

Supporting Information

P450 nomenclature

CYP194A2 from *R. palustris* CGA009 has already been named (CYP194A1 is found in *Bradyrhizobium japonicum* USDA 110) according to the CYP family assignments used for P450 nomenclature. Assignments are made based on the amino acid sequences of the P450 enzymes, 40% identity places a P450 in the same family, unless homologues with lower identity are demonstrated to be functionally equivalent, and 55% places it in the same subfamily. By analogy with the CYP199A subfamily; CYP199A1, *B. japonicum* USDA110; CYP199A2, *R. palustris* CGA009; CYP199A3, *Rhodococcus* sp. RHA1; CYP199A4, *R. palustris* HaA2, and in the absence of a CYP194A family member in *Rhodococcus* sp. RHA1 or any other published proteins from this family, we have assigned the CYP enzyme from *R. palustris* strain HaA2 as CYP194A3.

Figure S1. SDS-PAGE analysis of the [3Fe-4S] ferredoxin RPB3630 from *Rhodopseudomonas palustris* HaA2.

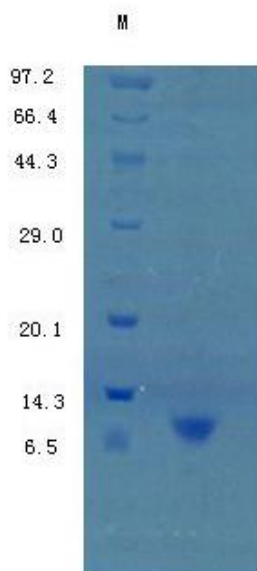


Figure S2 Hydrogen bonds in β -sheet B of RPB3630

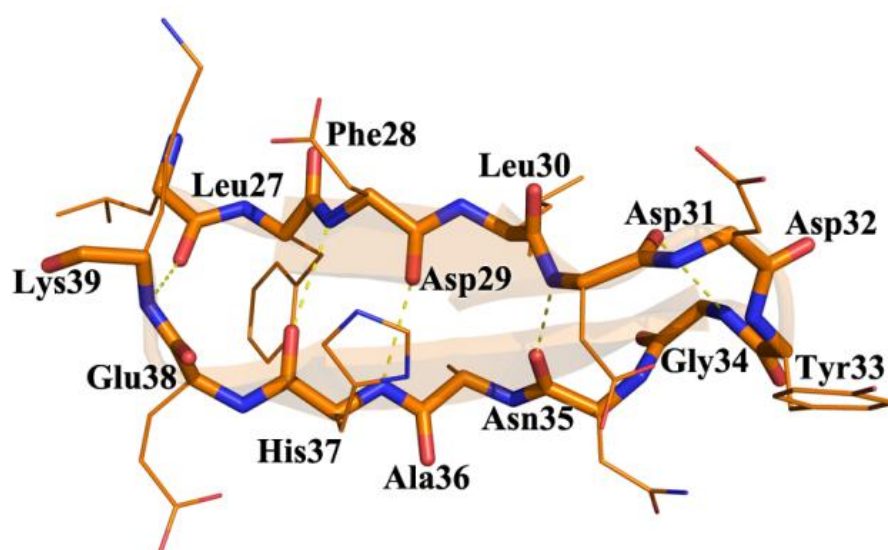


Figure S3 cluster environment comparison with [4Fe-4S] ferredoxin from *Bacillus thermoproteolyticus* (magenta). The residues from *Bacillus thermoproteolyticus* are labeled in italic.

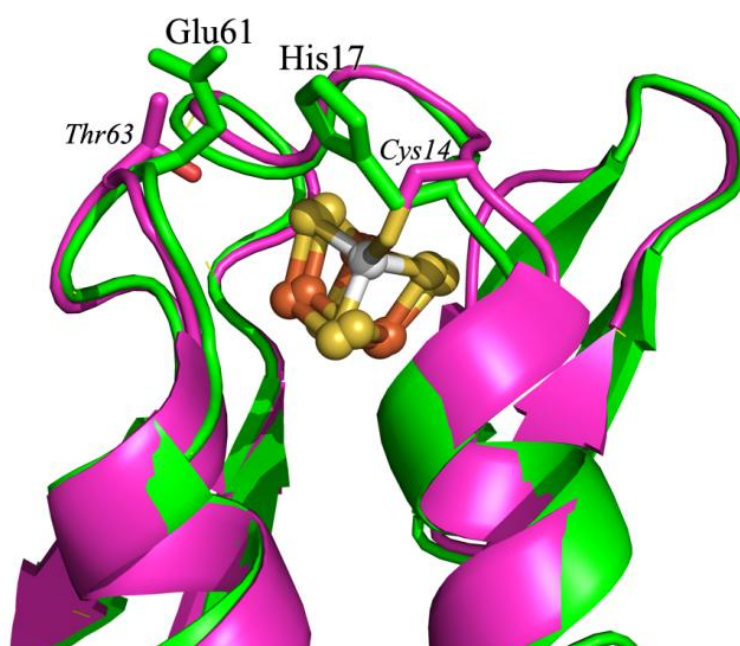
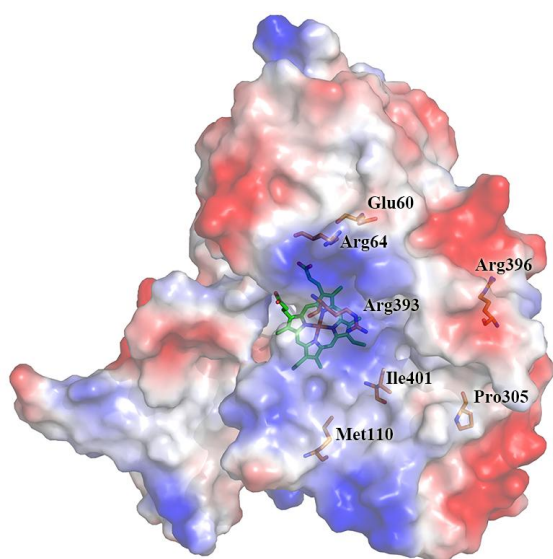
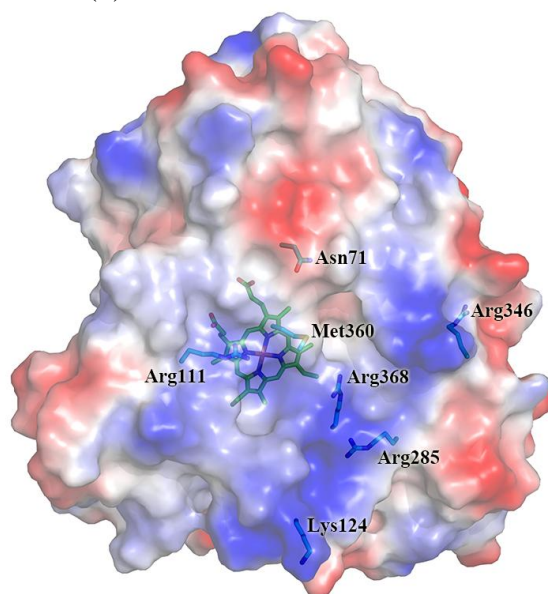


Figure S5. A comparison of the proximal faces of different cytochrome P450 enzymes: (a) CYP51 from *M. tuberculosis* (PDB: 1EA1), (b) CYP199A2 from *R. palustris* CGA009 (PDB: 2FR7), (c) CYP24A1 from rat mitochondria (PDB: 3K9Y), (d) CYP101D1 from *Novosphingobium aromaticivorans* DSM12444 (PDB: 3LXH) and (e) CYP101A1 (P450 cam), (PDB: 2CPP). Electrostatic interactions have been shown to be important in CYP-electron transfer partner recognition for (b), (c) and (d) and are less important for (e). All of the P45 enzymes have a prominent positively charge patch near the heme on the proximal surface.

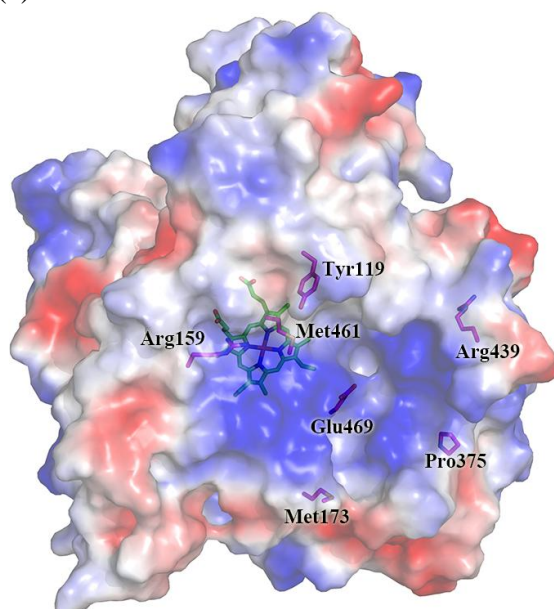
(a)



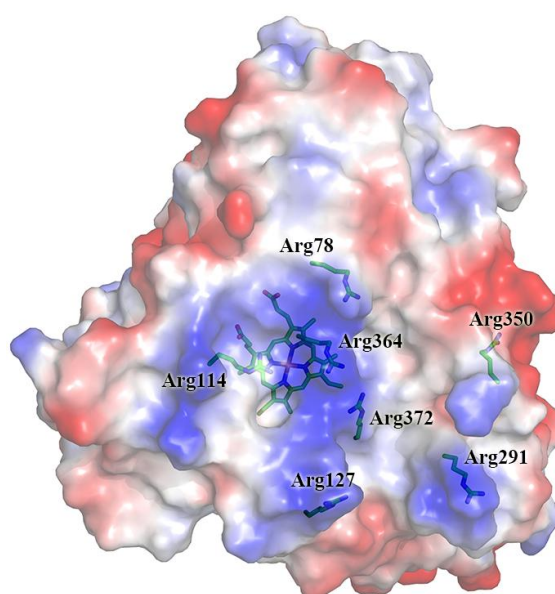
(b)



(c)



(d)



(e)

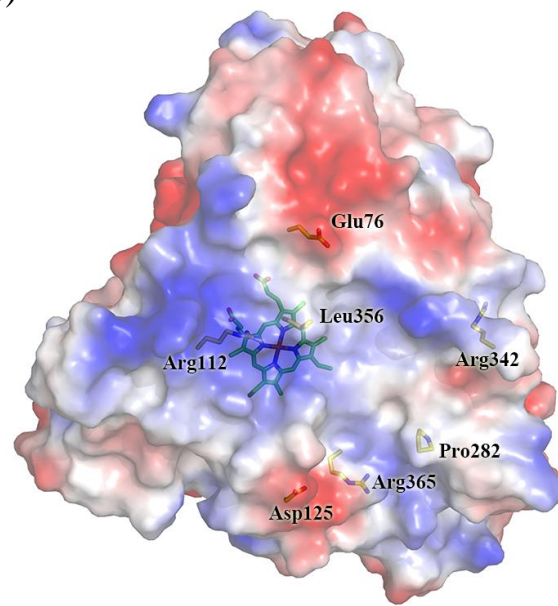


Table S1 Comparison of the residues comprising β -sheet B of RPB3630 with other structurally characterized ferredoxins. The β 3 sheet of RPB3630 is longer than the equivalent sheets in the other ferredoxins.

Sources	FeS cluster type	β 2	β 3	PDB code
<i>Rhodopseudomonas palustris</i> HaA2	[3Fe-4S]	Phe28-Asp31	Gly34-Glu38	4ID8
<i>Pyrococcus furiosus</i>	[3Fe-4S]	Phe25-Met27	Ala33-Pro35	1SJ1
<i>Desulfovibrio gigas</i>	[3Fe-4S]	Phe22-Met24	Ala31-Val33	1FXD
<i>Pyrococcus furiosus</i> (D14C mutant)	[4Fe-4S]	Phe25-Met27	Ala33-Pro35	2Z8Q
<i>Thermotoga maritima</i>	[4Fe-4S]	Phe24-Gly27	Ala32-Val34	1VJW
<i>Bacillus thermoproteolyticus</i>	[4Fe-4S]	Tyr25-Tyr27	Ala33-Val35	1IQZ