Supporting information

Constructing Molecular π-Orbital Active Spaces for Multireference Calculations of Conjugated Systems

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I. Geometries

Tables S1-S4 provide the structures used in the calculations:

Table S1. Benzene Geometry

atom	x	y	z
C	0.000000	0.001262	0.000000
C	0.000000	2.782738	0.000000
C	1.204419	0.696631	0.000000
C	-1.204419	0.696631	0.000000
C	1.204419	2.087369	0.000000
C	-1.204419	2.087369	0.000000
H	-2.141507	2.628401	0.000000
H	2.141507	2.628401	0.000000
H	-2.141507	0.155599	0.000000
H	2.141507	0.155599	0.000000
H	0.000000	-1.080796	0.000000
H	0.000000	3.864796	0.000000

Table S2. Octatetraene Geometry

atom	x	y	z
C	-0.205041	4.293236	0.000000
C	0.403263	3.101312	0.000000
C	-0.282048	1.831603	0.000000
C	0.338471	0.633305	0.000000
C	-0.338471	-0.633305	0.000000
C	0.282048	-1.831603	0.000000
C	-0.403263	-3.101312	0.000000
C	0.205041	-4.293236	0.000000
H	0.357619	5.215665	0.000000
H	-1.284763	4.375963	0.000000
H	1.488449	3.064021	0.000000
H	-1.367965	1.860302	0.000000
H	1.424632	0.609319	0.000000
H	-1.424632	-0.609319	0.000000
H	1.367965	-1.860302	0.000000
H	-1.488449	-3.064021	0.000000
H	1.284763	-4.375963	0.000000
H	-0.357619	-5.215665	0.000000

Table S3. Free Base Porphine Geometry

atom	x	y	z
C	-0.682956	-4.256282	0.000000
C	-1.083580	-2.853519	0.000000
N	0.000000	-2.024853	0.000000
C	1.083580	-2.853519	0.000000
C	0.682956	-4.256282	0.000000
C	-2.425952	-2.443542	0.000000
C	-2.900522	-1.126914	0.000000
C	-4.268346	-0.689607	0.000000
C	-4.268346	0.689607	0.000000
C	-2.900522	1.126914	0.000000
N	-2.123164	0.000000	0.000000
C	-2.425952	2.443542	0.000000
C	-1.083580	2.853519	0.000000
C	-0.682956	4.256282	0.000000
C	0.682956	4.256282	0.000000
C	1.083580	2.853519	0.000000
N	0.000000	2.024853	0.000000
C	2.425952	2.443542	0.000000
C	2.900522	1.126914	0.000000
C	4.268346	0.689607	0.000000
C	4.268346	-0.689607	0.000000
C	2.900522	-1.126914	0.000000
N	2.123164	0.000000	0.000000
C	2.425952	-2.443542	0.000000
H	5.133687	-1.357782	0.000000
H	5.133687	1.357782	0.000000
H	1.362163	5.114185	0.000000
H	-1.362163	5.114185	0.000000
H	-5.133687	1.357782	0.000000
H	-5.133687	-1.357782	0.000000
H	-1.362163	-5.114185	0.000000
H	1.362163	-5.114185	0.000000
H	3.190898	-3.230970	0.000000
H	3.190898	3.230970	0.000000
H	-3.190898	3.230970	0.000000
H	-3.190898	-3.230970	0.000000
H	-1.096774	0.000000	0.000000
H	1.096774	0.000000	0.000000

Table S4. Slr1694 BLUF Photoreceptor Active Site Geometry

atom	x	y	z
C	21.359973	-3.067032	-11.453970
H	20.736725	-2.615690	-12.226104
H	21.998101	-2.304441	-11.000487
C	20.573349	-3.838760	-10.442056
C	19.226183	-4.188699	-10.672492
H	18.696215	-3.727069	-11.499923
C	18.601690	-5.130623	-9.899132
H	17.571353	-5.420766	-10.073128
C	19.327922	-5.806791	-8.845872
O	18.842534	-6.796447	-8.241562
H	17.326327	-7.259783	-8.748288
C	21.248458	-4.387332	-9.322176
H	22.270729	-4.077495	-9.125361
C	20.658680	-5.336188	-8.537456
H	21.172691	-5.804691	-7.705622
C	16.740968	-8.534141	-10.884039
H	16.512940	-9.493663	-11.347243
H	16.612913	-7.734526	-11.618765
C	15.868989	-8.269312	-9.667402
O	16.344800	-7.355543	-8.800275
N	14.742183	-8.766387	-9.368884
H	13.850492	-8.587494	-7.749536
H	14.334631	-9.377384	-10.069403
C	9.793169	-13.835317	-14.749996
H	8.808204	-14.312494	-14.724704
H	9.654719	-12.875928	-15.262634
C	10.288733	-13.620459	-13.354870
C	9.852099	-14.297170	-12.222043
H	9.034356	-14.994721	-12.111409
N	10.633240	-13.942360	-11.142072
H	10.482669	-14.239065	-10.192461
C	11.608119	-13.062448	-11.553940
C	11.425513	-12.845736	-12.939905
C	12.327772	-12.016355	-13.623103
H	12.210331	-11.836444	-14.687347
C	13.374372	-11.443031	-12.923714
H	14.083938	-10.806548	-13.443068
C	12.652663	-12.473317	-10.839583
H	12.773575	-12.633820	-9.773386
C	13.534064	-11.674360	-11.544506
H	14.372267	-11.228037	-11.020139

N	9.945743	-8.554741	-5.554349
C	9.214074	-8.787103	-6.688104
O	7.993992	-8.832283	-6.718554
N	9.925128	-9.000667	-7.883045
H	9.371377	-9.207091	-8.704453
C	11.291455	-8.968092	-8.042885
O	11.834122	-9.203346	-9.119557
C	12.001371	-8.644103	-6.821001
N	13.349597	-8.517776	-6.832504
C	14.023753	-8.192493	-5.672567
C	15.395795	-7.935781	-5.715303
H	15.887854	-7.978265	-6.680091
C	16.108326	-7.590302	-4.579237
C	17.584838	-7.311033	-4.669670
H	17.824672	-6.305405	-4.307366
H	17.936723	-7.387025	-5.700441
H	18.164290	-8.014473	-4.061364
C	15.420435	-7.491854	-3.355195
C	16.148907	-7.107223	-2.095901
H	15.471841	-7.083387	-1.239447
H	16.610648	-6.118016	-2.185886
H	16.954171	-7.813651	-1.867696
C	14.051731	-7.741129	-3.313076
H	13.545884	-7.633267	-2.362966
C	13.321027	-8.102209	-4.449051
N	11.941542	-8.361500	-4.407377
C	11.257001	-8.502026	-5.627058
C	11.199075	-8.248990	-3.091997
H	11.806169	-8.676808	-2.299841
H	10.256373	-8.776726	-3.209519
H	22.002821	-3.824651	-11.902159
H	17.771968	-8.516929	-10.530570
H	11.004556	-7.185015	-2.956989
H	10.408717	-14.445089	-15.410897

II. Computed electronic states

Tables S5-S7 provide the electronic states obtained from the CASSCF and CASSCF+NEVPT2 calculations. Table S8 presents the ground state (GS), locally-excited (LE) state of the flavin, and two charge-transfer states associated with electron transfer from Tyr8 (CT_{Tyr}) or Trp91 (CT_{Trp}) to the flavin computed as a function of the two proton transfer coordinates defined in Figure 4.

Table S5. Electronic States of Benzene (in a.u.)

State	CASSCF	CASSCF+NEVPT2
X^1A_g	-230.843710	-231.857062
1^1B_{2u}	-230.664655	-231.660801
1^1B_{1u}	-230.556643	-231.633952
1^1E_{1u}	-230.505161	-231.603119
	-230.505157	-231.603004
2^1E_{2g}	-230.545552	-231.542930
	-230.545549	-231.543077

Table S6. Electronic States of Octatetraene (in a.u.)

State	CASSCF	CASSCF+NEVPT2
$1^1A_g^-$	-308.906986	-310.267727
$1^1B_u^+$	-308.662424	-310.120090
$2^1A_g^-$	-308.731103	-310.090787
$1^1B_u^-$	-308.686352	-310.044467
$3^1A_g^-$	-308.659277	-310.016871

Table S7. Electronic States of Porphine (in a.u.)

State	CASSCF	CASSCF+NEVPT2
X^1A_g	-983.356081	-986.674745
1^1B_{3u}	-983.230447	-986.602473
1^1B_{2u}	-983.222183	-986.587543
2^1B_{2u}	-983.156750	-986.562226
2^1B_{3u}	-983.156051	-986.560985

Table S8. Potential Energy Surface for the BLUF Photoreceptor (a.u.)

r(O –H), Å	*r*(N–H), Å	GS	LE	CT_{Tyr}	CT_{Trp}
1.0	1.0	-1825.936867	-1825.830961	-1825.820405	-1825.796714
1.0	1.1	-1825.932846	-1825.822860	-1825.820812	-1825.803618
1.0	1.2	-1825.913300	-1825.801845	-1825.806885	-1825.789010
1.0	1.3	-1825.898835	-1825.793443	-1825.798354	-1825.769031
1.0	1.4	-1825.884675	-1825.781405	-1825.791848	-1825.758609
1.0	1.5	-1825.872783	-1825.772145	-1825.789646	-1825.754995
1.0	1.6	-1825.864556	-1825.771141	-1825.793305	-1825.759220
1.0	1.7	-1825.862471	-1825.769304	-1825.800555	-1825.765108
1.0	1.8	-1825.865144	-1825.776767	-1825.813279	-1825.775268
1.0	1.9	-1825.867817	-1825.782929	-1825.823374	-1825.785386
1.0	2.0	-1825.868101	-1819.866511	-1825.829710	-1825.791077
1.1	1.0	-1825.931740	-1825.826299	-1825.824169	-1825.790793
1.1	1.1	-1825.920605	-1825.814625	-1825.818554	-1825.781207
1.1	1.2	-1825.909055	-1825.797351	-1825.812117	-1825.786676
1.1	1.3	-1825.894781	-1825.789733	-1825.803914	-1825.765152
1.1	1.4	-1825.880978	-1825.777669	-1825.798667	-1825.755394
1.1	1.5	-1825.875955	-1825.777337	-1825.791452	-1825.751420
1.1	1.6	-1825.869836	-1825.770968	-1825.797539	-1825.746076
1.1	1.7	-1825.860325	-1825.766504	-1825.807962	-1825.762420
1.1	1.8	-1825.862940	-1825.774672	-1825.820826	-1825.773195
1.1	1.9	-1825.866005	-1825.781283	-1825.831552	-1825.783665
1.1	2.0	-1825.863741	-1819.947893	-1825.837976	-1825.790006
1.2	1.0	-1825.913663	-1825.808399	-1825.819012	-1825.769103
1.2	1.1	-1825.911443	-1825.806078	-1825.820691	-1825.772347
1.2	1.2	-1825.900031	-1825.795963	-1825.813921	-1825.772041
1.2	1.3	-1825.886553	-1825.781799	-1825.807034	-1825.757002
1.2	1.4	-1825.876206	-1825.778633	-1825.798664	-1825.751942
1.2	1.5	-1825.869240	-1825.770455	-1825.797775	-1825.744646
1.2	1.6	-1825.862971	-1825.767421	-1825.801963	-1825.747600
1.2	1.7	-1825.853882	-1825.761024	-1825.812910	-1825.756208
1.2	1.8	-1825.855603	-1825.769381	-1825.823814	-1825.766208
1.2	1.9	-1825.859692	-1825.775531	-1825.834036	-1825.768440
1.2	2.0	-1825.858163	N/A	-1825.843165	-1825.794049
1.3	1.0	-1825.904609	-1825.799856	-1825.823004	-1825.761124
1.3	1.1	-1825.902377	-1825.797638	-1825.825373	-1825.764473
1.3	1.2	-1825.894826	-1825.797810	-1825.819123	-1825.763934
1.3	1.3	-1825.881622	-1825.785911	-1825.818690	-1825.755908
1.3	1.4	-1825.868941	-1825.775229	-1825.806267	-1825.749707
1.3	1.5	-1825.862201	-1825.764066	-1825.803695	-1825.738116
1.3	1.6	-1825.856323	-1825.761413	-1825.808192	-1825.741775
1.3	1.7	-1825.848321	-1825.755688	-1825.820057	-1825.750964

1.3	1.8	-1825.850666	-1825.764331	-1825.831150	-1825.762341
1.3	1.9	-1825.854518	-1825.770897	-1825.842430	-1825.771625
1.3	2.0	-1825.855727	-1825.774522	-1825.849671	-1825.777912
1.4	1.0	-1825.899241	-1825.800737	-1825.831897	-1825.762517
1.4	1.1	-1825.898007	-1825.797635	-1825.834371	-1825.763918
1.4	1.2	-1825.886838	-1825.791210	-1825.828919	-1825.757491
1.4	1.3	-1825.873803	-1825.780084	-1825.822909	-1825.749906
1.4	1.4	-1825.863166	-1825.769155	-1825.818823	-1825.744641
1.4	1.5	-1825.841520	-1825.760974	-1825.818561	-1825.743206
1.4	1.6	-1825.845251	-1825.749692	-1825.824980	-1825.740327
1.4	1.7	-1825.846270	-1825.750574	-1825.840360	
1.4	1.8	-1825.847945	-1825.761793	-1825.846251	-1825.759352
1.4	1.9	-1825.852197	-1825.769138	-1825.857783	-1825.771786
1.4	2.0	-1825.853170	-1819.856454	-1825.867747	-1825.787072
1.5	1.0	-1825.895445	-1825.797452	-1825.839917	-1825.759089
1.5	1.1	-1825.894053	-1825.795239	-1825.842250	-1825.760054
1.5	1.2	-1825.884581	-1825.788593	-1825.837842	-1825.755188
1.5	1.3	-1825.871965	-1825.776983	-1825.832027	-1825.748222
1.5	1.4	-1825.860095	-1825.767241	-1825.828116	-1825.742269
1.5	1.5	-1825.851844	-1825.760235	-1825.828543	-1825.742031
1.5	1.6	-1825.843892	-1825.751926	-1825.835599	-1825.739603
1.5	1.7	-1825.844292	-1825.754227	-1825.845060	-1825.748423
1.5	1.8	-1825.847557	-1825.762343	-1825.856638	-1825.751379
1.5	1.9	-1825.852404	-1825.761586	-1825.872865	-1825.781371
1.5	2.0	-1825.855394	N/A	-1825.883187	N/A
1.6	1.0	-1825.890982	-1825.792721	-1825.844945	-1825.754553
1.6	1.1	-1825.888761	-1825.790633	-1825.847346	-1825.756545
1.6	1.2	-1825.880532	-1825.784420	-1825.842926	-1825.751302
1.6	1.3	-1825.868170	-1825.774348	-1825.837403	-1825.744669
1.6	1.4	-1825.856487	-1825.763518	-1825.833956	-1825.739881
1.6	1.5	-1825.849355	-1825.758480	-1825.829781	-1825.737327
1.6	1.6	-1825.841635	-1825.750007	-1825.842091	-1825.737415
1.6	1.7	-1825.842031	-1825.752844	-1825.852159	-1825.746148
1.6	1.8	-1825.846055	-1825.761363	-1825.864540	-1825.757839
1.6	1.9	-1825.851102	-1825.769240	-1825.876796	-1825.769628
1.6	2.0	-1825.854962	N/A	-1825.891323	N/A

III. Identification of the states in the BLUF photoreceptor

To identify the electronic states, the partial charges on all atoms may be inspected for each state at a given geometry, but such an analysis is very time-consuming. To characterize the states more efficiently, we used the following algorithm. First, we computed the one-electron transition reduced density matrices (RDMs). Using these RDMs, we obtained the change in partial charge for each atom corresponding to a given state transition. Then we summed up the partial charges for the atoms belonging to each fragment and generated the output in the form shown in Table S9. In this case, the first excited state (#1) is the LE state because there is no change in charge for any of the fragments with respect to the ground state. The second excited state (#2) is the CT state associated with Tyr8, and the third excited state (#3) is the CT state associated with Trp91.

Table S9. Example of the Output with the Change in Charge for each Fragment for the Relevant Excited States with Respect to the Ground State

State	FMN	Tyr	Trp	Gln
#1	-0.01	0.01	0.00	0.01
#2	**-0.98**	**0.96**	-0.01	0.04
#3	**-0.98**	-0.02	**0.97**	-0.03