

The partial charges of the hemes and the linked residues (two histidines modeled by methyl-imidazoles and two cysteines modeled by methyl-thiols) obtained from a density functional calculation (functionals VWN and PW91) using the ADF program package. The electrostatic potentials obtained from the density functional calculation were fitted using the CHELPG-algorithm combined with a singular value decomposition. The atom names are in Protein Data Bank standard.

Table S1: Charges that change upon oxidation.

Residue	Atom	Charge	
		oxidized	reduced
Heme	FE	0.729	0.597
	NA	-0.104	-0.091
	C1A	0.25	0.20
	C2A	-0.075	-0.125
	C3A	-0.075	-0.125
	C4A	0.25	0.20
	NB	-0.104	-0.091
	C1B	0.25	0.20
	C2B	-0.075	-0.125
	C3B	-0.075	-0.125
	C4B	0.25	0.20
	NC	-0.104	-0.091
	C1C	0.25	0.20
	C2C	-0.075	-0.125
	C3C	-0.075	-0.125
	C4C	0.25	0.20
ND	-0.104	-0.091	
C1D	0.25	0.20	
C2D	-0.075	-0.125	
C3D	-0.075	-0.125	
C4D	0.25	0.20	
Histidine	ND1	-0.380	-0.429
	HD1	0.384	0.384
	CG	0.177	0.166
	CD2	-0.255	-0.255
	HD2	0.170	0.170
	CE1	0.012	0.012
	HE1	0.125	0.125

Table S2: Charges that do not change upon oxidation.

Residue	Atom	Charge
Heme	FE	0.24
	NA	-0.18
	C1A	0.12
	C2A	-0.06
	C3A	-0.06
	C4A	0.12
	NB	-0.18
	C1B	0.12
	C2B	-0.06
	C3B	-0.06
	C4B	0.12
	NC	-0.18
	C1C	0.12
	C2C	-0.06
	C3C	-0.06
	C4C	0.12
	ND	-0.18
	C1D	0.12
	C2D	-0.06
	C3D	-0.06
C4D	0.12	
CHA	-0.10	
HA	0.10	
CHB	-0.10	
HB	0.10	
CHC	-0.10	
HC	0.10	
CHD	-0.10	
HD	0.10	
CMA	-0.144	
HMA1	0.048	

Residue	Atom	Charge	Residue	Atom	Charge
	HMA2	0.048		HBD1	-0.07
	HMA3	0.048		HBD2	-0.07
	CAA	0.01		CGD	0.66
	HAA1	-0.07		O1D	-0.70
	HAA2	-0.07		O2D	-0.70
	CBA	0.01			
	HBA1	-0.07	Cystein	N	-0.4157
	HBA2	-0.07		HN	0.2719
	CGA	0.66		CA	0.0213
	O1A	-0.70		HA	0.1124
	O2A	-0.70		CB	-0.1231
	CMB	-0.144		HB1	0.1112
	HMB1	0.048		HB2	0.1112
	HMB2	0.048		SG	-0.3186
	HMB3	0.048		C	0.5973
	CAB	0.13		O	-0.5679
	HAB	0.07			
	CBB	-0.03	Histidine	N	-0.415
	HBB1	0.01		HN	0.271
	HBB2	0.01		CA	0.018
	HBB3	0.01		HA	0.088
	CMC	-0.144		CB	-0.264
	HMC1	0.048		HB1	0.105
	HMC2	0.048		HB2	0.108
	HMC3	0.048		NE2	-0.171
	CAC	0.13		CD2	-0.255
	HAC	0.07		HD2	0.170
	CBC	-0.03		CE1	0.012
	HBC1	0.01		HE1	0.125
	HBC2	0.01		C	0.597
	HBC3	0.01		O	-0.567
	CMD	-0.144			
	HMD1	0.048			
	HMD2	0.048			
	HMD3	0.048			
	CAD	0.01			
	HAD1	-0.07			
	HAD2	-0.07			
	CBD	0.01			

Table S3: Interaction of the hemes and the heme propionates with the residues that show a moderate solution redox potential dependence. The protonation probabilities of these residues are depicted in Figure 4 in the main text.

	Interaction Energy [kcal/mol]			
	Asp 32	Glu 41	Tyr 66	Lys 77
Heme I	0.80	0.53	0.11	0.19
Propionate A	0.08	0.12	0.03	0.03
Propionate B	0.26	0.16	0.16	0.12
Heme II	0.60	0.36	0.25	0.35
Propionate A	0.24	0.08	0.23	0.34
Propionate B	0.15	0.12	0.04	0.11
Heme III	0.60	0.13	0.27	0.40
Propionate A	0.10	0.03	0.07	0.06
Propionate B	0.11	0.02	0.03	0.09
Heme IV	0.13	0.04	2.45	0.14
Propionate A	0.04	0.01	0.91	0.04
Propionate B	0.13	0.05	0.77	0.09

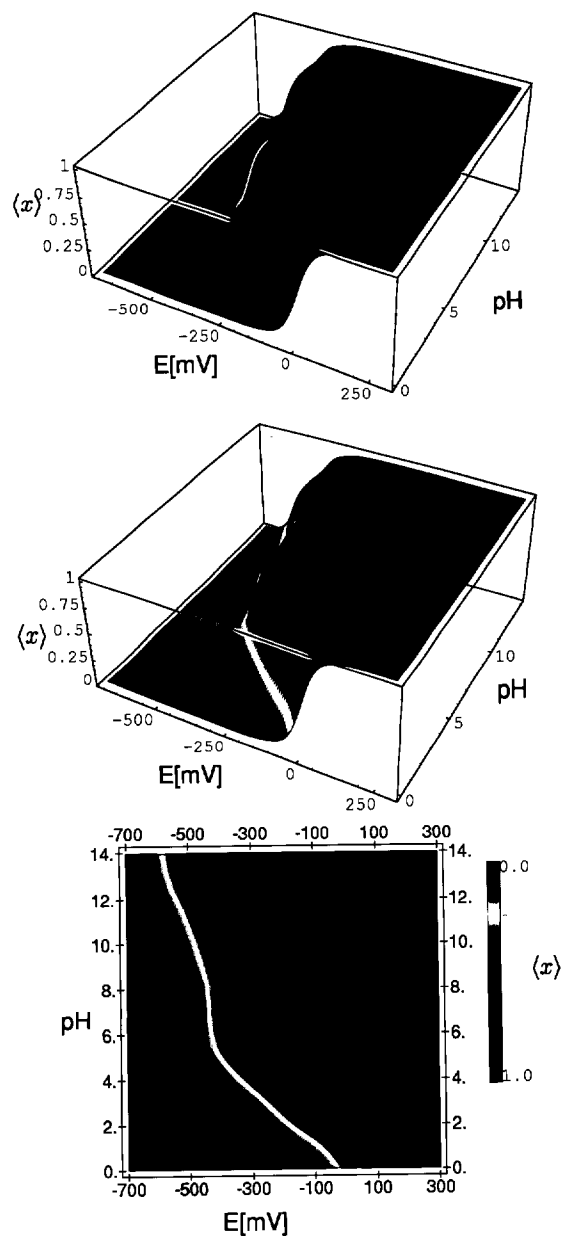


Figure S1: How to read the pH vs. E vs. Oxidation Probability Plots. In the upper diagram the oxidation probability $\langle x \rangle$ is depicted as a function of the solution pH and redox potential. In the middle diagram, additional (redundant) color coding is used to display the oxidation probability. In the lower diagram, only color coding is used to display the oxidation probability $\langle x \rangle$ as a function of the solution pH and redox potential. The color coding is used in the lower diagram is also used in Figure 4 in the main text. The protonation probability is displayed in an analogous manner.