SUPPORTING INFORMATION

Structural Analysis of Aliphatic vs. Aromatic Substrate Specificity in a Copper Amine Oxidase from *Hansenula polymorpha*

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Table S1: Unit cell parameters for native-HPAO-1 and substrate-HPAO-1 complexes.

structure	space group	unit cell lengths (Å)	β angle (°)
native HPAO-1	$P2_1$	a = 104.15, b = 223.08, c = 104.25	95.77
ethylamine-HPAO-1	$P2_1$	a = 104.41, b = 232.83, c = 105.12	96.66
benzylamine-HPAO-1	$P2_1$	a = 104.24, b = 233.71, c = 105.05	96.57

Table S2: Species in the substrate-HPAO-1 active sites. A = axial copper ligand, E = equatorial copper ligand, * = evidence of second overlapping binding site. Occupancies are listed in parentheses.

Substrate	Chain	Electronic form of cofactor	Chain	Copper ligands	Chain	Species bound in active site
ethylamine	all	aminoquinol (1)	A	A = H_2O_2	A	ethylamine (1)*
			B	A = H_2O_2	B	ethylamine (1)
			C	A = H_2O E = H_2O	C	ethylamine (1)*
			D	A = H_2O	D	ethylamine (1)*
			E	A = H_2O_2 E = H_2O	E	ethylamine (1)
			F	A = H_2O_2	F	ethylamine (1)*
benzylamine	all	aminoquinol (1)	A	A = H_2O_2	all	benzylamine (1)
			B	A = H_2O_2		
			C	A = H_2O E = H_2O		
			D	A = H_2O		
			E	A = H_2O_2		
			F	A = H_2O_2		

Table S3: Average B-values for active site constituents.

Active site constituent	Average B-value ($Å^2$)	
	ethylamine complex	benzylamine complex
Copper ions	23.3	30.8
H_2O copper ligands	41.3	29.4
H_2O_2 copper ligands	22.0	30.2
ethylamine	35.2	--
benzylamine	--	38.0

Figure S1: Domain organization in HPAO-1. One monomer is drawn in cartoon and colored by domain (D2, purple; D3, green; D4, blue; connecting loops, yellow; β-hairpin arms, red). The second monomer is drawn as a semi-transparent surface rendering. TPQ atoms are drawn as space-filling spheres and colored by atom type (carbon, white), and copper ions are drawn as gold spheres.

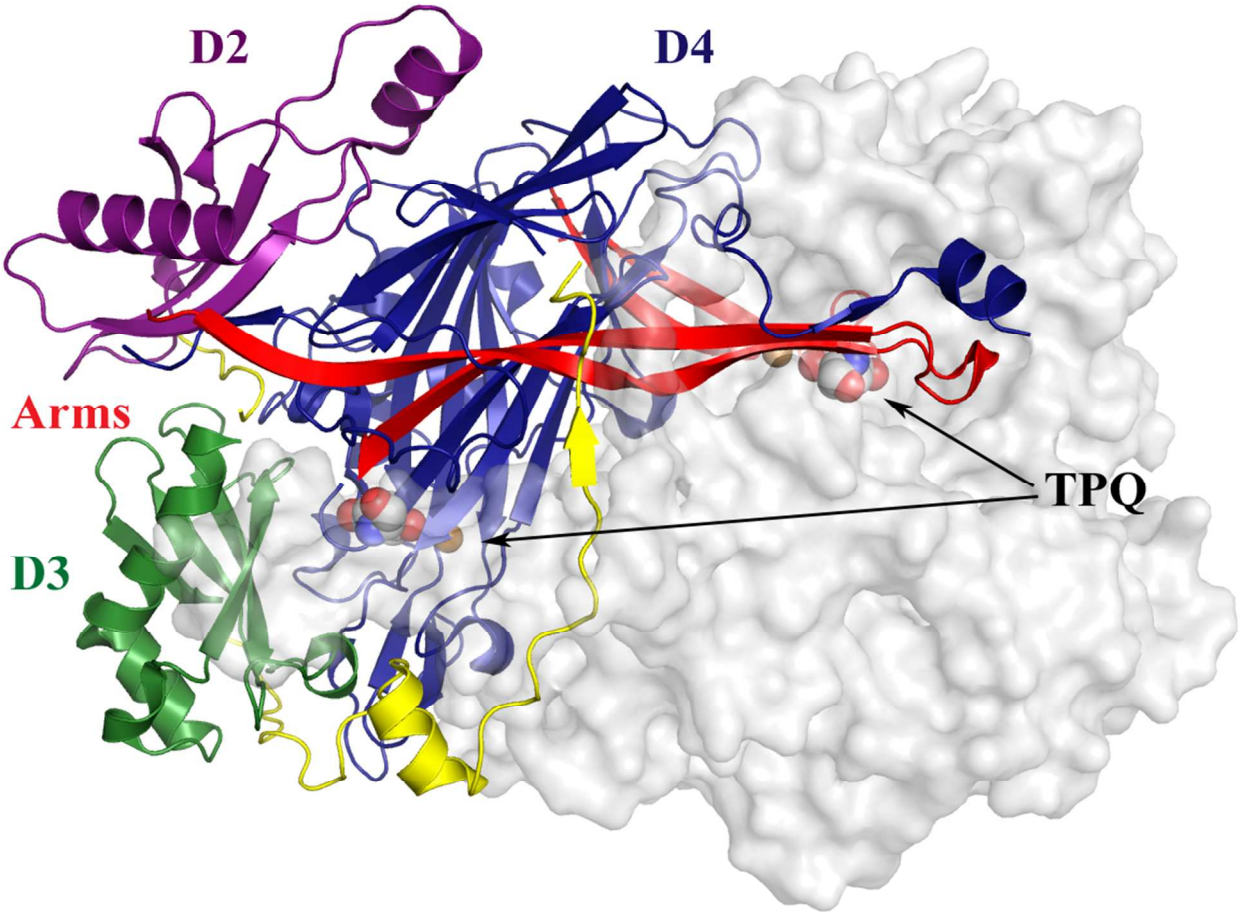

Figure S2: Electron density suggesting an alternate ethylamine conformer. Peaks in the F_o-F_c map near the site of ethylamine binding in all polypeptide chains in the EtAm-HPAO-1 structure are superimposed onto one active site and shown as green mesh contoured to 3.5σ.