-2.74288	0.051867
n	2.0068	0.5198	-0.60574	-0.438223
h	2.8272	1.30932	1.24274	0.100727
h	3.60472	2.28554	-2.77689	0.238293
c	-0.47657	-4.18438	0.47648	0.014209
h	0.56542	-4.39609	0.71994	0.061970
h	-0.61933	-4.19701	-0.60549	0.003686
h	-1.13009	-4.9064	0.97029	0.079195
s	-0.85323	-2.46422	1.15053	-0.435822
c	-2.60001	-2.19502	0.44871	0.397841
h	-2.56608	-2.44868	-0.61558	-0.051071
h	-2.79384	-1.12736	0.55147	-0.019878
c	-3.65377	-3.01152	1.2078	-0.155854
h	-3.48337	-4.08739	1.0884	0.081146
h	-3.59892	-2.78116	2.28122	0.071229
c	-5.08564	-2.68317	0.68999	0.114069
h	-5.12162	-2.90378	-0.38441	0.090876
n	-5.41354	-1.26816	0.89396	-1.004984
c	-6.08799	-3.62979	1.37431	0.858375
o	-6.92398	-3.30341	2.22639	-0.603853
o	-5.94028	-4.93376	0.92788	-0.796684
h	-6.57689	-5.54369	1.36724	0.521624
h	-5.50203	-1.02525	1.88109	0.410926
h	-6.24462	-0.97069	0.38499	0.398944

Table S3. Cartesian coordinates (Å) and the atomic ChelpG charges describing the optimized structure of the cyt c_4 heme group in the oxidized state ($m_s = 4$).

atom	*x*	*y*	*z*	*q*
c	-2.2497	1.38996	-2.07543	-0.135067
h	-1.81005	0.15403	-5.15092	0.072763
c	-2.58667	0.23133	-4.37852	-0.201486
c	-0.51652	-1.63484	-3.02714	-0.231498
c	-1.01609	-0.49772	-2.40278	0.207577
h	4.4661	-4.02271	5.15118	0.165934
c	3.02752	-6.07253	-3.58111	-0.365956
c	2.67415	-5.46722	-2.41956	-0.085268
c	1.89458	-3.40924	-1.0699	0.004781
c	2.71347	-2.88284	1.20231	0.057036
fe	0.70925	-0.84656	0.11401	0.780685
n	1.92909	-1.7476	1.43258	-0.059715
n	0.23959	0.52397	1.50509	-0.168893
n	-0.6697	-0.05602	-1.12162	-0.330551
n	1.0021	-2.34537	-1.20382	-0.170301
c	2.7009	-3.64643	0.03855	-0.184783
h	3.36722	-4.49902	-0.0006	0.143850
c	1.87243	-4.25081	-2.2638	0.048227
h	3.02029	-5.93021	-1.49553	0.117663
h	3.61731	-6.98542	-3.57161	0.165092
h	2.76954	-5.6762	-4.55832	0.179228
c	0.93976	-3.68376	-3.13131	-0.020470
c	0.4991	-4.18643	-4.47851	-0.153122
h	-0.50731	-3.83966	-4.73671	0.058708
h	0.48755	-5.28314	-4.49729	0.077054
h	1.17671	-3.85589	-5.27974	0.068573
c	0.42001	-2.50254	-2.46745	0.156761
c	2.24575	-1.33136	2.72452	0.012401
c	3.5368	-3.18374	2.36053	-0.028027
c	4.53247	-4.3064	2.44937	-0.055011
h	4.89538	-4.61205	1.46263	0.025541
h	4.10197	-5.19567	2.93214	0.062421
h	5.40329	-4.00506	3.04347	0.043157
c	3.23726	-2.2217	3.32303	0.061064
c	3.78629	-2.04033	4.669	-0.113391
h	3.70667	-1.03567	5.08422	0.119446
c	4.37334	-2.98282	5.44807	-0.324996
h	4.75545	-2.7266	6.43281	0.153968
c	1.6912	-0.22798	3.36651	-0.171942
h	1.9948	-0.02731	4.38659	0.137099
c	0.75309	0.62693	2.79965	0.109195
c	-0.66835	1.57811	1.38226	0.116600
c	0.1612	1.76096	3.49932	0.011280
c	-0.72603	2.35279	2.61858	-0.077385
c	0.48154	2.149	4.91746	-0.241506
h	0.20458	1.35564	5.62481	0.077640
h	-0.05507	3.05498	5.21398	0.106916

h	1.55377	2.3464	5.05068	0.092506
h	-0.88296	-1.85991	-4.02185	0.136473
c	-1.9932	0.39807	-3.00529	-0.027370
h	-3.2046	-0.67483	-4.44672	0.086757
h	-3.22457	1.08147	-4.64058	0.090782
c	-1.4267	1.09726	-0.90911	0.150055
c	-3.20074	2.55519	-2.19255	0.211888
c	-1.43387	1.85748	0.25626	-0.167133
h	-2.08769	2.7211	0.29656	0.149654
c	-1.65154	3.52176	2.85464	0.106719
h	-2.66845	3.22362	2.57509	-0.018686
h	-1.68232	3.7545	3.92382	0.042590
h	-3.2419	2.9003	-3.23349	0.003109
h	-2.84282	3.39848	-1.59551	-0.062904
c	-4.6441	2.18758	-1.73134	-0.203485
h	-5.11295	1.48713	-2.42893	0.084988
h	-4.6089	1.68786	-0.75184	0.045490
c	-1.28125	4.82975	2.06842	-0.244618
h	-0.55362	4.59617	1.28102	0.045835
h	-0.82848	5.57217	2.7304	0.091447
c	-2.48386	5.47441	1.39454	0.824877
o	-2.86921	6.64062	1.54046	-0.598738
o	-3.10585	4.57043	0.55257	-0.658903
h	-3.91797	4.86892	0.052	0.514695
c	-5.53175	3.40633	-1.59487	0.913290
o	-5.2296	4.48634	-1.04508	-0.677736
o	-6.77872	3.2184	-2.13872	-0.754720
h	-7.35275	4.01208	-2.02267	0.522844
c	5.33672	3.7887	-1.74946	0.275430
h	4.39844	4.355	-1.71226	0.032474
c	6.47695	4.75808	-1.40746	0.785107
c	5.27169	2.6634	-0.67045	-0.242932
h	6.21121	2.09034	-0.71037	0.093834
h	5.21701	3.12265	0.32129	0.117743
n	5.48896	3.21547	-3.10777	-0.777331
h	6.4415	2.87724	-3.26673	0.329684
h	5.2536	3.88854	-3.8393	0.325900
o	6.2032	5.47314	-0.25733	-0.768969
h	6.93095	6.09611	-0.02669	0.524183
o	7.5237	4.88599	-2.05527	-0.585407
c	4.09424	1.74922	-0.86524	0.177264
n	3.70227	1.32301	-2.13893	-0.177380
c	3.22493	1.12771	0.01712	-0.111461
c	2.63324	0.48511	-2.00817	0.174332
h	2.11963	0.01591	-2.83063	0.054029
n	2.32071	0.3417	-0.70808	-0.449888
h	3.18712	1.19037	1.09227	0.090514
h	4.18018	1.71042	-2.965	0.228188
c	-1.28198	-4.1869	0.72326	0.042286
h	-0.32228	-4.5577	1.0893	0.064367
h	-1.27792	-4.16804	-0.3692	-0.009948
h	-2.08999	-4.81755	1.0999	0.056077

s	-1.46507	-2.43034	1.38461	-0.471563
c	-3.06289	-1.89718	0.50755	0.408434
h	-2.95749	-2.15985	-0.55145	-0.064289
h	-3.08891	-0.80941	0.59414	-0.011116
c	-4.32149	-2.52319	1.12336	-0.168747
h	-4.29335	-3.61532	1.03614	0.086276
h	-4.3715	-2.27763	2.19375	0.065605
c	-5.61202	-2.00911	0.42022	0.121110
h	-5.52904	-2.22577	-0.65277	0.084636
n	-5.7762	-0.5601	0.60037	-0.988456
c	-6.81644	-2.80954	0.94574	0.854757
o	-7.70715	-2.37437	1.68819	-0.606469
o	-6.79165	-4.12039	0.49365	-0.795319
h	-7.55574	-4.63827	0.83913	0.520008
h	-5.91585	-0.30713	1.57992	0.405383
h	-6.53118	-0.17327	0.03436	0.390654

Table S4. Cartesian coordinates (Å) and the atomic ChelpG charges describing the optimized structure of deprotonated (dp) cyt c_4 heme group in the oxidized state (m_s = 2).

atom	*x*	*y*	*z*	*q*
c	-0.037	3.40639	2.51728	-0.188174
h	-0.66035	2.12155	5.52095	0.064701
c	0.15194	2.64597	4.99818	-0.249533
c	0.1429	-0.07428	3.49171	-0.238920
c	0.11821	1.15324	2.83478	0.163577
h	0.98785	-4.88195	-5.06277	0.172958
c	-0.7221	-5.71176	3.81936	-0.390987
c	-0.34976	-5.01623	2.71461	-0.077490
c	-0.16	-2.87373	1.28543	0.016739
c	-0.06447	-2.89038	-1.19406	0.025943
fe	0.03209	-0.09908	0.03009	1.040443
n	0.09562	-1.52007	-1.39553	-0.069916
n	0.17194	1.29746	-1.39613	-0.257675
n	0.05598	1.31874	1.45003	-0.308953
n	-0.00758	-1.50531	1.47617	-0.232885
c	-0.21498	-3.51091	0.04589	-0.191202
h	-0.34343	-4.58666	0.04337	0.128903
c	-0.20668	-3.56677	2.57502	0.026283
h	-0.13356	-5.60064	1.8199	0.120131
h	-0.77984	-6.79701	3.79529	0.151218
h	-0.99674	-5.23471	4.75438	0.181941
c	-0.05174	-2.58831	3.55502	-0.039123
c	0.02776	-2.76941	5.0465	-0.049025
h	0.52018	-1.9219	5.53491	0.028315
h	0.59578	-3.67363	5.29779	0.041156
h	-0.96849	-2.87568	5.50075	0.033455
c	0.05111	-1.3176	2.85959	0.119092
c	0.28193	-1.35487	-2.76336	0.006500
c	0.01248	-3.60579	-2.45971	-0.044856
c	-0.16508	-5.08953	-2.6298	-0.003408
h	-0.74476	-5.52823	-1.81042	0.011259
h	0.80066	-5.61524	-2.66838	0.040247
h	-0.69215	-5.31105	-3.56571	0.022528
c	0.25568	-2.65115	-3.44297	0.047849
c	0.42667	-2.81356	-4.88729	-0.094459
h	0.26966	-1.91572	-5.48586	0.120823
c	0.76582	-3.94282	-5.55915	-0.378000
h	0.85508	-3.93548	-6.64232	0.151551
c	0.43291	-0.12377	-3.40247	-0.235065
h	0.59359	-0.11969	-4.4743	0.147111
c	0.35307	1.11247	-2.76648	0.143416
c	0.06941	2.67496	-1.21666	0.208565
c	0.39019	2.39765	-3.45774	-0.007001
c	0.1984	3.3738	-2.49769	-0.102819
c	0.59752	2.56386	-4.93933	-0.231465
h	1.56783	2.15992	-5.26046	0.068784
h	0.57056	3.62053	-5.22218	0.099324

h	-0.18049	2.04879	-5.52024	0.078967
h	0.18335	-0.05767	4.57521	0.146180
c	0.07988	2.44844	3.50738	0.026145
h	1.09949	2.27319	5.41205	0.084923
h	0.07947	3.70694	5.25652	0.110369
c	-0.04161	2.69097	1.24249	0.166317
c	-0.11034	4.90521	2.65077	0.281580
c	-0.06931	3.32911	0.00392	-0.255035
h	-0.15258	4.41822	-0.0155	0.213278
c	0.16257	4.87213	-2.64859	0.094472
h	0.89272	5.31671	-1.96112	-0.022528
h	0.4751	5.14144	-3.66406	0.036898
h	-0.41513	5.1738	3.66929	-0.008887
h	-0.86271	5.30855	1.96494	-0.067859
c	1.25245	5.60109	2.33925	-0.254406
h	2.02631	5.21532	3.0113	0.048739
h	1.52999	5.38521	1.30119	0.056357
c	-1.22351	5.53441	-2.34189	-0.208185
h	-1.92469	4.77723	-1.96304	0.010916
h	-1.66737	5.95722	-3.24791	0.061306
c	-1.15918	6.66139	-1.27963	0.792688
o	-1.8396	7.70919	-1.44444	-0.686764
o	-0.38275	6.38458	-0.23414	-0.680331
h	0.01701	7.2474	0.80433	0.510783
c	1.15475	7.11565	2.5322	0.853147
o	0.42048	7.79448	1.64829	-0.769354
o	1.73364	7.68171	3.51365	-0.675626
c	-6.27437	1.31989	-1.04471	0.283170
h	-5.74282	2.2784	-1.05801	0.048338
c	-7.49278	1.44866	-1.96733	0.772004
c	-5.31542	0.22337	-1.60766	-0.241152
h	-5.84509	-0.74175	-1.59049	0.088425
h	-5.08742	0.45097	-2.65313	0.118894
n	-6.67327	1.01607	0.3496	-0.780440
h	-7.39687	0.29434	0.38314	0.327849
h	-7.00384	1.8441	0.84668	0.324746
o	-7.14845	1.99659	-3.18633	-0.765937
h	-7.92514	2.08582	-3.78525	0.523552
o	-8.64587	1.09207	-1.68531	-0.590453
c	-4.03606	0.13666	-0.82617	0.180118
n	-4.03279	0.18922	0.57341	-0.208882
c	-2.71146	-0.00934	-1.19726	-0.104854
c	-2.74796	0.08974	1.01203	0.219521
h	-2.44298	0.12509	2.04356	0.043154
n	-1.92389	-0.03556	-0.04226	-0.491458
h	-2.27968	-0.08434	-2.18075	0.091771
h	-4.91113	0.38757	1.06919	0.242386
c	3.21083	-1.42055	1.15961	0.013047
h	2.78681	-2.3865	0.8784	0.060277
h	2.88261	-1.14774	2.16462	-0.010156
h	4.30059	-1.45433	1.09494	0.078043
s	2.56697	-0.1618	-0.08972	-0.460834

c	3.18138	1.45669	0.69186	0.478860
h	2.85553	1.45203	1.73711	-0.059505
h	2.65557	2.24973	0.15761	-0.075952
c	4.69515	1.65362	0.56225	-0.181541
h	5.24873	0.9002	1.13635	0.059100
h	4.99502	1.57182	-0.49189	0.070215
c	5.07802	3.07672	1.08679	0.212491
h	4.71996	3.16309	2.12082	0.055112
n	4.46052	4.12657	0.2803	-0.993917
c	6.60813	3.18713	1.13333	0.830194
o	7.31662	3.85429	0.36696	-0.603817
o	7.14731	2.40615	2.1495	-0.791996
h	8.12903	2.47927	2.17134	0.512536
h	4.9507	4.32856	-0.58768	0.398505
h	4.20723	4.97119	0.78443	0.392640

Table S5. Cartesian coordinates (Å) and the atomic ChelpG charges describing the optimized structure of cyt c_4 heme group in the reduced state ($m_s = 1$).

atom	*x*	*y*	*z*	*q*
c	-2.42175	1.02995	-2.21764	-0.229901
h	-1.79309	-0.15326	-5.27005	0.070186
c	-2.58145	-0.20178	-4.50567	-0.242189
c	-0.27201	-1.74955	-3.09801	-0.260104
c	-0.95079	-0.69048	-2.4933	0.171810
h	5.10381	-3.25995	5.11181	0.179660
c	3.94749	-5.58998	-3.65001	-0.437832
c	3.54696	-4.97318	-2.50727	-0.052250
c	2.39916	-3.09613	-1.14229	-0.007388
c	3.09479	-2.4584	1.16351	0.031418
fe	0.7431	-0.81713	0.07322	0.719555
n	2.13499	-1.47612	1.39349	-0.006345
n	0.09407	0.52248	1.44489	-0.169222
n	-0.68622	-0.19374	-1.22048	-0.284595
n	1.34053	-2.2111	-1.27727	-0.136978
c	3.21954	-3.19689	-0.01601	-0.211262
h	4.02259	-3.92428	-0.05253	0.138470
c	2.53567	-3.92888	-2.34818	-0.001614
h	4.03968	-5.29134	-1.58759	0.110388
h	4.70851	-6.36627	-3.621	0.152407
h	3.55651	-5.33393	-4.62929	0.182851
c	1.52142	-3.53052	-3.21316	-0.027346
c	1.18485	-4.09009	-4.56924	-0.077042
h	0.15939	-3.84687	-4.868	0.023253
h	1.28317	-5.18341	-4.57479	0.043622
h	1.85511	-3.70234	-5.35146	0.035558
c	0.79858	-2.45727	-2.53801	0.106214
c	2.35439	-1.02628	2.68546	-0.012323
c	3.94621	-2.63599	2.33795	-0.056183
c	5.112	-3.58257	2.43455	0.020505
h	5.49294	-3.86222	1.44628	0.000182
h	4.84311	-4.51252	2.9583	0.026457
h	5.93898	-3.12547	2.99291	0.007605
c	3.47909	-1.74922	3.30128	0.012439
c	3.96558	-1.49206	4.65628	-0.052612
h	3.64456	-0.54691	5.09654	0.106378
c	4.75778	-2.28122	5.42803	-0.427280
h	5.05693	-1.96006	6.42304	0.149169
c	1.61196	-0.02334	3.31737	-0.215427
h	1.86436	0.21818	4.34439	0.138022
c	0.5636	0.69454	2.74083	0.088633
c	-0.93113	1.44525	1.2897	0.147079
c	-0.19346	1.74785	3.42997	0.022501
c	-1.12418	2.21595	2.527	-0.170525
c	0.04023	2.17797	4.8544	-0.241175
h	-0.08782	1.34148	5.5558	0.061527
h	-0.6574	2.96842	5.15235	0.094720

h	1.05815	2.56792	4.9978	0.080364
h	-0.59205	-2.03369	-4.0954	0.143533
c	-2.0363	0.06467	-3.12643	0.001048
h	-3.03699	-1.20013	-4.57672	0.079319
h	-3.35071	0.52888	-4.78013	0.087881
c	-1.57629	0.8526	-1.03159	0.146218
c	-3.49293	2.08195	-2.36235	0.317542
c	-1.69418	1.6145	0.13368	-0.244634
h	-2.44923	2.39226	0.14761	0.179775
c	-2.2052	3.25108	2.72291	0.162817
h	-3.16274	2.82185	2.4043	-0.038193
h	-2.30874	3.48686	3.78808	0.015088
h	-3.67111	2.29345	-3.42449	-0.025121
h	-3.17142	3.01872	-1.89409	-0.090721
c	-4.84784	1.64506	-1.7067	-0.254952
h	-5.23393	0.74966	-2.19962	0.092558
h	-4.67091	1.408	-0.65133	0.045143
c	-1.98076	4.5919	1.93387	-0.230560
h	-1.24791	4.42136	1.13631	0.040540
h	-1.59215	5.37502	2.59049	0.078745
c	-3.2529	5.10624	1.28091	0.787807
o	-3.80168	6.20027	1.48935	-0.617649
o	-3.74148	4.17792	0.38514	-0.625755
h	-4.58657	4.38415	-0.10665	0.501438
c	-5.88048	2.74184	-1.78836	0.911175
o	-5.82345	3.86579	-1.24158	-0.683216
o	-6.96074	2.41578	-2.58208	-0.754158
h	-7.60461	3.16123	-2.62629	0.508753
c	4.5705	4.35437	-1.55172	0.279026
h	3.56024	4.76615	-1.44536	0.035184
c	5.56432	5.44379	-1.12956	0.781666
c	4.69798	3.13329	-0.58823	-0.238038
h	5.69745	2.69137	-0.72927	0.085301
h	4.64369	3.48569	0.44631	0.111538
n	4.76931	3.94018	-2.95634	-0.805407
h	5.74758	3.7194	-3.15254	0.333849
h	4.43652	4.6363	-3.62381	0.325037
o	5.20174	6.02975	0.07048	-0.766814
h	5.85096	6.71521	0.35054	0.515249
o	6.58619	5.77032	-1.75085	-0.602049
c	3.62483	2.10708	-0.8119	0.164235
n	3.23221	1.70558	-2.09293	-0.225689
c	2.86928	1.34332	0.06312	-0.104087
c	2.2687	0.7386	-1.96507	0.192939
h	1.77547	0.25396	-2.78966	0.033387
n	2.03259	0.49586	-0.66833	-0.467867
h	2.87114	1.34048	1.13979	0.077965
h	3.60271	2.17023	-2.92267	0.240630
c	-0.55038	-4.17764	0.54307	0.053876
h	0.49527	-4.40769	0.75439	0.047830
h	-0.7176	-4.1916	-0.53636	-0.015793
h	-1.20187	-4.89163	1.05342	0.041554

s	-0.85614	-2.44012	1.20776	-0.488850
c	-2.60849	-2.14278	0.54851	0.404992
h	-2.60197	-2.37941	-0.52106	-0.059773
h	-2.77774	-1.07174	0.66266	-0.018419
c	-3.66705	-2.95241	1.30937	-0.176561
h	-3.49766	-4.02788	1.18249	0.084624
h	-3.59835	-2.73057	2.38447	0.057390
c	-5.10643	-2.62253	0.81347	0.159175
h	-5.14376	-2.80828	-0.26789	0.076035
n	-5.44526	-1.22137	1.06731	-1.017787
c	-6.09612	-3.60393	1.46428	0.853244
o	-6.93312	-3.33387	2.33754	-0.621712
o	-5.95281	-4.88988	0.95508	-0.800133
h	-6.57875	-5.51456	1.38831	0.512447
h	-5.39698	-0.96822	2.05309	0.413090
h	-6.33039	-0.92809	0.65913	0.392918

Table S6. Cartesian coordinates (Å) and the atomic ChelpG charges describing the optimized structure of cyt c_4 heme group in the reduced state ($m_s = 4$).

atom	*x*	*y*	*z*	*q*
c	-0.01637	3.45663	2.49651	-0.204127
h	-0.79618	2.18916	5.47481	0.055959
c	0.04991	2.69365	4.98375	-0.239493
c	0.05348	-0.03727	3.46947	-0.252792
c	0.05397	1.19337	2.81303	0.152488
h	0.56409	-4.92742	-5.20892	0.185766
c	-0.39321	-5.75409	3.86216	-0.456551
c	-0.16154	-5.01799	2.74092	-0.070256
c	-0.06591	-2.87785	1.29118	-0.033281
c	-0.00456	-2.90912	-1.20318	-0.053564
fe	0.03	-0.08845	0.01022	0.670963
n	0.07295	-1.53335	-1.41619	0.083125
n	0.1195	1.32282	-1.43232	-0.131149
n	0.04078	1.35876	1.42944	-0.205181
n	0.00215	-1.50366	1.47021	-0.132667
c	-0.08075	-3.52392	0.0512	-0.159731
h	-0.14148	-4.60702	0.05874	0.102379
c	-0.09979	-3.56616	2.59154	0.006617
h	-0.00139	-5.58463	1.82188	0.128442
h	-0.40046	-6.84158	3.81579	0.139866
h	-0.5943	-5.31087	4.83218	0.184651
c	-0.03842	-2.56683	3.56249	-0.041730
c	-0.01043	-2.73134	5.05932	-0.039042
h	0.28749	-1.80679	5.56552	0.014979
h	0.69908	-3.51704	5.35529	0.026829
h	-0.99582	-3.0211	5.45699	0.020738
c	0.01589	-1.29673	2.8495	0.092022
c	0.16344	-1.3621	-2.78738	-0.068674
c	0.0338	-3.62917	-2.47188	-0.032452
c	-0.05772	-5.1233	-2.63531	0.021893
h	-0.39201	-5.61548	-1.7154	0.004547
h	0.91338	-5.5641	-2.91053	0.015563
h	-0.76856	-5.38786	-3.43101	-0.002819
c	0.15019	-2.66529	-3.47176	0.013926
c	0.22296	-2.8181	-4.92267	-0.034614
h	0.11414	-1.89298	-5.49103	0.105280
c	0.41149	-3.95022	-5.65524	-0.471599
h	0.43584	-3.90462	-6.7423	0.145651
c	0.2436	-0.1203	-3.43345	-0.213556
h	0.3293	-0.11811	-4.5154	0.134132
c	0.21678	1.12477	-2.80517	0.084747
c	0.08447	2.70044	-1.25484	0.146470
c	0.26238	2.41433	-3.51176	-0.017178
c	0.17593	3.39752	-2.54862	-0.118506
c	0.3862	2.56781	-5.00579	-0.224811
h	1.31532	2.11659	-5.38562	0.053638
h	0.38958	3.62573	-5.29222	0.087027

h	-0.44922	2.08534	-5.53583	0.068003
h	0.06086	-0.01343	4.55511	0.139022
c	0.02913	2.49803	3.48914	-0.000334
h	0.97061	2.29232	5.43381	0.070972
h	-0.00263	3.75731	5.24153	0.094494
c	-0.00439	2.72977	1.21854	0.110136
c	-0.06139	4.96024	2.62428	0.284019
c	0.0024	3.35932	-0.02795	-0.229390
h	-0.0333	4.44765	-0.04875	0.203822
c	0.2077	4.90022	-2.69098	0.113266
h	0.979	5.30159	-2.02126	-0.040794
h	0.50342	5.16749	-3.71405	0.021980
h	-0.3835	5.23845	3.63662	-0.018995
h	-0.79527	5.37338	1.92215	-0.069649
c	1.31445	5.64312	2.33833	-0.249965
h	2.07027	5.2375	3.02117	0.045965
h	1.60508	5.42734	1.30377	0.050195
c	-1.1339	5.62783	-2.33702	-0.226600
h	-1.82002	4.91546	-1.85601	0.019495
h	-1.63238	6.00105	-3.23869	0.052657
c	-0.96272	6.81721	-1.35659	0.808744
o	-1.56826	7.90479	-1.57791	-0.720248
o	-0.19014	6.54728	-0.31333	-0.680021
h	0.19725	7.34759	0.74437	0.516594
c	1.24182	7.16411	2.55433	0.871816
o	0.57819	7.86901	1.62279	-0.798973
o	1.76271	7.69734	3.56692	-0.697555
c	-6.32691	1.24405	-1.08688	0.296601
h	-5.77172	2.18935	-1.08705	0.048307
c	-7.4952	1.38382	-2.07075	0.771495
c	-5.36274	0.12052	-1.58807	-0.246325
h	-5.9025	-0.83929	-1.53397	0.079390
h	-5.11971	0.30001	-2.64047	0.114837
n	-6.79609	0.96433	0.28652	-0.817205
h	-7.50211	0.22629	0.3052	0.332375
h	-7.14702	1.79533	0.76247	0.325296
o	-7.09497	1.95419	-3.26635	-0.766613
h	-7.84403	2.02618	-3.90212	0.513563
o	-8.66368	1.01708	-1.86692	-0.609418
c	-4.08729	0.06997	-0.79783	0.161274
n	-4.07413	0.12537	0.60087	-0.246826
c	-2.75873	-0.04249	-1.17669	-0.100092
c	-2.76941	0.0604	1.02153	0.232534
h	-2.45422	0.10545	2.05	0.015846
n	-1.9522	-0.04491	-0.03512	-0.500217
h	-2.33447	-0.10942	-2.1646	0.078604
h	-4.92867	0.30218	1.12809	0.248374
c	3.23804	-1.42328	1.10393	0.085415
h	2.80889	-2.37914	0.79569	0.041245
h	2.89664	-1.17984	2.11339	-0.035127
h	4.33006	-1.46621	1.05587	0.026604
s	2.59118	-0.13259	-0.11188	-0.524833

c	3.20316	1.45126	0.72749	0.491335
h	2.84302	1.42746	1.76176	-0.067625
h	2.69604	2.26218	0.20157	-0.067390
c	4.72358	1.64131	0.65866	-0.199793
h	5.24488	0.85894	1.22669	0.064552
h	5.06096	1.58554	-0.3864	0.068251
c	5.11265	3.04117	1.24092	0.164231
h	4.69951	3.10906	2.25497	0.070617
n	4.56828	4.12599	0.43769	-0.966693
c	6.64162	3.10196	1.37143	0.844726
o	7.42775	3.68464	0.60979	-0.623516
o	7.09893	2.37055	2.4682	-0.791776
h	8.08254	2.39927	2.51791	0.499758
h	5.03808	4.29514	-0.44732	0.394447
h	4.3065	4.97209	0.9315	0.381190