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Supporting Information

The Oxygen Reactivity of an Artificial Hydrogenase Designed in a Reengineered Copper Storage Protein

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Table S1. Key geometric parameters.

	R_{Ni-S1} Å	R_{Ni-S2} Å	R_{Ni-S3} Å	R_{Ni-S4} Å	R_{Ni-O1} Å	R_{O1-O2} Å	R_{O2-S4} Å	∠S1-S2-S3-S4 degree
I-1	2.459	2.350	2.447	2.362				48.0
I-2	2.400	2.330	2.459	2.322				48.2
I-2'	2.458	2.331	2.525	3.969	1.884	1.459	1.617	55.4
I-3	2.473	2.419	2.457	2.437	2.144	1.444	/	27.5
I-3'	2.412	2.377	2.405	2.374	2.157	1.451	/	24.4
I-4	2.476	2.318	2.508	2.260	1.815	/	/	48.7

Table S2. Key spin densities and relative reaction Gibbs free energies from **I-1**

	$\rho^{\alpha\beta}_{Ni}$ e	$\rho^{\alpha\beta}_{S1}$ e	$\rho^{\alpha\beta}_{S2}$ e	$\rho^{\alpha\beta}_{S3}$ e	$\rho^{\alpha\beta}_{S4}$ e	$\rho^{\alpha\beta}_{O1}$ e	$\rho^{\alpha\beta}_{O2}$ e	ΔG kcal/mol
I-1	1.484	0.111	0.156	0.116	0.130	0.169	0.009	0.00
I-2	0.851	0.047	0.036	0.036	0.041			-176.36
I-2'	1.516	0.120	0.131	0.068	0.004	0.150	0.001	54.21
I-3	1.527	0.110	0.123	0.081	0.111	0.035	0.002	-282.17
I-3'	1.311	-0.061	-0.112	-0.121	-0.046	0.041	0.002	177.58
I-4	0.867	0.039	-0.074	0.076	-0.052	0.152	0.867	-354.95

Table S3. Key geometric parameters in **I-1** models

	R_{Ni-S1} Å	R_{Ni-S2} Å	R_{Ni-S3} Å	R_{Ni-S4} Å	∠S1-S2-S3-S4 Degree
^{1}I-1-SP	2.301	2.275	2.313	2.279	32.0
^{1}I-1-TH	2.314	2.274	2.339	2.246	54.4
^{3}I-1-SP	2.459	2.350	2.447	2.362	48.0
^{3}I-1-TH	2.459	2.358	2.432	2.380	62.8

Table S4. Key spin densities and relative energies in **I-1** models

	$\rho^{\alpha\beta}_{Ni}$ e	$\rho^{\alpha\beta}_{S1}$ e	$\rho^{\alpha\beta}_{S2}$ e	$\rho^{\alpha\beta}_{S3}$ e	$\rho^{\alpha\beta}_{S4}$ e	ΔE kcal/mol	ΔE_{ZPE} kcal/mol	ΔH kcal/mol	ΔG kcal/mol
^{1}I-1-SP	0.000	0.000	0.000	0.000	0.000	6.40	6.39	6.46	7.07
^{1}I-1-TH	0.000	0.000	0.000	0.000	0.000	57.62	57.68	56.96	61.14
^{3}I-1-SP	1.484	0.111	0.156	0.116	0.130	0.00	0.00	0.00	0.00
^{3}I-1-TH	1.494	0.073	0.151	0.095	0.170	66.81	66.70	66.27	68.73

Table S5. Key geometric parameters in **I-2'** models

	R_{Ni-S1} Å	R_{Ni-S2} Å	R_{Ni-S3} Å	R_{Ni-S4} Å	R_{Ni-O1} Å	R_{O1-O2} Å	$R_{O2-S3/4}$ Å	∠S1-S2-S3-S4 degree
I-2'-F-up	2.404	2.407	4.163	2.422	1.888	1.475	1.631	50.1
I-2'-AF-up	2.803	2.421	2.954	2.265	1.775	1.511	1.720	62.3
I-2'-F-dn	2.458	2.331	2.525	3.969	1.884	1.459	1.617	55.4
I-2'-AF-dn	2.373	2.270	2.410	4.135	1.874	1.465	1.617	47.3

Table S6. Key spin densities and relative energies in **I-2'** models

	$\rho^{\alpha\beta}_{Ni}$ e	$\rho^{\alpha\beta}_{S1}$ e	$\rho^{\alpha\beta}_{S2}$ e	$\rho^{\alpha\beta}_{S3}$ e	$\rho^{\alpha\beta}_{S4}$ e	$\rho^{\alpha\beta}_{O1}$ e	$\rho^{\alpha\beta}_{O2}$ e	ΔE kcal/mol	ΔE_{ZPE} kcal/mol	ΔH kcal/mol	ΔG kcal/mol
I-2'-F-up	1.589	0.052	0.076	0.000	0.101	0.169	0.009	15.06	13.37	14.03	11.27
I-2'-AF-up	0.160	-0.177	0.046	0.002	-0.042	0.001	-0.014	93.11	87.00	87.01	84.56
I-2'-F-dn	1.516	0.120	0.131	0.068	0.004	0.150	0.001	0.00	0.00	0.00	0.00
I-2'-AF-dn	0.024	-0.071	0.036	-0.020	-0.002	0.031	0.002	3.75	4.01	3.51	5.61

Table S7. Key geometric parameters in **I-3'** models

	R_{Ni-S1} Å	R_{Ni-S2} Å	R_{Ni-S3} Å	R_{Ni-S4} Å	R_{Ni-O1} Å	R_{O1-O2} Å	$R_{O2-S3/4}$ Å	∠S1-S2-S3-S4 degree
I-3'-Ni-4S-1	2.412	2.377	2.405	2.374	2.157	1.451	/	24.4
I-3'-Ni-4S-2	2.401	2.418	2.503	2.478	2.138	1.445	/	48.1

Table S8. Key spin densities and relative energies in **I-3'** models

	$\rho^{\alpha\beta}_{Ni}$ e	$\rho^{\alpha\beta}_{S1}$ e	$\rho^{\alpha\beta}_{S2}$ e	$\rho^{\alpha\beta}_{S3}$ e	$\rho^{\alpha\beta}_{S4}$ e	$\rho^{\alpha\beta}_{O1}$ e	$\rho^{\alpha\beta}_{O2}$ e	ΔE kcal/mol	ΔE_{ZPE} kcal/mol	ΔH kcal/mol	ΔG kcal/mol
I-3'-Ni-4S-1	1.311	-0.061	-0.112	-0.121	-0.046	0.041	0.002	0.00	0.00	0.00	0.00
I-3'-Ni-4S-2	1.308	-0.091	0.124	-0.169	-0.173	0.019	-0.002	-3.43	-2.24	-2.79	0.03

Table S9. Key geometric parameters in **I-3** models

	R_{Ni-S1} Å	R_{Ni-S2} Å	R_{Ni-S3} Å	R_{Ni-S4} Å	R_{Ni-O1} Å	R_{O1-O2} Å	∠S1-S2-S3-S4 degree
^{1}I-3-Ni-4S-1	2.304	2.275	2.302	2.264	3.166	1.446	29.6
^{3}I-3-Ni-4S-1	2.473	2.419	2.457	2.437	2.144	1.444	27.5
^{1}I-3-Ni-4S-2	2.303	2.293	2.316	2.270	2.674	1.448	31.9
^{3}I-3-Ni-4S-2	2.461	2.383	2.470	2.414	2.194	1.438	52.9

Table S10. Key spin densities and relative energies in **I-3** models

	$\rho^{\alpha\beta}_{Ni}$ e	$\rho^{\alpha\beta}_{S1}$ e	$\rho^{\alpha\beta}_{S2}$ e	$\rho^{\alpha\beta}_{S3}$ e	$\rho^{\alpha\beta}_{S4}$ e	$\rho^{\alpha\beta}_{O1}$ e	$\rho^{\alpha\beta}_{O2}$ e	ΔE kcal/mol	ΔE_{ZPE} kcal/mol	ΔH kcal/mol	ΔG kcal/mol
^{1}I-3-Ni-4S-1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	9.01	8.30	9.39	6.26
^{3}I-3-Ni-4S-1	1.527	0.110	0.123	0.081	0.111	0.035	0.002	7.52	5.18	6.82	0.13
^{1}I-3-Ni-4S-2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	15.94	15.60	16.51	13.49
^{3}I-3-Ni-4S-2	1.506	0.112	0.141	0.091	0.113	0.029	0.000	0.00	0.00	0.0	0.00

Table S11. Key geometry parameters in **I-4** models

	R_{Ni-S1} Å	R_{Ni-S2} Å	R_{Ni-S3} Å	R_{Ni-S4} Å	R_{Ni-O1} Å	R_{S4-O1} Å	∠S1-S2-S3-S4 degree
I-4-Ni-4S-1	2.476	2.318	2.508	2.260	1.815	/	48.7
I-4-Ni-4S-2	2.382	2.316	2.434	2.465	1.772	/	55.6

Table S12. Key spin densities and relative energies in **I-4** models

	$\rho^{\alpha\beta}_{Ni}$ e	$\rho^{\alpha\beta}_{S1}$ e	$\rho^{\alpha\beta}_{S2}$ e	$\rho^{\alpha\beta}_{S3}$ e	$\rho^{\alpha\beta}_{S4}$ e	$\rho^{\alpha\beta}_{O1}$ e	ΔE kcal/mol	ΔE_{ZPE} kcal/mol	ΔH kcal/mol	ΔG kcal/mol
I-4-Ni-4S-1	0.867	0.039	-0.074	0.076	-0.052	0.152	0.00	0.00	0.00	0.00
I-4-Ni-4S-2	0.775	0.025	-0.033	-0.027	0.254	0.016	2.65	2.72	2.61	2.84

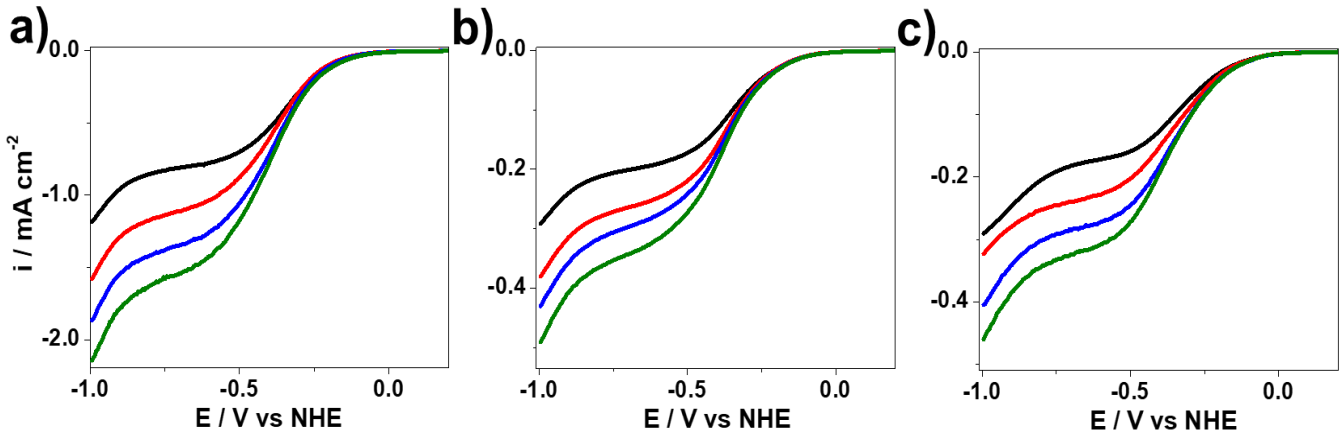

Figure S1: The linear sweep voltammograms (LSVs) of Ni(II)-NBP at different rotation rates, 125 rpm (black), 250 rpm (red), 375 rpm (blue) and 500 rpm (olive) under oxic conditions at (a) pH 6, (b) pH 7, and (c) pH 9.

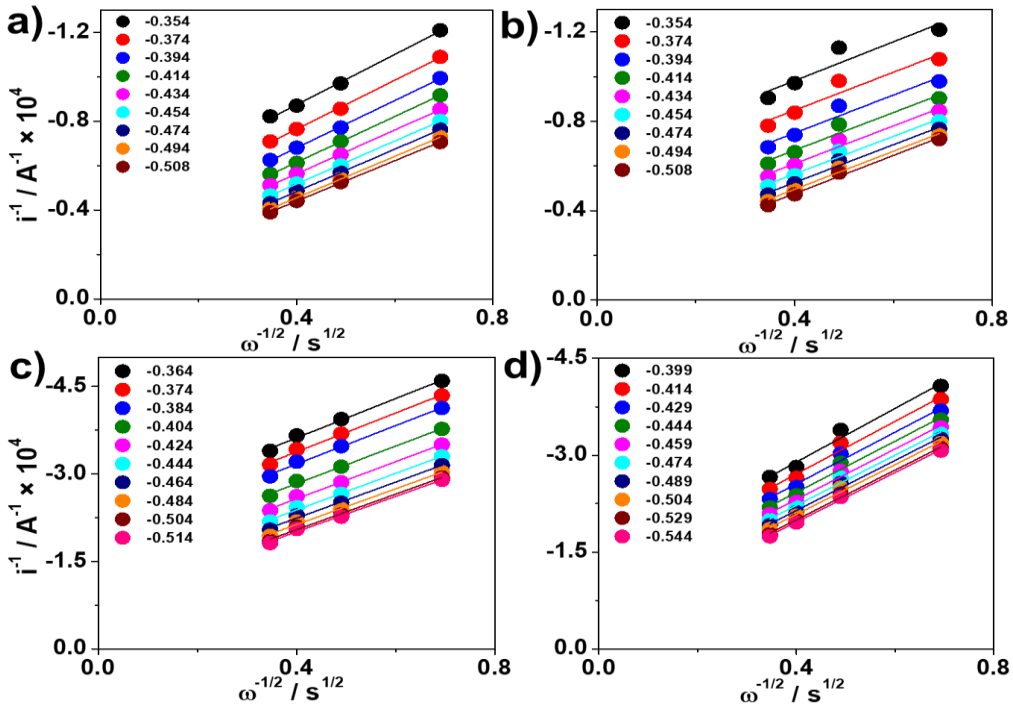

Figure S2: The Koutecký-Levich (K-L) Analyses of the LSVs of Ni(II)-NBP at different rotation rates under ambient O_2 at varying pH (a) pH 5 (b) pH 6 (c) pH 7 and (d) pH 9. The corresponding potential values are shown on each plot.

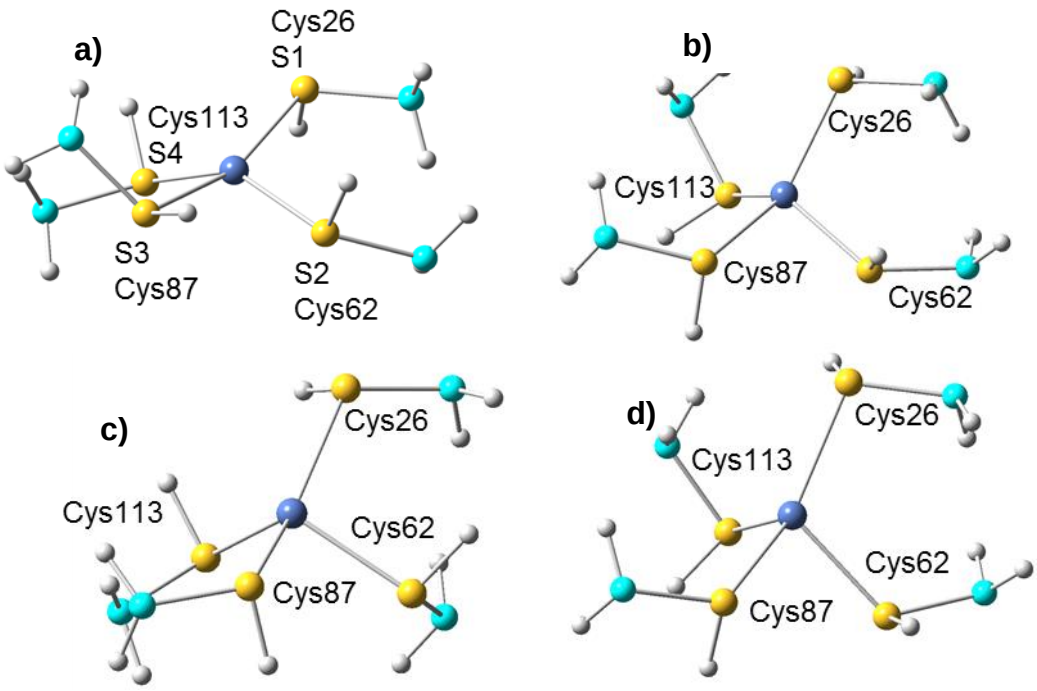

Figure S3. QM region of optimized **I-1**: **a**) ^{1}I-1-SP; **b**) ^{1}I-1-TH; **c**) ^{3}I-1-SP; **d**) ^{3}I-1-TH.

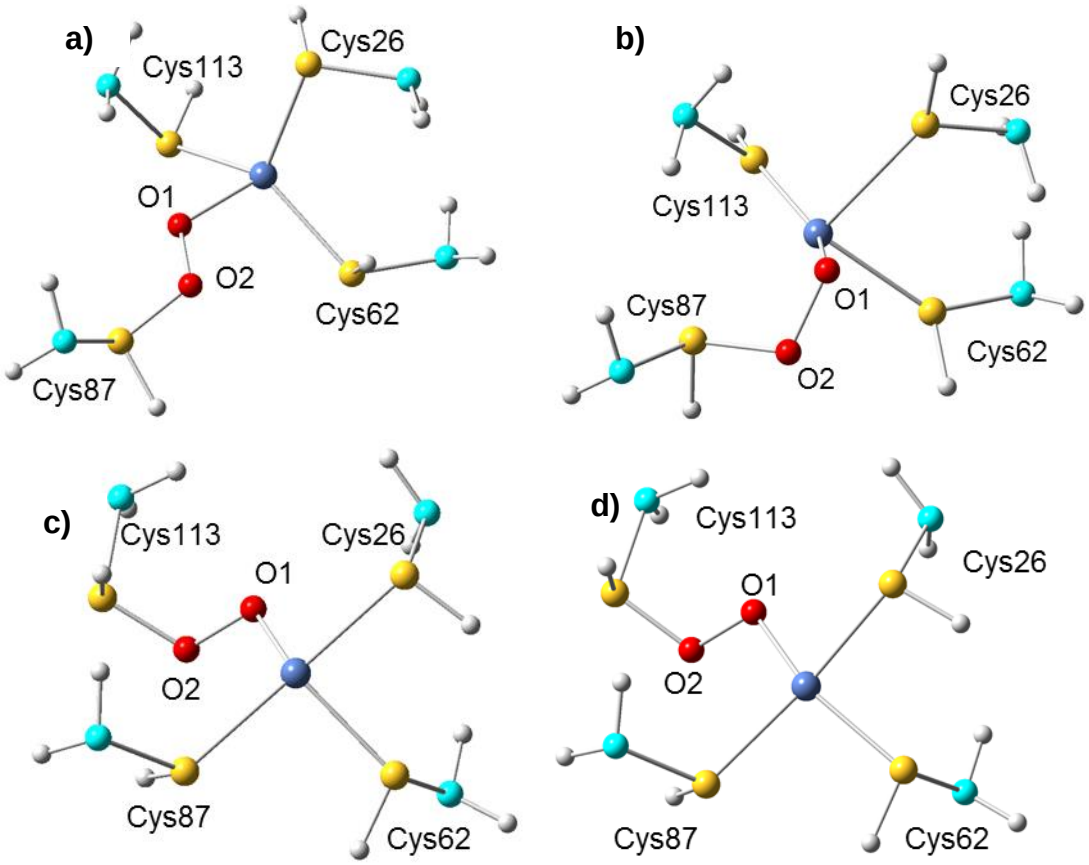

Figure S4. QM region of optimized **I-2'** models: **a**) I-2'-F-up; **b**) I-2'-AF-up; **c**) I-2'-F-dn; **d**) I-2'-AF-dn. Atom color scheme: Ni- blue gray, S- yellow, O- red, C- cyan, H- grey.

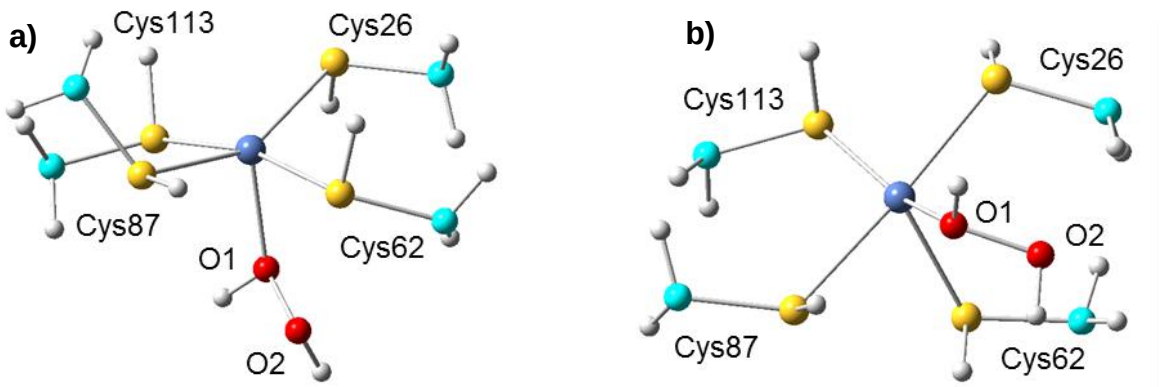

Figure S5. QM region of optimized **I-3'**: **a)** I-3'-Ni-4S-1; **b)** I-3'-Ni-4S-2.

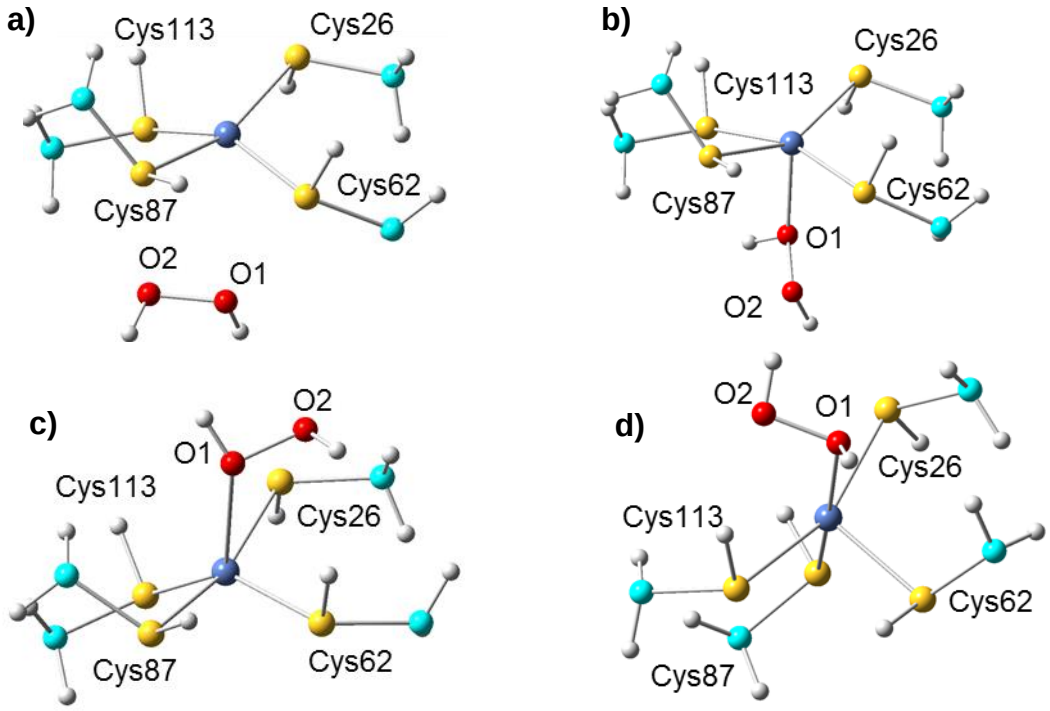

Figure S6. QM region of optimized **I-3**: **a**) ^{1}I-3-Ni-4S-1; **b**) ^{3}I-3-Ni-4S-1; **c**) ^{1}I-3-Ni-4S-2; **d**) ^{3}I-3-Ni-4S-2.

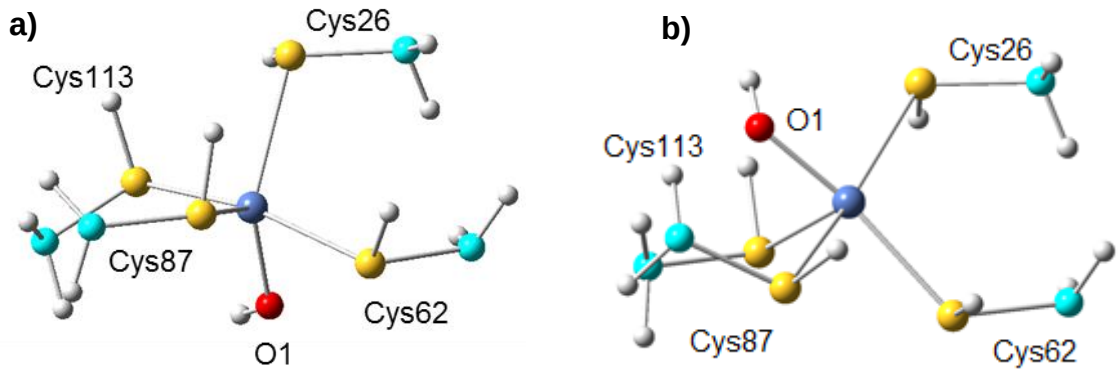

Figure S7. QM region of optimized **I-4**: **a**) I-4-Ni-4S-1; **b**) I-4-Ni-4S-2; **c**) I-4-Ni-3S-1; **d**) I-4-Ni-3S-2.