Table S1- Data Collection and Refinement Statistics

Crystal	**Fdh_1min**	**Fdh_1min-Staraniso**	**Fdh_1.5min**	**Fdh_1.5min-Staraniso**
PDB_{code}		8BQG		8BQH
Diffraction Data				
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions (Å) (º)	a=64.54, b=122.78, c=148.99	a=64.54, b=122.78, c=148.99	a=64.36, b=127.46, c=128.95	a=64.36, b=127.46, c=128.95
Wavelength (Å)	0.8856	0.8856	0. 8856	0. 8856
Beamline	ESRF ID23-1	ESRF ID23-1	ESRF ID23-1	ESRF ID23-1
No. Crystals	1	1	1	1
Resolution range of data (Å) (last shell)	94.75 – 2.19 (2.23 – 2.19)	94.75 – 1.95 (2.07 – 1.95)	90.65 – 1.90 (1.93 – 1.90)	90.65 – 1.61 (1.78 – 1.61)
Completeness (%) (last shell)	97.72 (99.22)	91.96 (46.32)	99.35 (100.00)	94.17 (64.00)
Rmerge (last shell)	0.090 (0.709)	0.102 (1.055)	0.120 (0.803)	0.130 (0.877)
Rmeas (last shell)	0.102(0.808)	0.116 (1.212)	0.132 (0.883)	0.143 (0.989)
I/σI (last shell)	10.9 (2.1)	9.2 (1.5)	10.4 (2.2)	9.5 (1.7)
CC 1/2 (last shell)	0.997 (0.704)	0.997 (0.435)	0.996 (0.779)	0.996 (0.656)
Redundancy (last shell)	4.3 (4.2)	4.3 (4.1)	5.6 (5.8)	5.7 (4.7)
Refinement				
Reflections used in refinement (work (free))		69752 (3564)		90038 (4778)
Rwork		0.193		0.151
Rfree		0.243		0.175
Nº of non-hydrogen atoms		9509		9927
Protein		9191		9134
Ligands		168		229
Ions		2		7
Solvent		148		557
Geometry and *B*-factors				
RMSD bond lengths (Å)		0.010		0.012
RMSD bond angles (º)		1.618		1.601
Average B-factor ALL ($Å^2$)		38.30		19.36
Protein ($Å^2$)		40.86		20.06
Ligands ($Å^2$)		34.75		22.61
Ions ($Å^2$)		32.68		31.75
Solvent ($Å^2$)		34.24		25.26
Ramachandran favoured (%)		95.72		96.98
Ramachandran outliers (%)		0.26		1.04
Molprobity score		1.87		1.31
Clashscore		4.77		3.30

Crystal	**Fdh_3min**	**Fdh_5min**	**Fdh_5min-Staraniso**
PDB_{code}	8BQI		8BQJ
Diffraction Data			
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions (Å) (º)	a=64.99, b=123.75, c=150.36	a=64.94, b=123.35, c=150.55	a=64.94, b=123.35, c=150.55
Wavelength (Å)	0. 8856	0. 8856	0. 8856
Beamline	ESRF ID23-1	ESRF ID23-1	ESRF ID23-1
No. Crystals	1	1	1
Resolution range of data (Å) (last shell)	150.36 – 2.36 (2.43 – 2.36)	95.41 – 2.58 (2.62 – 2.58)	95.41 – 2.11 (2.36 – 2.11)
Completeness (%) (last shell)	98.30 (91.50)	99.08 (99.69)	92.88 (62.30)
Rmerge (last shell)	0.139 (1.258)	0.110 (0.806)	0.121 (0.851)
Rmeas (last shell)	0.170 (1.524)	0.127 (0.927)	0.139 (0.978)
I/σI (last shell)	9.0 (1.2)	10.4 (2.2)	9.1 (1.8)
CC 1/2 (last shell)	0.992 (0.409)	0.994 (0.621)	0.994 (0.552)
Redundancy (last shell)	4.8 (4.8)	4.3 (4.2)	4.3 (3.9)
Refinement			
Reflections used in refinement (work (free))	47534 (2409)		43543 (2296)
Rwork	0.213		0.214
Rfree	0.248		0.245
Nº of non-hydrogen atoms	9442		9431
Protein	9201		9191
Ligands	174		159
Ions	2		2
Solvent	65		79
Geometry and *B*-factors			
RMSD bond lengths (Å)	0.003		0.003
RMSD bond angles (º)	1.282		1.234
Average B-factor ALL ($Å^2$)	44.55		38.78
Protein ($Å^2$)	47.73		41.62
Ligands ($Å^2$)	40.83		33.80
Ions ($Å^2$)	37.43		31.59
Solvent ($Å^2$)	39.63		29.84
Ramachandran favoured (%)	94.78		95.21
Ramachandran outliers (%)	0.34		0.43
Molprobity score	1.67		1.54
Clashscore	2.54		3.42

Crystal	**Fdh_22min**	**Fdh_22-Staraniso**	**Fdh_FormO2**	**Fdh_FormO2-Staraniso**
PDB_{code}		8BQK		8BQL
Diffraction Data				
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions (Å) (º)	a=64.58, b=123.87, c=149.18	a=64.58, b=123.87, c=149.18	a=64.80, b=127.59, c=148.62	a=64.80, b=127.59, c=148.62
Wavelength (Å)	0.7749	0.7749	0.9686	0.9686
Beamline	ESRF ID23-1	ESRF ID23-1	ESRF ID30B	ESRF ID30B
No. Crystals	1	1	1	1
Resolution range of data (Å) (last shell)	95.30 – 1.80 (1.83 – 1.80)	95.30 – 1.59 (1.70 – 1.59)	96.81 – 2.11 (2.15 – 2.11)	96.81 – 1.91 (2.01 – 1.91)
Completeness (%) (last shell)	99.13 (99.24)	92.25 (63.11)	99.37 (99.89)	94.46 (61.60)
Rmerge (last shell)	0.070 (0.656)	0.077 (1.125)	0.168 (1.088)	0.186 (1.686)
Rmeas (last shell)	0.079 (0.745)	0.040 (1.234)	0.177 (1.142)	0.195 (1.767)
I/σI (last shell)	13.0 (2.2)	11.3 (1.5)	10.2 (2.2)	9.1 (1.3)
CC 1/2 (last shell)	0.998 (0.670)	0.998 (0.579)	0.997 (0.737)	0.997 (0.620)
Redundancy (last shell)	4.5 (4.5)	4.7 (5.9)	10.7 (11.1)	11.0 (11.1)
Refinement				
Reflections used in refinement (work (free))		123277 (6509)		78325 (4045)
Rwork		0.170		0.188
Rfree		0.192		0.225
Nº of non-hydrogen atoms		9875		9769
Protein		9219		9228
Ligands		196		166
Ions		2		2
Solvent		458		373
Geometry and *B*-factors				
RMSD bond lengths (Å)		0.007		0.004
RMSD bond angles (º)		1.387		1.278
Average B-factor ALL ($Å^2$)		28.48		33.79
Protein ($Å^2$)		30.01		36.02
Ligands ($Å^2$)		29.19		28.03
Ions ($Å^2$)		23.15		25.68
Solvent ($Å^2$)		33.81		31.61
Ramachandran favoured (%)		96.32		96.67
Ramachandran outliers (%)		0.26		0.34
Molprobity score		1.35		1.18
Clashscore		3.12		2.00

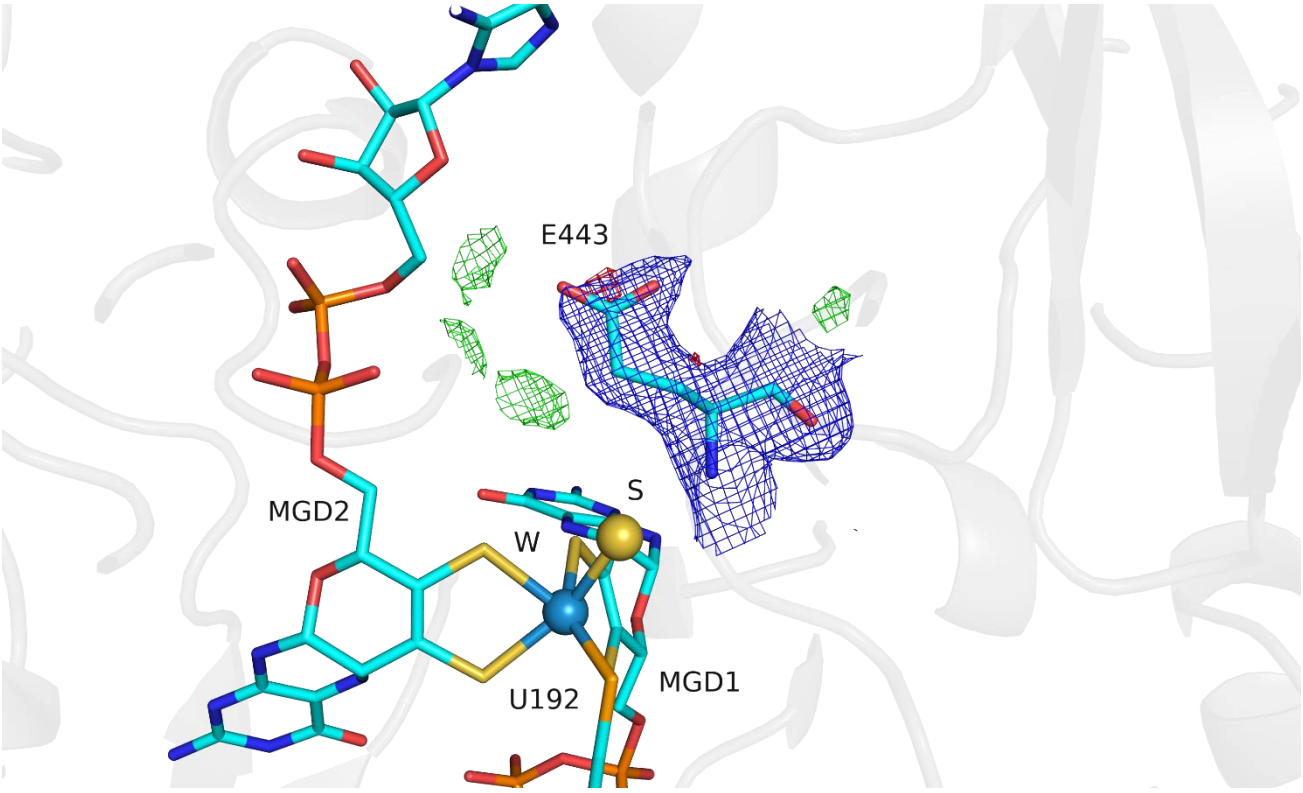

Figure S1. *Dv*FdhAB formate-soaked Fdh_5min structure (light blue). U192, E443 and the two MGD co-factors are shown as sticks. The 2fo-fc map is shown as a blue mesh, at 1.0 σ, and the fo-fc map is shown as a green and red mesh, respectively, for positive and negative values, at 3.0 σ.