−Supporting Information−

Geometry, Spin Coupling, and Dielectric Control of Redox Potentials in [4Fe–4S] Clusters

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Table S1. Calculated Adiabatic Electron Affinity (AEA_{ZPE}) for each of the five ferredoxin [4Fe-4S] clusters with commonly used exchange-correlation functionals (E_{XC}). The across-cluster range is the difference between the maximum and minimum values across the clusters (Δ(Max-Min)). σ is the standard deviation across all methods for each cluster. These calculations include zero-point vibrational energy (ZPE) and van der Waals corrections.

		AEA_{ZPE} / eV					
E_{XC}	***E_{XC} Type***	**#1**	**#2**	**#3**	**#4**	**#5**	**Δ(Max-Min)**
PWLDA	LDA	-4.465	-4.341	-4.349	-4.568	-4.531	0.227
BP86	GGA	-4.239	-4.187	-4.188	-4.270	-4.203	0.083
PBE	GGA	-4.203	-4.356	-4.335	-4.377	-4.411	0.208
BLYP	GGA	-4.367	-4.285	-4.307	-4.429	-4.333	0.144
TPSS	Meta-GGA	-4.132	-4.275	-4.301	-4.423	-4.308	0.291
revTPSS	Meta-GGA	-4.361	-4.338	-4.365	-4.423	-4.371	0.085
r2SCAN	Meta-GGA	-4.305	-4.314	-4.270	-4.290	-4.329	0.059
B3LYP	GGA Hybrid	-3.645	-3.648	-3.649	-3.638	-3.626	0.023
PBE0	GGA Hybrid	-3.556	-3.566	-3.564	-3.546	-3.561	0.020
TPSSh	Meta-GGA Hybrid	-3.971	-3.979	-3.980	-3.997	-3.982	0.026
TPSS0	Meta-GGA Hybrid	-3.406	-3.434	-3.448	-3.411	-3.412	0.042
r2SCANh	Meta-GGA Hybrid	-3.991	-3.990	-3.998	-3.996	-4.020	0.030
CAM-B3LYP	Range-Separated Hybrid	-3.150	-3.082	-3.173	-3.186	-3.155	0.104
	Mean	-3.984	-3.984	-3.994	-4.043	-4.019	0.103
	1σ	0.417	0.420	0.404	0.455	0.441	0.089

Table S2. Calculated zero-point energy (ΔZPE) correction for each exchange correlation functional used to calculate the Adiabatic Electron Affinity (AEA_{ZPE}) for each of the five ferredoxin [4Fe-4S] clusters.

	ΔZPE / eV				
E_{XC}	**#1**	**#2**	**#3**	**#4**	**#5**
PWLDA	0.053	0.054	0.054	0.050	0.055
BP86	0.070	0.070	0.067	0.072	0.070
PBE	0.030	0.050	0.050	0.022	0.025
BLYP	0.074	0.071	0.072	0.075	0.071
TPSS	0.021	0.049	0.049	0.052	0.050
revTPSS	0.053	0.050	0.050	0.050	0.049
B3LYP	0.043	0.043	0.044	0.042	0.067
PBE0	0.040	0.042	0.043	0.039	0.040
TPSSh	0.070	0.073	0.067	0.077	0.067
TPSS0	0.042	0.039	0.043	0.040	0.043
CAM-B3LYP	0.067	0.062	0.043	0.041	0.039
r2SCAN	0.057	0.057	0.055	0.059	0.056
r2SCANh	0.045	0.046	0.049	0.044	0.046
r2SCAN0	0.041	0.041	0.059	0.079	0.043

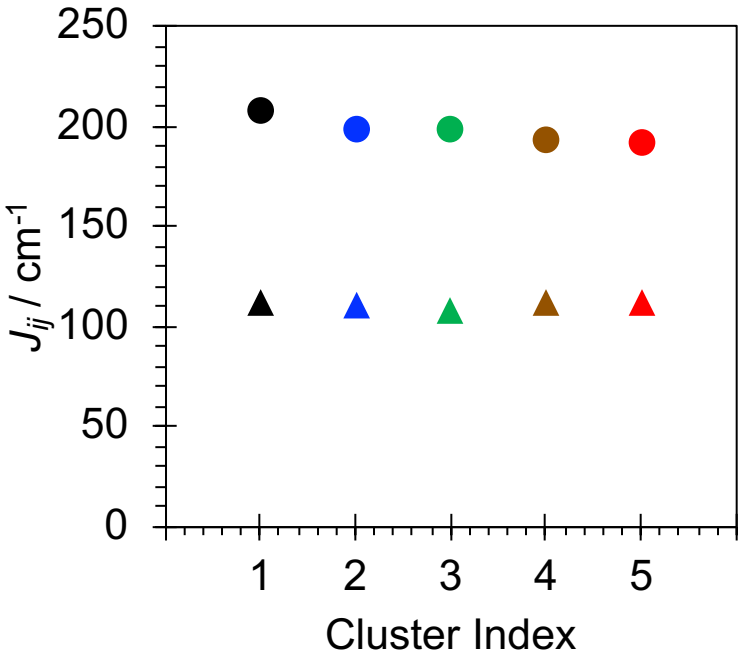

Figure S1. Extended Broken Symmetry DFT calculated exchange coupling constants (J_{ij}) for each of the five [4Fe-4S] clusters in the reduced (triangles) and oxidized (circles) state.

Table S3. Calculated zero-point energy (ΔZPE) correction for each value of dielectric constant (ε) used to calculate the Adiabatic Electron Affinity (AEA_{ZPE}) for each of the five ferredoxin [4Fe-4S] clusters.

ΔZPE / eV					
ε	**#1**	**#2**	**#3**	**#4**	**#5**
1	0.070	0.070	0.067	0.072	0.070
2	0.048	0.047	0.045	0.050	0.049
4	0.045	0.037	0.035	0.045	0.038
6	0.044	0.033	0.032	0.041	0.035
8	0.036	0.031	0.031	0.039	0.033
10	0.035	0.030	0.031	0.038	0.033
15	0.034	0.028	0.030	0.037	0.032
20	0.034	0.028	0.029	0.036	0.032
25	0.034	0.027	0.029	0.035	0.031
30	0.033	0.027	0.029	0.036	0.031
35	0.033	0.027	0.029	0.036	0.031
40	0.033	0.027	0.029	0.035	0.031
45	0.033	0.027	0.029	0.035	0.031
50	0.033	0.026	0.029	0.035	0.031
55	0.033	0.026	0.029	0.035	0.031
60	0.033	0.026	0.029	0.035	0.031
65	0.033	0.026	0.029	0.035	0.031
70	0.033	0.026	0.029	0.035	0.031
75	0.033	0.026	0.029	0.035	0.031
80	0.033	0.026	0.029	0.035	0.031

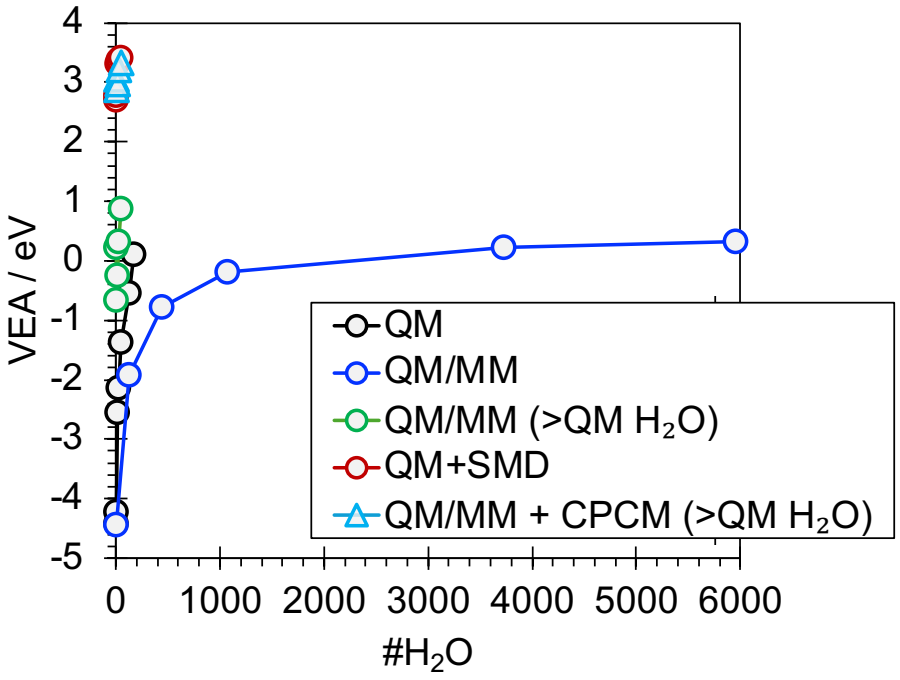

Figure S2. Calculated VEA of the [4Fe-4S] cluster as a function of the number of water molecules (#H_2O): (i) QM DFT with all water molecules treated at the QM level; (ii) QM/MM with all water molecules treated as MM point charges; (iii) QM/MM with a growing subset of water molecules included in the QM region (> QM H_2O); (iv) QM with implicit solvent (SMD, ε = 78); and (v) QM/MM with CPCM implicit solvent and an increasing number of QM water molecules (QM/MM + CPCM, > QM H_2O).