Supplementary Information

Structural and electronic properties of the active site of [ZnFe] SulE

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S1. Relevant atomic distances [Å] at the [ZnFe] center of SulE harboring O_2 molecule according to DFT calculations on the isolated model systems. Distances around the experimental values are highlighted.

Model	d_{Zn-Fe} [Å] (exp. 3.83 Å)				d_{Zn-O2} [Å] (exp. 2.74 Å)				d_{Fe-O1} [Å] (exp. 2.12 Å)			
	FeII		FeIII		FeII		FeIII		FeII		FeIII	
	high	low	high	low	high	low	high	low	high	low	high	low
E95xE92x	4.13	4.11	4.16	4.03	3.71	2.99	4.09	3.93	**2.20**	**1.87**	**2.08**	**1.99**
E95tE92x	4.03	4.10	4.37	4.37	3.99	2.93	5.64	3.45	**2.04**	**1.75**	5.15	**2.05**
E95pE92x	4.27	4.12	4.53	4.53	3.90	2.82	4.62	4.64	3.16	**1.75**	3.96	3.99
E95xE92h	**3.71**	**3.73**	**3.63**	-	2.34	**2.31**	3.40	-	2.35	**1.78**	**2.06**	-
E95tE92h	**3.93**	4.06	4.44	4.47	4.69	3.40	4.84	4.87	5.31	**1.74**	4.94	6.00
E95pE92h	**3.96**	**3.89**	4.45	4.47	**2.42**	**2.44**	4.87	4.95	**2.14**	**1.73**	4.95	4.92

S2. O-O bond distances [Å] according to DFT calculations on the isolated model systems.

Model	d_{O-O} [Å] (exp. 1.25 Å)			
	FeII		FeIII	
	high	low	high	low
E95xE92x	1.25	1.27	1.24	1.26
E95tE92x	1.25	1.26	1.21	1.22
E95pE92x	1.21	1.26	1.21	1.21
E95xE92h	1.29	1.29	1.31	-
E95tE92h	1.22	1.29	1.21	1.21
E95pE92h	1.31	1.28	1.21	1.21

S3. Relevant atomic distances [Å] at the [ZnFe] center of SulE harboring H_2O_2 molecule according to DFT calculations on the isolated model systems. Distances around the experimental values are highlighted.

Model	d_{Zn-Fe} [Å] (exp. 3.83 Å)				d_{Zn-O2} [Å] (exp. 2.74 Å)				d_{Fe-O1} [Å] (exp. 2.12 Å)			
	FeII		FeIII		FeII		FeIII		FeII		FeIII	
Conf. "a"	high	low	high	low	high	low	high	low	high	low	high	low
E95xE92x	**3.84**	**3.82**	4.26	**3.91**	**2.19**	**2.19**	2.95	**2.31**	**2.05**	**1.98**	**1.93**	**1.84**
E95tE92x	**3.97**	**3.97**	4.14	4.05	**2.56**	**2.59**	**2.40**	**2.40**	2.37	**2.06**	**2.24**	**2.03**
E95xE92h	**3.79**	**3.75**	**3.78**	4.05	3.36	3.32	3.68	3.45	**2.16**	**2.02**	**1.99**	**1.84**
E95tE92h	**3.97**	**3.79**	4.29	4.23	3.53	3.30	3.52	3.56	3.74	**2.13**	2.30	**2.05**
Conf. "b"												
E95xE92x	**3.73**	**3.61**	4.14	4.12	**1.97**	**1.99**	2.95	2.79	**2.25**	**2.07**	**2.08**	**1.96**
E95pE92x	4.21	4.13	4.49	4.43	4.33	2.95	3.33	3.15	4.87	**2.07**	2.36	**2.06**
E95xE92h	4.20	**3.97**	**3.89**	4.02	3.73	3.61	3.60	3.74	2.38	**2.04**	**2.19**	4.11
E95pE92h	**3.88**	**3.89**	4.29	4.35	3.73	3.64	3.83	3.32	2.52	**2.10**	2.47	**2.05**

S4. QM O-O bond distances [Å] for high and low spin Fe for all 16 models and both Fe oxidation states at the active site of [ZnFe] sulerythrin with H_2O_2 as substrate.

Model	d_{O-O} [Å] (exp. 1.25 Å)			
	FeII		FeIII	
Conf. "a"	high	low	high	low
E95xE92x	1.48	1.48	1.43	1.45
E95tE92x	1.46	1.46	1.45	1.45
E95xE92h	1.47	1.47	1.46	1.46
E95tE92h	1.46	1.47	1.44	1.44
Conf. "b"				
E95xE92x	1.47	1.47	1.45	1.46
E95pE92x	1.45	1.46	1.46	1.46
E95xE92h	1.46	1.46	1.44	1.45
E95pE92h	1.45	1.45	1.44	1.45

S5. Relevant atomic distances [Å] of the [ZnFe] center of SulE harboring O_2 molecule according to DFT calculations on the most plausible model systems in vacuum. Distances around the experimental values are highlighted. O-O bond distances are compared to the experimental resolved value of diCo-SulE (exp. 1.50 Å) (PDB 709D). Binding distances around the experimental values are highlighted.

Model	d_{Zn-Fe} [Å] (exp. 3.83 Å)		d_{O-O} [Å] (exp. 1.50 Å)		d_{Zn-O2} [Å] (exp. 2.74 Å)		d_{Fe-O1} [Å] (exp. 2.12 Å)	
	FeII		FeII		FeII		FeII	
	high	low	high	low	high	low	high	low
E95xE92x	-	4.24	-	1.23	-	3.36	-	**2.19**
E95tE92x	4.09	4.09	1.27	1.27	3.19	3.16	**1.75**	**1.75**
E95xE92h	**3.89**	-	1.27	-	**2.92**	-	**1.74**	-

S6. Relevant atomic distances [Å] at the [ZnFe] center of SulE harboring H_2O_2 molecule according to DFT calculations on the most plausible model systems in vacuum. Distances around the experimental values are highlighted. O-O bond distances are compared to the experimental resolved value of diCo-SulE (exp. 1.50 Å) (PDB 709D). Binding distances around the experimental values are highlighted.

Model	d_{Zn-Fe} [Å] (exp. 3.83 Å)		d_{O-O} [Å] (exp. 1.50 Å)		d_{Zn-O2} [Å] (exp. 2.74 Å)		d_{Fe-O1} [Å] (exp. 2.12 Å)	
	FeII		FeII		FeII		FeII	
	high	low	high	low	high	low	high	low
E95tE92x_a	**3.84**	**3.91**	**1.45**	**1.45**	3.07	3.43	**2.06**	**2.11**
E95xE92h_a	**3.79**	**3.78**	**1.46**	**1.46**	**2.90**	**2.86**	**2.06**	**2.07**
E95tE92h_a	-	**3.90**	**-**	**1.45**	-	3.14	**-**	**2.10**