Supporting information for:

Distance-Independent Charge Recombination Kinetics in Cytochrome *c* - Cytochrome *c* Peroxidase Complexes: Compensating Changes in the Electronic Coupling and Reorganization Energies

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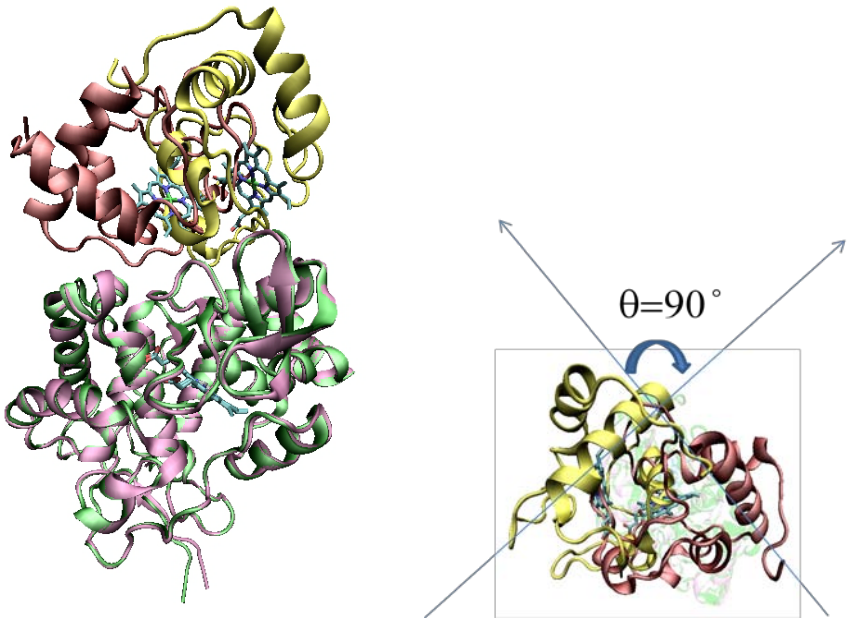
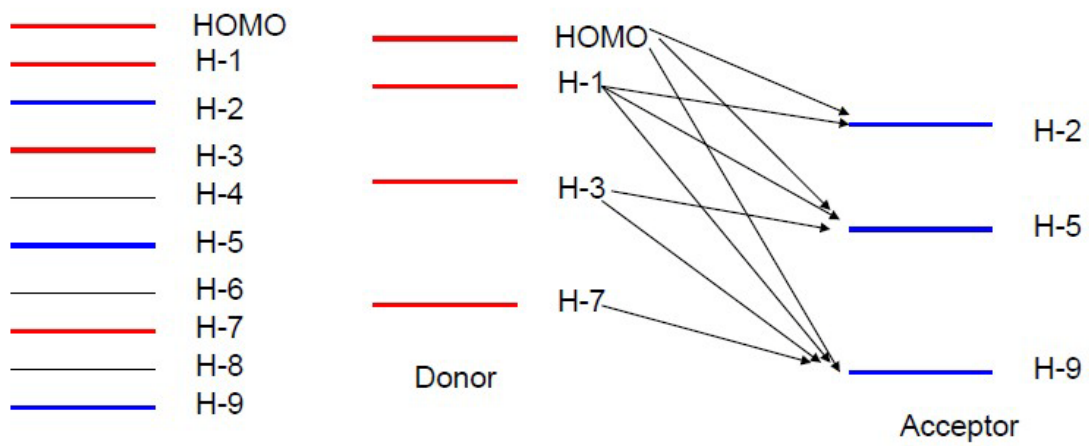


(a) (b)

Figure S1. Aligned conformations of five CcP:Cc complexes. For the WT CcP:Cc complex and F82S (W) mutants, Cc is in red and CcP is in green. For the F82I(Y) mutants, Cc is in yellow and CcP is in mauve. a) Side view of the aligned conformations b): Top view of the aligned conformations. (PDB ID: 1U74, 2B10, 2B11, 2B0Z, and 2B12 for WT CcP:Cc complex, F82S,F82W,F82I and F82Y, respectively.) The 90 degree rotations are observed in F82I(Y) with respect to WT CcP:Cc and F82S(W).



(a) (b)

Figure S2. Schematic diagram for the two state GMH approach. (a) Orbitals are divided into two sets. The red lines represent the occupied orbitals localized on the donor site (heme). The blue lines are the occupied orbitals localized on the acceptor site (ZnP and Trp191) (b) For each orbital pair between donor and acceptor groups, the two state generalized Mulliken-Hush approach is employed to compute H_{ij} in eq. 5.

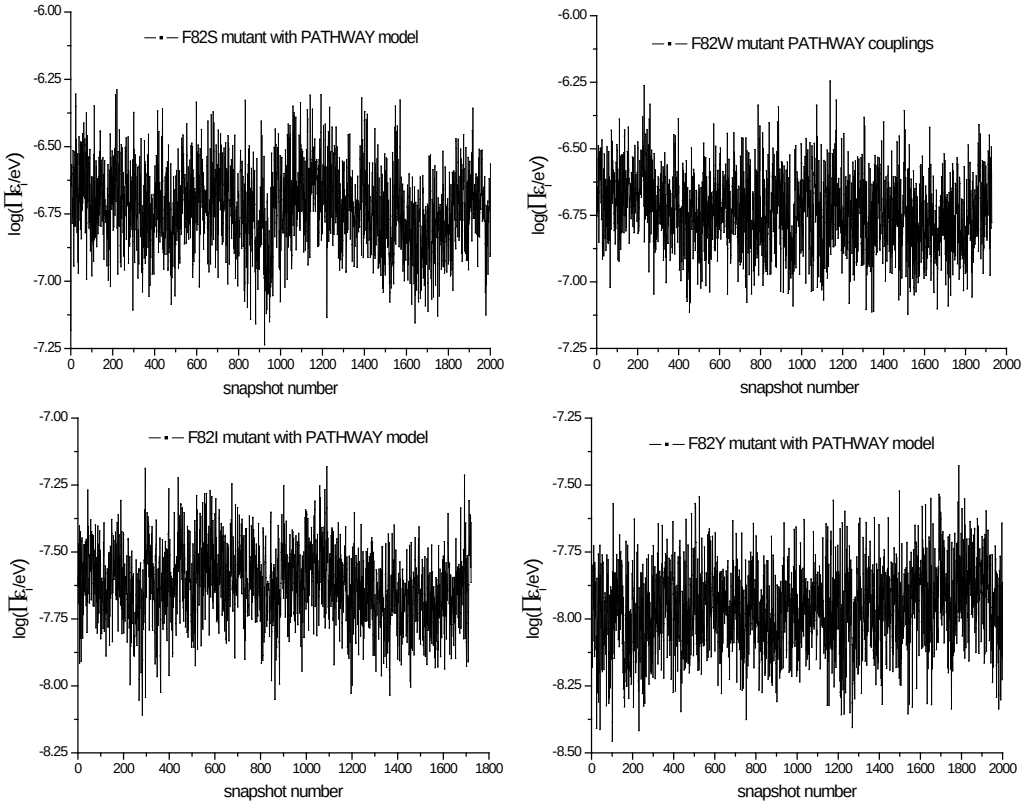


Figure S3. Logarithm of electronic coupling versus snapshot for four CcP:Cc mutants computed by the PATHWAY model.

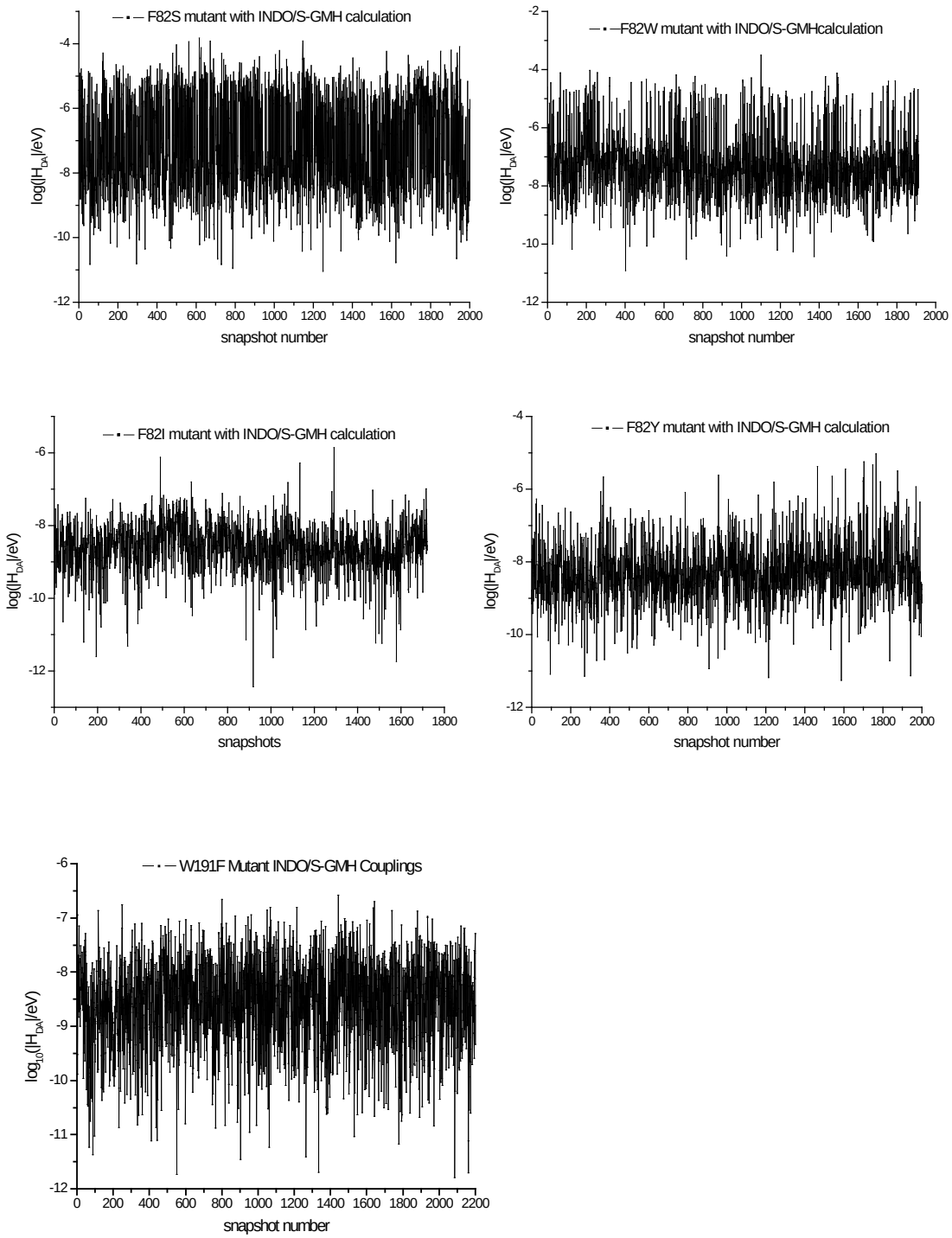
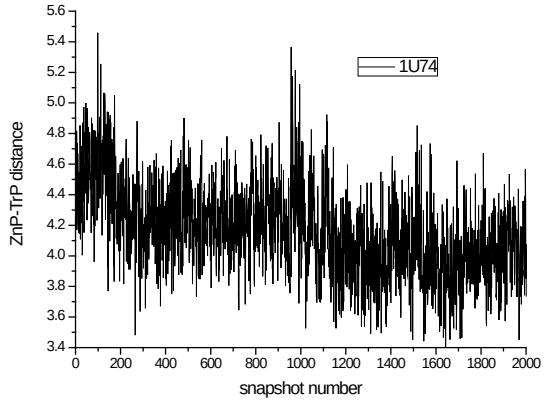
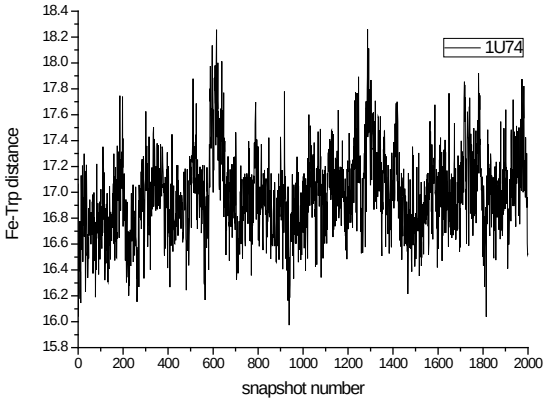
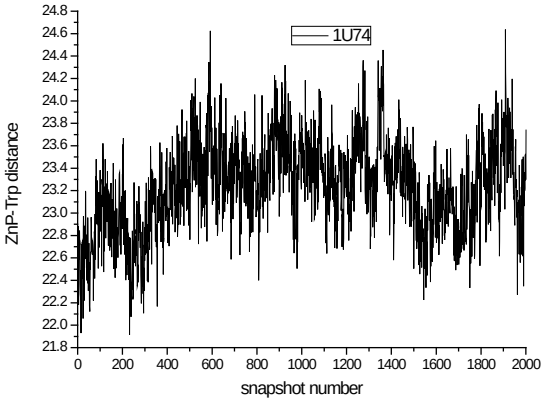


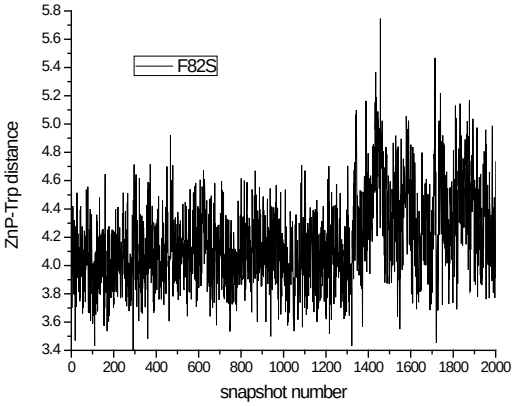
Figure S4. Logarithm of electronic coupling versus snapshots for five CcP:Cc mutants computed by INDO/S-GMH approach.

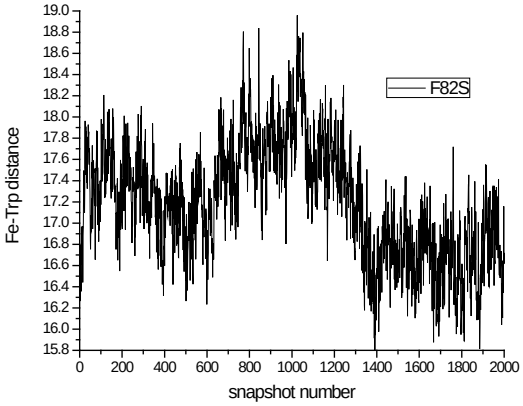

1U74
ZnP-TrP distance
snapshot number

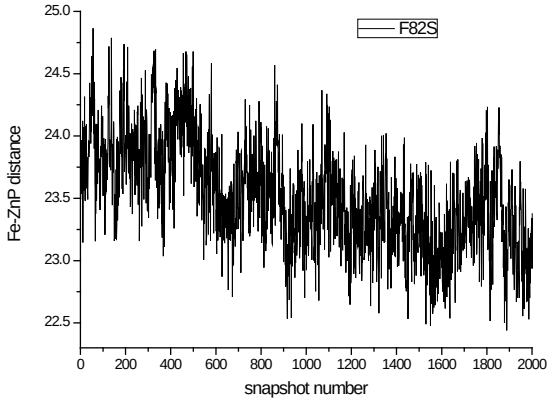

1U74
Fe-Trp distance
snapshot number


1U74
ZnP-Trp distance
snapshot number

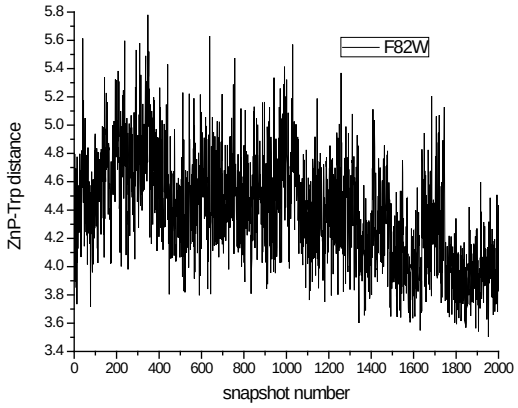
a) 1U74

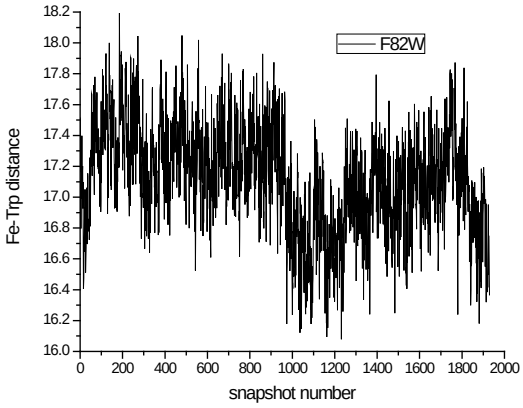

F82S
ZnP-Trp distance
snapshot number

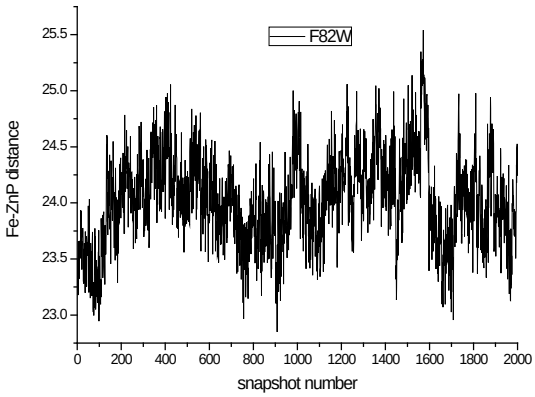

F82S
Fe-Trp distance
snapshot number


F82S
Fe-ZnP distance
snapshot number

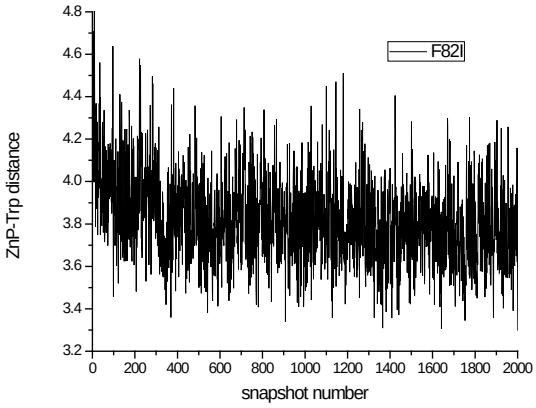
b)F82S

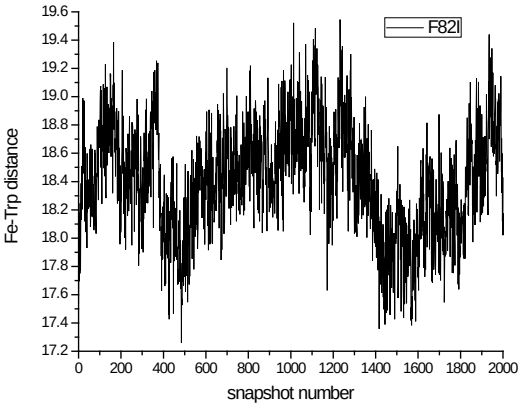

F82W
ZnP-Trp distance
snapshot number

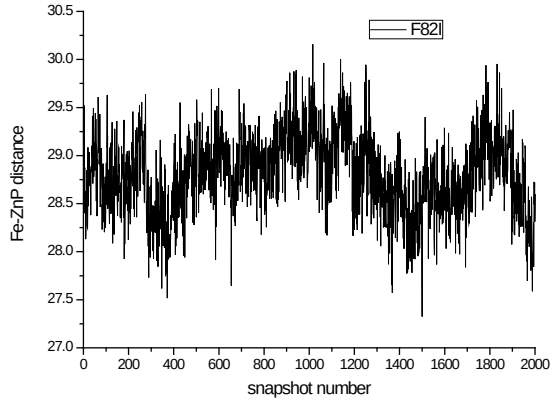

F82W
Fe-Trp distance
snapshot number


F82W
Fe-ZnP distance
snapshot number

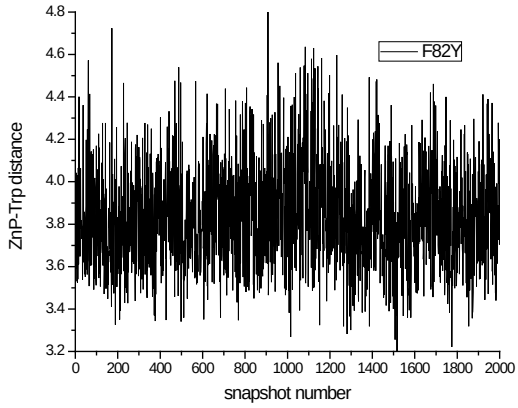
c)F82W

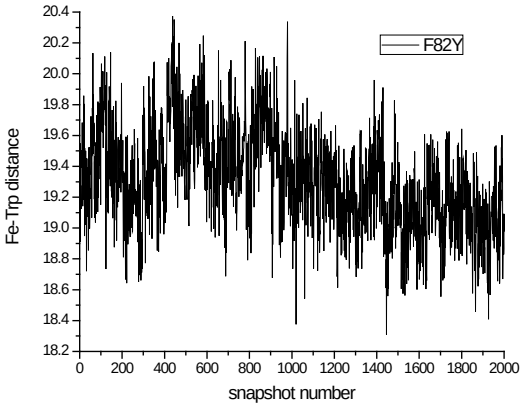

F82I
ZnP-Trp distance
snapshot number

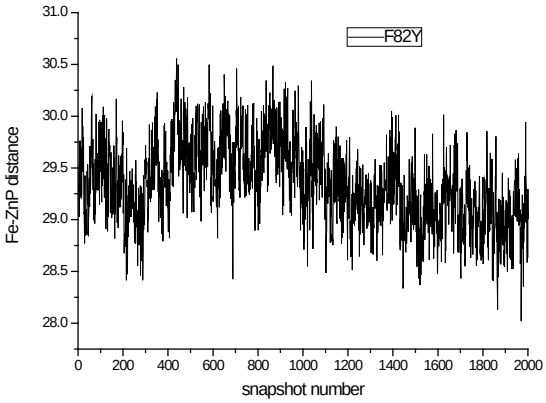

F82I
Fe-Trp distance
snapshot number



d)F82I



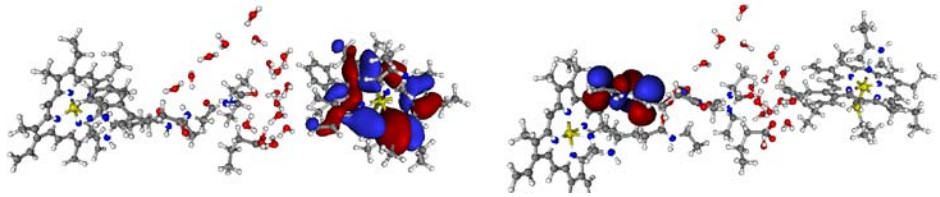




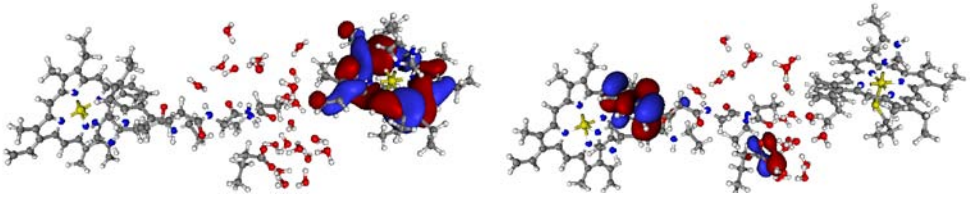
e)F82Y

Figure S5. Plots of Trp-ZnP, Fe-ZnP and Fe-Trp distances versus snapshots for WT CcP:Cc complex and four CcP:Cc mutants.

a) Snapshot 88



b) Snapshot 730



c) Snapshot 1209

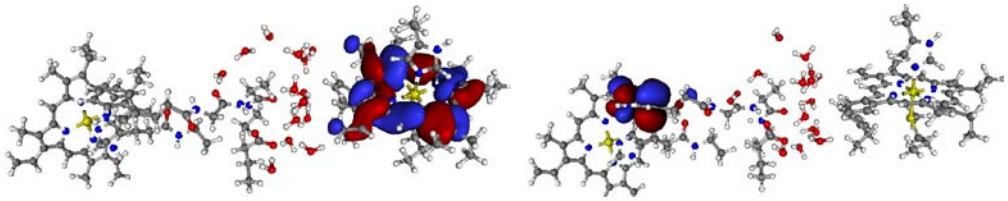
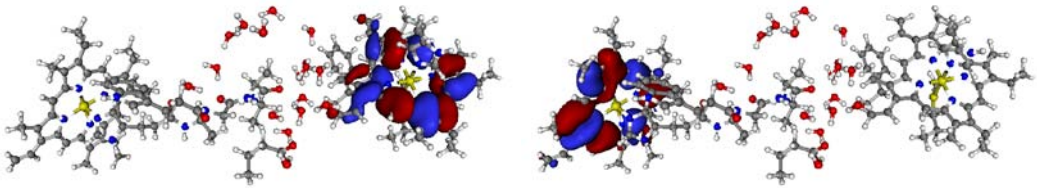
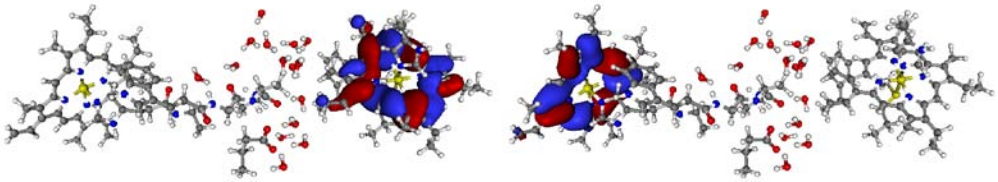


Figure S6-1. Orbitals with the largest ET couplings for a snapshot randomly selected with a large $|H_{DA}|$ value for the WT complex

a) Snapshot 3



b) Snapshot 788



c) Snapshot 1496

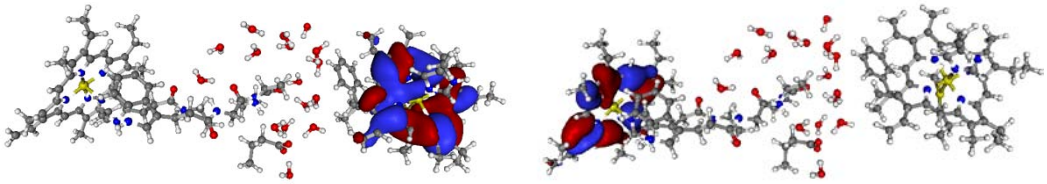
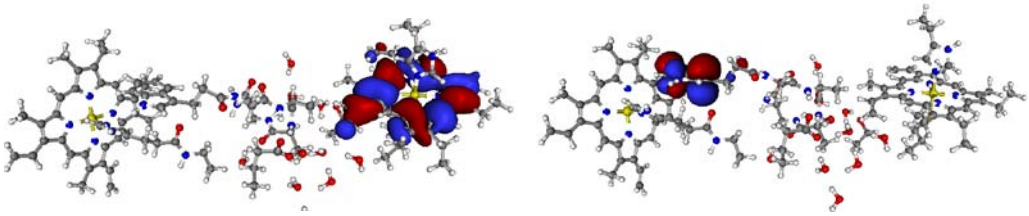
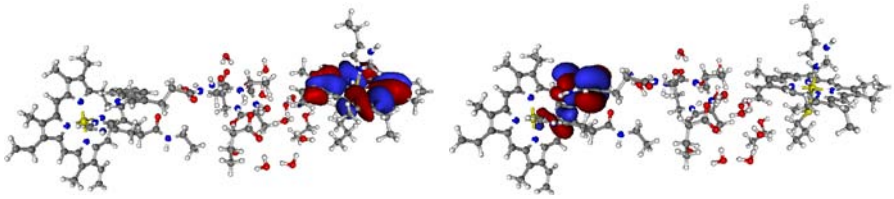


Figure S6-2. Orbitals with the largest ET couplings for a snapshot randomly selected with a small $|H_{DA}|$ value for the WT complex

a) Snapshot 370



b) Snapshot 889



c) Snapshot 1005

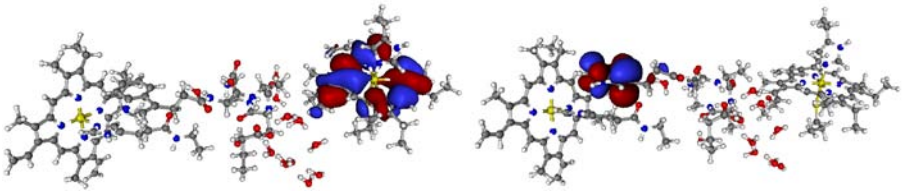
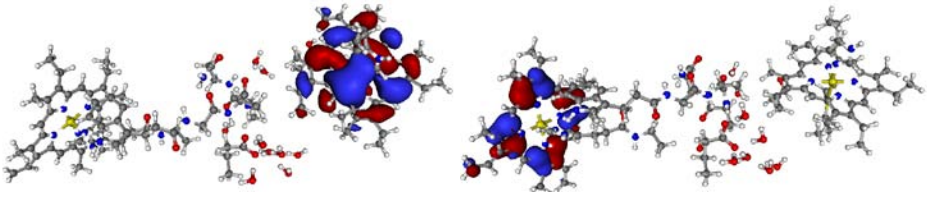
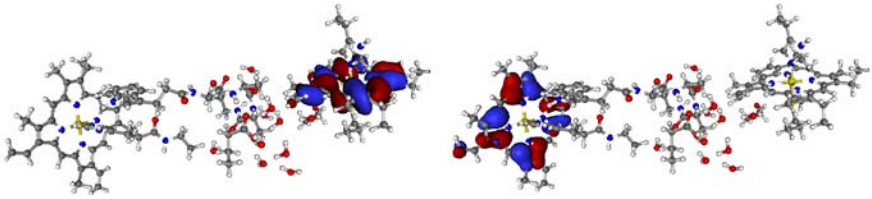


Figure S6-3. Orbitals with the largest ET couplings for a snapshot randomly selected with a large $|H_{DA}|$ value for the F82S mutant.

a) Snapshot 1023



b) Snapshot 1138



c) Snapshot 2072

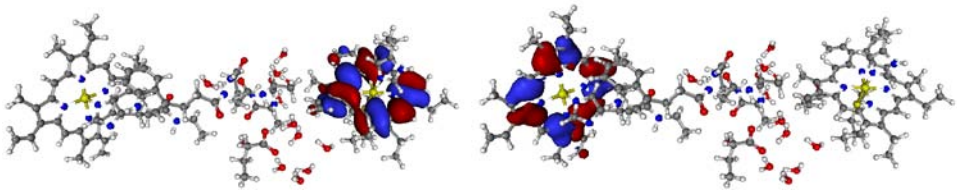
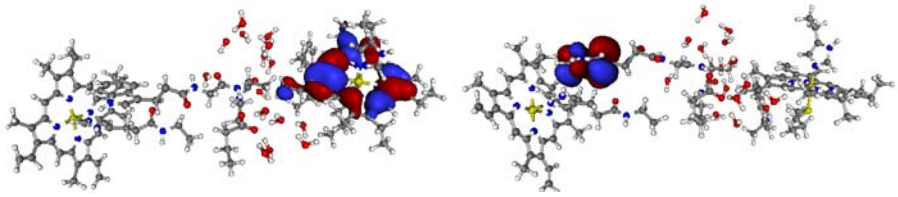
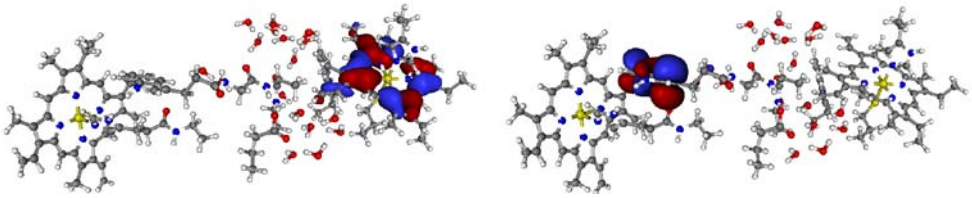


Figure S6-4. Orbitals with the largest ET couplings for a snapshot randomly selected with a small $|H_{DA}|$ value for the F82S mutant.

a) Snapshot 1200 for F82W



b) Snapshot 1616 for F82W



c) Snapshot 1919 for F82W

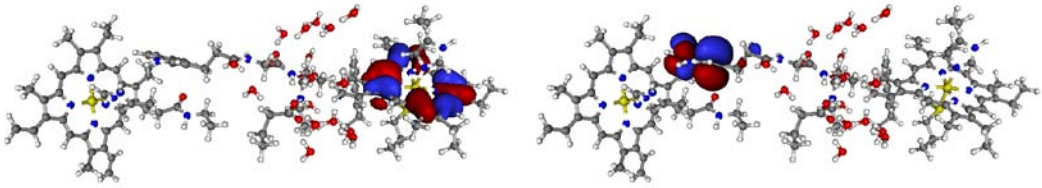
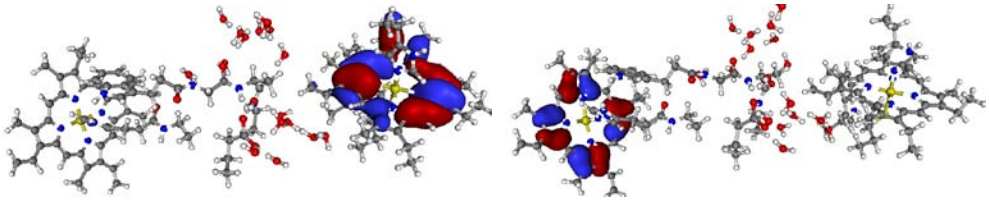
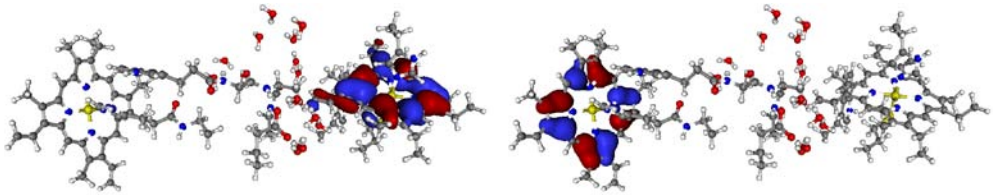


Figure S6-5. Orbitals with the largest ET couplings for a snapshot randomly selected with a large $|H_{DA}|$ value for the F82W mutant.

a) Snapshot 351 for F82W



b) Snapshot 1011 for F82W



c) Snapshot 1200 for F82W

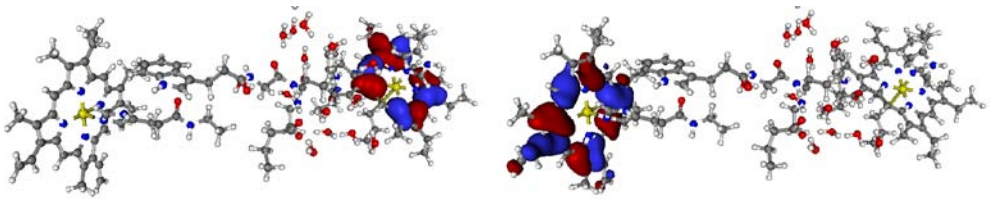
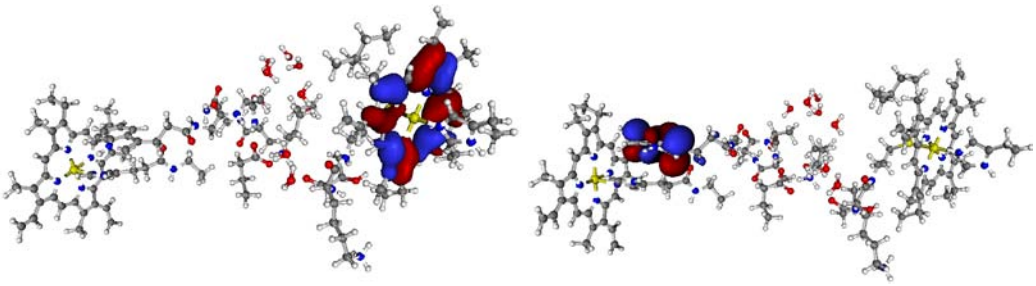
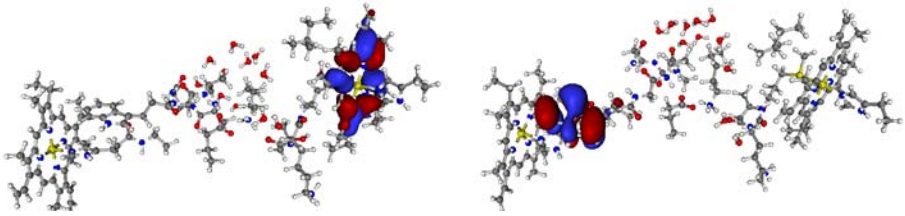


Figure S6-6. Orbitals with the largest ET couplings for a snapshot randomly selected with a small $|H_{DA}|$ value for the F82W mutant.

a) Snapshot 1417 for F82I



b) Snapshot 1518 for F82I



c) Snapshot 1900 for F82I

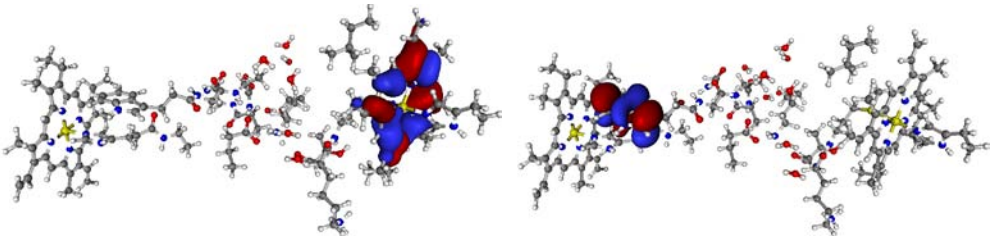
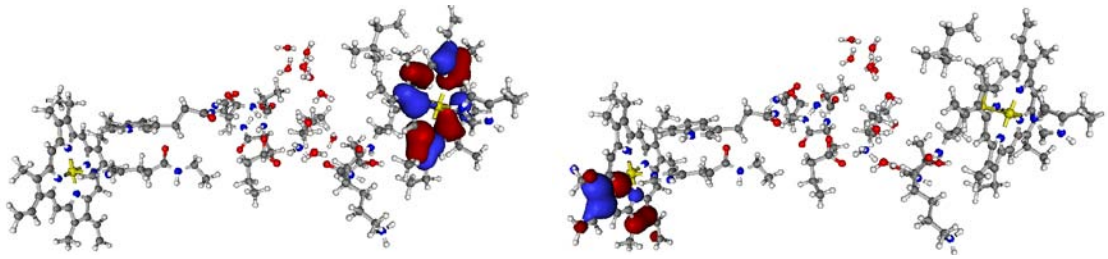
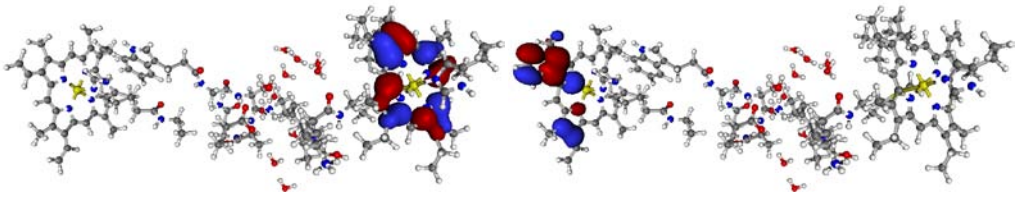


Figure S6-7. Orbitals with the largest ET couplings for a snapshot randomly selected with a large $|H_{DA}|$ value for the F82I mutant.

a) Snapshot 1194 for F82I



b) Snapshot 1885 for F82I



c) Snapshot 2512 for F82I

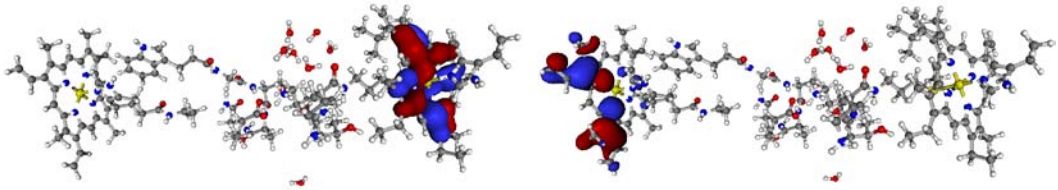
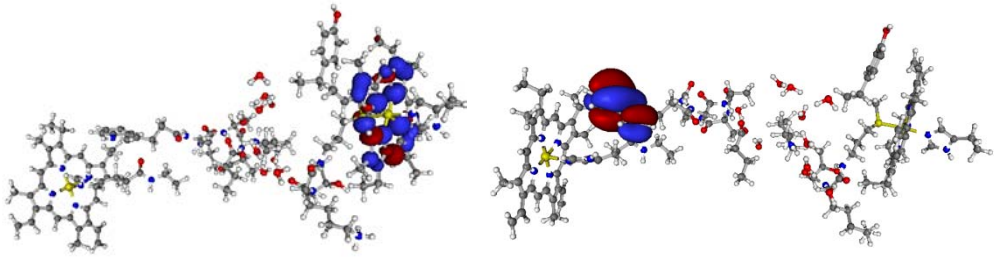
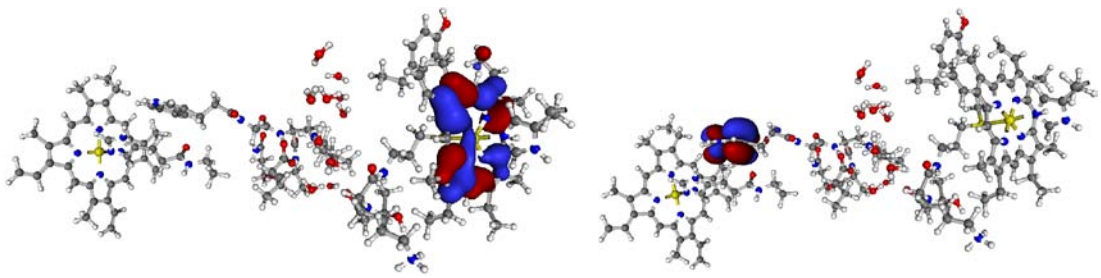


Figure S6-8. Orbitals with the largest ET couplings for a snapshot randomly selected with a small $|H_{DA}|$ value for the F82I mutant.

a) Snapshot 162 for F82Y



b) Snapshot 1541 for F82Y



c) Snapshot 1794 for F82Y

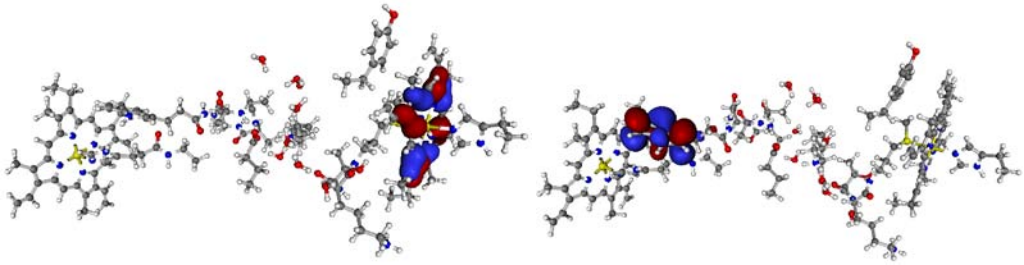
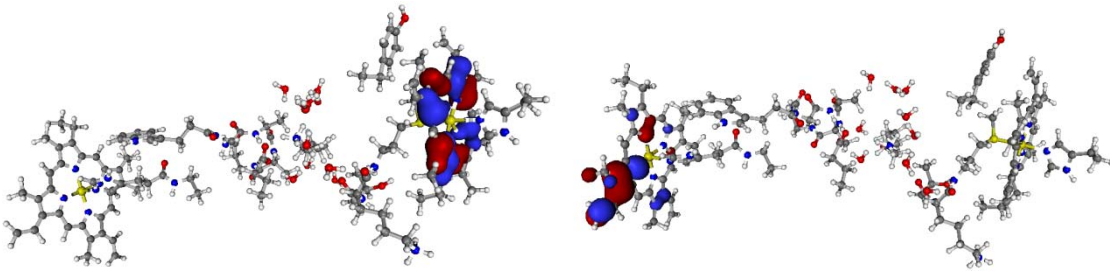
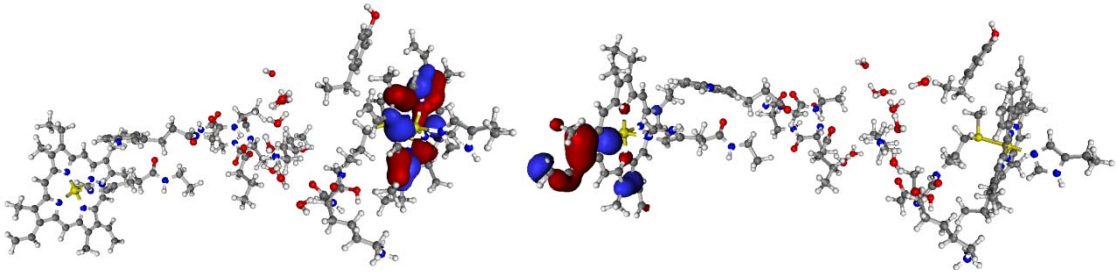


Figure S6-9. Orbitals with the largest ET couplings for a snapshot randomly selected with a large $|H_{DA}|$ value for the F82Y mutant.

a) Snapshot 302 for F82Y



b) Snapshot 1300 for F82Y



c) Snapshot 1893 for F82Y

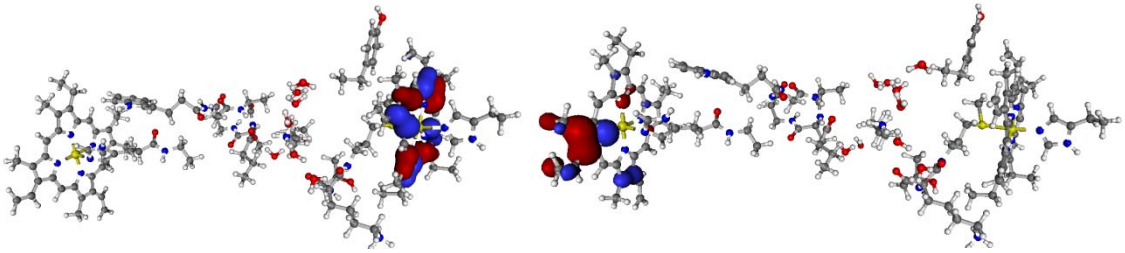
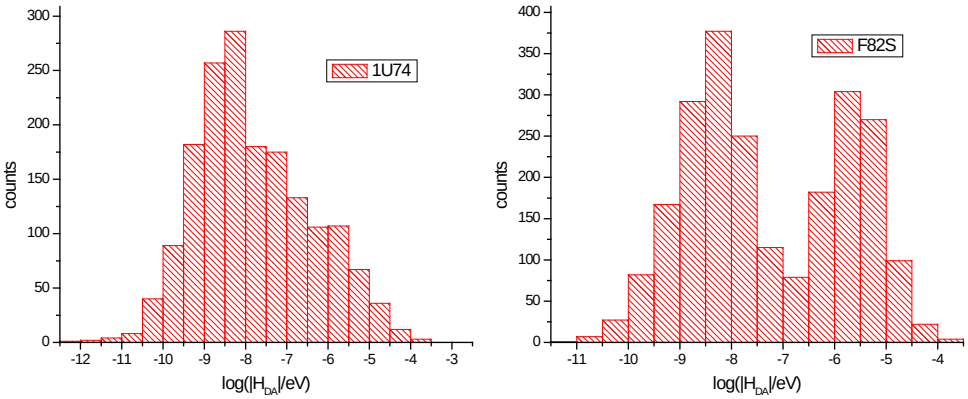


Figure S6-10. Orbitals with the largest ET couplings for a snapshot randomly selected with a small $|H_{DA}|$ value for the F82Y mutant.

Figure S6. Orbitals with the largest ET coupling component for snapshots randomly selected for each protein complex. The electron localized on donor side is shown on left side and the electron localized on acceptor side is shown on right side.



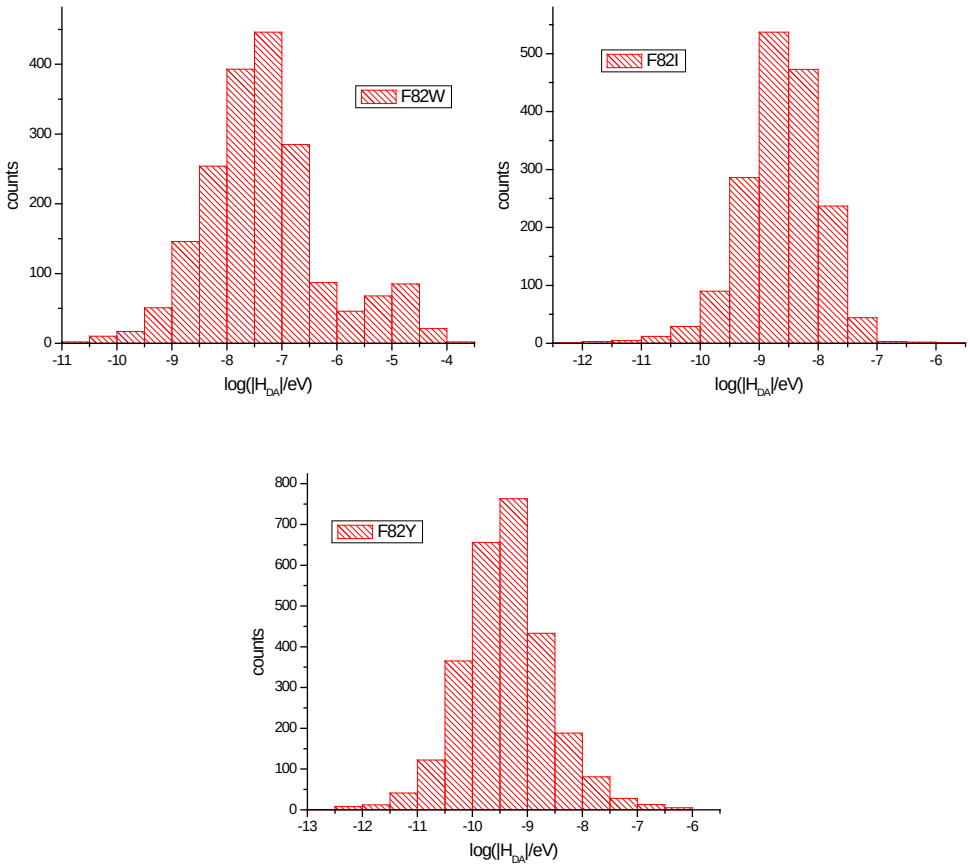


Figure S7. Distributions of the logarithm of the electronic coupling for the WT CcP:Cc complex and the four CcP:Cc mutants.

Table S1. Amino acids and functional groups included in the QM regions for WT CcP:Cc complex and mutants in INDO/S calculations. Note that the water molecules within five angstrom of Ala194 in CcP are also included in the INDO/S calculations.

	amino acids from CcP site	amino acids from Cc site	Donor	Acceptor
WT CcP:Cc	His175, Ala176, Trp191, Gly192,Ala193,Ala194, Asn195, Glu201	His23, Met80, Phe87	Heme	ZnP
F82S	His175, Ala176, Trp191, Gly192,Ala193,Ala194, Asn195, Glu201	His23, Met80, Ser87	Heme	ZnP
F82W	His175, Ala176, Trp191, Gly192,Ala193,Ala194, Asn195, Glu201	His23, Met80, Trp87	Heme	ZnP
F82Y	His175, Ala176, Trp191, Gly192,Ala193,Ala194, Asn195, Glu201	His23, Lys77, Lys84, Met85, Tyr87	Heme	ZnP
F82I	His175, Ala176, Trp191, Gly192,Ala193,Ala194, Asn195, Glu201	His23, Lys77, Lys84, Met85, Ile87	Heme	ZnP
W191F	His175, Ala176, Phe191, Gly192,Ala193,Ala194, Asn195, Glu201	His23, Met80, Trp87	Heme	ZnP

Table S2. Results of electrostatic potential charge analyses for snapshots with large $\langle H_{DA}^2 \rangle$ values (~10^{-10}) and small $\langle H_{DA}^2 \rangle$ values (~10^{-15}) based on the INDO/S-GMH approach. The values in the table indicate the percentage of the hole that is localized on ZnP or Trp191.

Residue	Frames with large $\langle H_{DA}^2 \rangle$	Frames with small $\langle H_{DA}^2 \rangle$
	Frame1097	Frame46
Trp191	0.16	0.08
ZnP	0.85	0.92
	Frame995	Frame491
Trp191	0.11	0.07
ZnP	0.89	0.93
	Frame96	Frame1030
Trp191	0.11	0.05
ZnP	0.89	0.95
	Frame1514	Frame1322
Trp191	0.01	0.03
ZnP	0.99	0.97
	Frame636	Frame378
Trp191	0.19	0.02
ZnP	0.81	0.98
	Average by five frames	Average by five frames
Trp191	0.12	0.02
ZnP	0.88	0.98

Table S3. Trp-ZnP, Fe-ZnP and Fe-Trp distances for WT CcP:Cc complex and four CcP:Cc mutants along the trajectories.

	ZnP-Trp distance/Å	Fe-Trp distance/Å	Fe-ZnP distance/Å
WT CcP:Cc	4.14±0.30	16.98±0.32	23.15±0.41
F82W	4.28±0.40	17.11±0.35	24.05±0.35
F82S	4.18±0.32	16.95±0.38	23.47±0.43
F82I	3.80±0.20	18.52±0.47	28.87±0.50
F82Y	3.83±0.24	19.23±0.37	29.24±0.43

Table S4. Frequency counts of Logarithm of electronic coupling of snapshots localized on Trp for WT CcP:Cc complex and four CcP:Cc mutants.

	$\mathrm{Log}\lvert H_{DA}\rvert$	counts	percentage
WT CcP:Cc	> -6	225	13.1%
F82W	> -6	222	11.6%
F82S	> -6	396	14.5%
F82I	> -7	6	0.3%
F82Y	> -7	18	0.7%

Table S5. Eigenvalues (eV) of frontier orbitals localized on donor (Heme) and acceptor (ZnP or Trp191) sites within the 10 highest occupied orbitals for both positively charged system and neutralized system for F82Y mutant (frame142), and for WT complex (frame730).

F82Y		F82Y		WT	
Lys positive charged		Lys neutralized			
Orbital	Orbital	Orbital	Orbital	Orbital	Orbital
-6.178	ZnP	-4.797	Heme	-4.175	Heme
-6.760	ZnP	-4.805	ZnP	-4.849	Heme
-7.709	Heme	-5.198	Heme	-4.896	ZnP
-7.997	Trp191	-5.380	ZnP	-5.459	Heme
-8.150	Heme	-6.183	Trp191	-5.639	Heme
-8.239	ZnP	-6.208	Heme	-5.691	Heme
-8.375	ZnP	-6.333	Heme	-6.187	Trp191
-8.756	ZnP			-6.190	Trp191

Table S6. Energies of orbitals localized on donor and acceptor within the 10 highest occupied orbitals for both positive charged system and neutralized system for F82Y mutant.

	Lys positive charged		Lys neutralized	
	Orbital	Orbital	Orbital	Orbital
Frame_142	-6.178	ZnP	-4.797	Heme
	-6.760	ZnP	-4.805	ZnP
	-7.709	Heme	-5.198	Heme
	-7.997	Trp191	-5.380	ZnP
	-8.150	Heme	-6.183	Trp191
	-8.239	ZnP	-6.208	Heme
	-8.375	ZnP	-6.333	Heme
	-8.756	ZnP		
Frame_1022	-6.137	ZnP	-4.754	Heme
	-6.707	ZnP	-4.770	ZnP
	-7.603	Heme	-5.311	Heme
	-7.689	Trp191	-5.332	ZnP
	-8.113	Heme	-5.824	Trp191
	-8.115	ZnP	-6.228	Heme
	-8.239	ZnP	-6.265	Heme
	-8.486	ZnP		
Frame_320	-6.105	ZnP	-4.766	ZnP
	-6.719	ZnP	-4.776	Heme
	-7.467	Trp191	-5.201	Heme
	-7.554	Heme	-5.264	ZnP
	-8.070	ZnP	-6.057	Heme
	-8.137	Heme	-6.116	Heme
	-8.288	ZnP	-6.129	Trp191
	-8.326	ZnP		
Frame_1893	-6.205	ZnP	-4.770	ZnP
	-6.672	ZnP	-4.802	Heme
	-7.650	Trp191	-5.231	Heme
	-7.664	Heme	-5.242	ZnP
	-8.020	ZnP	-5.946	Trp191
	-8.129	Heme	-6.211	Heme
	-8.195	ZnP		
	-8.300	ZnP		