Supporting Information

Broken-Symmetry DFT Computations for the Reaction Pathway of IspH, an Iron-Sulfur Enzyme in Pathogenic Bacteria

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Table S1. Geometric parameters for the lowest–energy 1e^- reduced RO(H)–bound states that are omitted from Table 2 in text. Bond lengths are shown in Å.

		$RO^-P^-E^H$			$RO^-P^HE^H$			$RO^HP^-E^H$		
	Exp	**Ox**	**Red**	**Δ**	**Ox**	**Red**	**Δ**	**Ox**	**Red**	**Δ**
Cluster bond lengths:										
Fe1 – S5	2.344	2.275	2.295	0.02	2.281	2.337	**0.06**	2.200	2.245	0.04
Fe1 – S6	2.393	2.351	2.369	0.02	2.351	2.337	-0.01	2.282	2.267	-0.02
Fe1 – S7	2.364	2.378	2.395	0.02	2.370	2.380	0.01	2.319	2.324	0.01
Fe2 – S5	2.217	2.340	2.310	-0.03	2.347	2.347	0.00	2.328	2.333	0.00
Fe2 – S6	2.186	2.212	2.260	**0.05**	2.213	2.213	0.00	2.206	2.213	0.01
Fe2 – S8	2.181	2.385	2.427	0.04	2.380	2.409	0.03	2.357	2.395	0.04
Fe3 – S5	2.319	2.328	2.336	0.01	2.330	2.330	0.00	2.305	2.328	0.02
Fe3 – S7	2.281	2.240	2.284	0.04	2.239	2.246	0.01	2.240	2.258	0.02
Fe3 – S8	2.306	2.377	2.400	0.02	2.372	2.402	0.03	2.361	2.382	0.02
Fe4 – S6	2.308	2.321	2.331	0.01	2.322	2.335	0.01	2.326	2.321	0.00
Fe4 – S7	2.217	2.320	2.321	0.00	2.323	2.301	-0.02	2.322	2.307	-0.01
Fe4 – S8	2.276	2.279	2.305	0.03	2.280	2.349	**0.07**	2.241	2.301	**0.06**
Fe2 – S_{C12}	2.283	2.305	2.339	0.03	2.303	2.364	**0.06**	2.256	2.309	**0.05**
Fe3 – S_{C197}	2.285	2.314	2.328	0.01	2.306	2.361	**0.05**	2.275	2.330	**0.06**
Fe4 – S_{C96}	2.264	2.321	2.373	**0.05**	2.314	2.356	0.04	2.295	2.356	**0.06**
HMBPP bond lengths:										
Fe1 – O_{C4}	2.046	1.891	1.930	0.04	1.899	1.934	0.03	2.214	2.257	0.04
Fe1 – C_3	3.039	3.497	3.497	0.00	3.406	3.396	-0.01	3.531	3.573	0.04
Fe1 – C_2	2.913	3.136	3.156	0.02	3.107	3.086	-0.02	3.272	3.304	0.03

Table S2. Net spin populations (NSPs) computed for the lowest–energy, 1e^- reduced RO(H)–bound valence isomers not included in Table 3 in the text.

	$RO^-P^-E^H$					
	αββα			βααβ		
	OX	**RED**	**ΔNSP**	**OX**	**RED**	**ΔNSP**
Fe1	3.355	3.439	0.085	-3.356	-3.253	0.102
Fe2	-3.279	-3.150	0.129	3.279	3.358	0.079
Fe3	-3.283	-3.071	0.212	3.283	3.359	0.076
Fe4	3.243	3.316	0.073	-3.242	-2.983	0.259
Sum	0.035	0.534	0.498	-0.036	0.482	0.517
S1	-0.102	-0.046	0.056	0.101	0.206	0.104
S2	0.048	0.188	0.140	-0.048	0.056	0.103
S3	0.060	0.213	0.153	-0.059	0.007	0.066
S4	-0.057	0.005	0.062	0.057	0.202	0.145
Sum	-0.051	0.359	0.411	0.052	0.471	0.419
C12	-0.190	-0.094	0.096	0.189	0.134	-0.055
C96	0.157	0.109	-0.049	-0.156	-0.063	0.093
C197	-0.154	-0.073	0.081	0.154	0.102	-0.051
Sum	-0.186	-0.058	0.128	0.187	0.173	-0.013
Cluster	-0.202	0.835	1.037	0.202	1.125	0.923
O_{C4}	0.182	0.143	-0.039	-0.182	-0.121	0.061
C_3	0.010	0.008	-0.002	-0.011	-0.006	0.004
C_2	-0.005	-0.004	0.001	0.005	0.004	-0.001
HMBPP	0.202	0.159	-0.043	-0.202	-0.132	0.070
Cluster + HMBPP	-0.001	0.993	0.994	0.001	0.993	0.993

	$RO^{-}P^{H}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**ΔNSP**	**OX**	**RED**	**ΔNSP**
Fe1	3.355	3.434	0.079	-3.356	-3.211	0.145
Fe2	-3.285	-3.178	0.107	3.282	3.353	0.071
Fe3	-3.279	-3.071	0.208	3.278	3.341	0.063
Fe4	3.250	3.340	0.090	-3.246	-2.991	0.255
Sum	0.041	0.525	0.484	-0.042	0.493	0.535
S1	-0.097	-0.014	0.083	0.098	0.227	0.129
S2	0.053	0.197	0.144	-0.050	0.036	0.086
S3	0.064	0.196	0.132	-0.063	0.001	0.064
S4	-0.062	-0.013	0.048	0.060	0.182	0.122
Sum	-0.042	0.365	0.407	0.045	0.446	0.401
C12	-0.192	-0.093	0.099	0.191	0.132	-0.059
C96	0.165	0.113	-0.052	-0.165	-0.064	0.101
C197	-0.159	-0.073	0.086	0.158	0.107	-0.052
Sum	-0.186	-0.053	0.133	0.185	0.175	-0.009
Cluster	-0.187	0.838	1.025	0.188	1.113	0.926
O_{C4}	0.168	0.135	-0.033	-0.169	-0.109	0.060
C_3	0.010	0.008	-0.002	-0.010	-0.005	0.005
C_2	-0.004	-0.004	0.001	0.004	0.003	-0.002
HMBPP	0.187	0.151	-0.036	-0.188	-0.117	0.071
Cluster + HMBPP	0.000	0.988	0.988	0.000	0.996	0.996

	$RO^{H}P^{-}E^{-}$					
	αββα			βααβ		
	OX	**RED**	**ΔNSP**	**OX**	**RED**	**ΔNSP**
Fe1	3.267	3.325	0.058	-3.270	-3.027	0.243
Fe2	-3.180	-3.039	0.141	3.181	3.286	0.105
Fe3	-3.202	-3.026	0.176	3.207	3.321	0.114
Fe4	3.207	3.303	0.097	-3.211	-3.081	0.131
Sum	0.092	0.563	0.472	-0.092	0.500	0.592
S1	-0.031	0.011	0.042	0.029	0.201	0.172
S2	0.082	0.221	0.139	-0.082	-0.015	0.067
S3	0.089	0.237	0.148	-0.088	-0.028	0.060
S4	-0.046	0.004	0.050	0.047	0.146	0.099
Sum	0.094	0.473	0.379	-0.094	0.304	0.398
C12	-0.221	-0.111	0.110	0.221	0.159	-0.063
C96	0.191	0.129	-0.062	-0.194	-0.084	0.110
C197	-0.186	-0.081	0.106	0.189	0.131	-0.058
Sum	-0.216	-0.063	0.153	0.216	0.206	-0.010
Cluster	-0.030	0.974	1.004	0.030	1.010	0.980
O_{C4}	0.023	0.015	-0.009	-0.023	-0.014	0.009
C_3	0.003	0.002	-0.001	-0.003	-0.001	0.001
C_2	0.000	0.000	-0.001	0.000	0.002	0.002
HMBPP	0.029	0.018	-0.011	-0.028	-0.013	0.016
Cluster + HMBPP	-0.001	0.992	0.993	0.001	0.997	0.996

	$RO^{H}P^{-}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**ΔNSP**	**OX**	**RED**	**ΔNSP**
Fe1	3.205	3.285	0.080	-3.206	-2.964	0.241
Fe2	-3.175	-3.026	0.149	3.174	3.280	0.106
Fe3	-3.197	-3.004	0.193	3.195	3.316	0.121
Fe4	3.222	3.289	0.067	-3.222	-3.095	0.127
Sum	0.055	0.544	0.489	-0.059	0.537	0.596
S1	-0.013	0.010	0.022	0.014	0.189	0.175
S2	0.086	0.226	0.140	-0.085	-0.023	0.062
S3	0.101	0.250	0.149	-0.101	-0.039	0.062
S4	-0.037	0.021	0.058	0.038	0.138	0.100
Sum	0.137	0.507	0.370	-0.133	0.267	0.400
C12	-0.233	-0.116	0.117	0.233	0.165	-0.069
C96	0.207	0.141	-0.066	-0.207	-0.091	0.116
C197	-0.185	-0.095	0.090	0.185	0.130	-0.055
Sum	-0.211	-0.070	0.141	0.212	0.203	-0.009
Cluster	-0.019	0.981	1.001	0.019	1.006	0.987
O_{C4}	0.013	0.008	-0.004	-0.013	-0.006	0.006
C_3	0.002	0.001	-0.002	-0.002	0.000	0.002
C_2	0.000	0.001	0.001	0.000	0.001	0.002
HMBPP	0.019	0.013	-0.006	-0.019	-0.008	0.012
Cluster + HMBPP	-0.001	0.994	0.995	0.000	0.998	0.998

	$RO^{H}P^{H}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**ΔNSP**	**OX**	**RED**	**ΔNSP**
Fe1	3.208	3.262	0.054	-3.207	-2.963	0.244
Fe2	-3.181	-3.069	0.111	3.181	3.286	0.106
Fe3	-3.193	-2.970	0.223	3.193	3.317	0.124
Fe4	3.223	3.318	0.095	-3.223	-3.099	0.124
Sum	0.056	0.540	0.483	-0.056	0.541	0.597
S1	-0.015	0.032	0.047	0.015	0.188	0.173
S2	0.090	0.219	0.129	-0.090	-0.023	0.067
S3	0.102	0.243	0.141	-0.102	-0.040	0.062
S4	-0.040	0.011	0.052	0.040	0.135	0.094
Sum	0.137	0.504	0.368	-0.136	0.260	0.397
C12	-0.235	-0.118	0.117	0.235	0.166	-0.069
C96	0.213	0.141	-0.072	-0.212	-0.095	0.117
C197	-0.188	-0.088	0.100	0.188	0.132	-0.056
Sum	-0.210	-0.065	0.146	0.210	0.203	-0.008
Cluster	-0.017	0.979	0.996	0.018	1.004	0.987
O_{C4}	0.012	0.008	-0.003	-0.012	-0.006	0.006
C_3	0.003	0.001	-0.002	-0.003	-0.001	0.002
C_2	0.001	0.001	0.000	-0.001	0.002	0.003
HMBPP	0.017	0.012	-0.006	-0.017	-0.004	0.013
Cluster + HMBPP	0.000	0.991	0.991	0.001	1.000	0.999

Table S3. Electrostatic potential (ESP) charge distributions computed for the lowest–energy, 1e^- reduced RO(H)–bound valence isomers not included in Table 4 in the text.

	$RO^{-}P^{-}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**Δq**	**OX**	**RED**	**Δq**
Fe1	0.584	0.628	0.044	0.584	0.614	0.030
Fe2	0.532	0.590	0.058	0.532	0.612	0.080
Fe3	0.632	0.656	0.024	0.633	0.717	0.084
Fe4	0.505	0.556	0.051	0.504	0.535	0.031
Sum	2.253	2.430	0.177	2.253	2.478	0.225
S1	-0.554	-0.692	-0.138	-0.554	-0.720	-0.166
S2	-0.301	-0.383	-0.082	-0.300	-0.395	-0.095
S3	-0.452	-0.601	-0.149	-0.451	-0.594	-0.142
S4	-0.708	-0.903	-0.195	-0.709	-0.933	-0.224
Sum	-2.015	-2.578	-0.563	-2.014	-2.641	-0.627
C12	-0.351	-0.490	-0.139	-0.351	-0.462	-0.111
C96	-0.424	-0.549	-0.125	-0.423	-0.566	-0.142
C197	-0.470	-0.597	-0.128	-0.469	-0.586	-0.116
Sum	-1.245	-1.636	-0.392	-1.244	-1.613	-0.369
Total cluster	-1.006	-1.784	-0.778	-1.006	-1.776	-0.771
O_{C4}	-0.509	-0.561	-0.052	-0.509	-0.566	-0.057
C3	0.060	0.067	0.007	0.059	0.070	0.011
C2	-0.228	-0.236	-0.008	-0.228	-0.226	0.002
Total HMBPP	-1.110	-1.203	-0.093	-1.110	-1.200	-0.090
Cluster + HMBPP	-2.116	-2.988	-0.872	-2.116	-2.976	-0.860

	$RO^{-}P^{H}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**Δq**	**OX**	**RED**	**Δq**
Fe1	0.549	0.574	0.025	0.551	0.573	0.023
Fe2	0.543	0.612	0.069	0.541	0.618	0.077
Fe3	0.610	0.632	0.022	0.607	0.678	0.071
Fe4	0.499	0.524	0.025	0.497	0.522	0.025
Sum	2.201	2.342	0.141	2.196	2.392	0.196
S1	-0.562	-0.678	-0.116	-0.562	-0.730	-0.168
S2	-0.290	-0.360	-0.070	-0.289	-0.364	-0.075
S3	-0.427	-0.538	-0.111	-0.426	-0.554	-0.128
S4	-0.689	-0.859	-0.170	-0.687	-0.896	-0.209
Sum	-1.968	-2.435	-0.467	-1.964	-2.544	-0.580
C12	-0.357	-0.484	-0.127	-0.357	-0.470	-0.113
C96	-0.404	-0.592	-0.188	-0.404	-0.561	-0.157
C197	-0.445	-0.586	-0.141	-0.442	-0.549	-0.107
Sum	-1.206	-1.662	-0.455	-1.203	-1.580	-0.377
Total cluster	-0.974	-1.755	-0.781	-0.970	-1.732	-0.762
O_{C4}	-0.497	-0.540	-0.043	-0.499	-0.556	-0.057
C3	0.084	0.099	0.016	0.085	0.093	0.008
C2	-0.272	-0.273	-0.002	-0.272	-0.274	-0.003
Total HMBPP	-0.800	-0.877	-0.077	-0.800	-0.905	-0.104
Cluster + HMBPP	-1.773	-2.632	-0.859	-1.771	-2.637	-0.866

	$RO^{H}P^{-}E^{-}$					
	αββα			βααβ		
	OX	**RED**	**Δq**	**OX**	**RED**	**Δq**
Fe1	0.538	0.558	0.019	0.520	0.529	0.009
Fe2	0.470	0.531	0.061	0.457	0.550	0.093
Fe3	0.588	0.668	0.080	0.601	0.711	0.111
Fe4	0.458	0.514	0.056	0.444	0.490	0.046
Sum	2.054	2.270	0.216	2.021	2.280	0.259
S1	-0.481	-0.611	-0.129	-0.475	-0.652	-0.177
S2	-0.301	-0.366	-0.065	-0.265	-0.338	-0.074
S3	-0.381	-0.539	-0.159	-0.374	-0.524	-0.149
S4	-0.627	-0.832	-0.205	-0.629	-0.848	-0.219
Sum	-1.790	-2.348	-0.558	-1.743	-2.361	-0.619
C12	-0.257	-0.408	-0.152	-0.255	-0.380	-0.125
C96	-0.346	-0.493	-0.147	-0.353	-0.511	-0.159
C197	-0.420	-0.593	-0.173	-0.430	-0.589	-0.158
Sum	-1.023	-1.494	-0.471	-1.038	-1.480	-0.442
Total cluster	-0.759	-1.571	-0.812	-0.759	-1.561	-0.802
O_{C4}	-0.402	-0.424	-0.021	-0.406	-0.437	-0.031
C3	0.023	0.029	0.005	0.015	0.017	0.002
C2	-0.166	-0.194	-0.028	-0.190	-0.219	-0.030
Total HMBPP	-0.682	-0.728	-0.046	-0.707	-0.866	-0.159
Cluster + HMBPP	-1.441	-2.299	-0.859	-1.466	-2.427	-0.961

	$RO^{H}P^{-}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**Δq**	**OX**	**RED**	**Δq**
Fe1	0.404	0.427	0.024	0.404	0.402	-0.001
Fe2	0.490	0.558	0.068	0.491	0.569	0.078
Fe3	0.599	0.641	0.042	0.599	0.686	0.087
Fe4	0.477	0.527	0.050	0.477	0.519	0.042
Sum	1.969	2.153	0.184	1.970	2.176	0.206
S1	-0.440	-0.586	-0.146	-0.440	-0.621	-0.181
S2	-0.302	-0.375	-0.073	-0.302	-0.369	-0.067
S3	-0.412	-0.550	-0.138	-0.412	-0.546	-0.135
S4	-0.600	-0.788	-0.188	-0.600	-0.804	-0.204
Sum	-1.753	-2.298	-0.545	-1.754	-2.340	-0.586
C12	-0.267	-0.414	-0.147	-0.268	-0.391	-0.124
C96	-0.332	-0.466	-0.133	-0.332	-0.486	-0.153
C197	-0.393	-0.552	-0.159	-0.393	-0.529	-0.136
Sum	-0.993	-1.432	-0.439	-0.993	-1.406	-0.413
Total cluster	-0.777	-1.577	-0.801	-0.777	-1.571	-0.794
O_{C4}	-0.119	-0.122	-0.003	-0.119	-0.133	-0.014
C3	-0.036	-0.033	0.002	-0.035	-0.043	-0.008
C2	-0.142	-0.162	-0.020	-0.142	-0.151	-0.009
Total HMBPP	-0.430	-0.488	-0.058	-0.430	-0.486	-0.055
Cluster + HMBPP	-1.207	-2.065	-0.858	-1.207	-2.056	-0.849

	$RO^{H}P^{H}E^{H}$					
	αββα			βααβ		
	OX	**RED**	**Δq**	**OX**	**RED**	**Δq**
Fe1	0.395	0.420	0.025	0.394	0.401	0.006
Fe2	0.505	0.569	0.064	0.505	0.587	0.082
Fe3	0.582	0.633	0.051	0.582	0.661	0.079
Fe4	0.468	0.520	0.052	0.468	0.508	0.039
Sum	1.949	2.142	0.193	1.949	2.157	0.207
S1	-0.452	-0.605	-0.153	-0.452	-0.639	-0.187
S2	-0.299	-0.372	-0.072	-0.299	-0.368	-0.069
S3	-0.395	-0.541	-0.146	-0.394	-0.530	-0.136
S4	-0.578	-0.766	-0.188	-0.579	-0.782	-0.203
Sum	-1.724	-2.284	-0.560	-1.725	-2.319	-0.594
C12	-0.275	-0.422	-0.147	-0.275	-0.401	-0.126
C96	-0.318	-0.454	-0.137	-0.317	-0.469	-0.152
C197	-0.370	-0.527	-0.158	-0.370	-0.497	-0.127
Sum	-0.962	-1.404	-0.441	-0.963	-1.367	-0.405
Total cluster	-0.737	-1.546	-0.808	-0.738	-1.529	-0.792
O_{C4}	-0.159	-0.154	0.006	-0.159	-0.173	-0.014
C3	0.000	0.002	0.001	0.001	-0.007	-0.007
C2	-0.187	-0.207	-0.021	-0.187	-0.196	-0.009
Total HMBPP	-0.121	-0.165	-0.043	-0.121	-0.180	-0.059
Cluster + HMBPP	-0.859	-1.710	-0.852	-0.859	-1.710	-0.850

Table S4. Relative energies (kcal mol^{-1}) of all valence isomers considered for 1e^- reduced RO(H)–bound states.

	Relative energies	
	DFT/COSMO	**DFT/SCRF**
$RO^-P^-E^H$ (RO^-)		
βαβα	29.6	15.4
βααβ	30.2	13.7
αββα	29.8	13.0
ααββ	29.5	14.9
$RO^-P^HE^H$ (RO^-)		
βαβα	19.2	14.1
βααβ	16.9	10.3
αββα	16.6	16.7
ααββ	19.6	12.9
$RO^HP^-E^-$ (ROH)		
βαβα	17.6	8.4
βααβ	17.6	5.1
αββα	20.2	4.1
ααββ	29.9	11.6
$RO^HP^HE^-$ (ROH)		
βαβα	6.7	5.9
βααβ	5.8	**0.0**
αββα	16.7	9.5
ααββ	16.3	10.1
$RO^HP^-E^H$ (ROH)		
βαβα	6.7	2.1
βααβ	5.3	0.3
αββα	7.3	2.0
ααββ	10.2	4.2
$RO^HP^HE^H$ (ROH)		
βαβα	0.9	5.9
βααβ	**0.0**	4.5
αββα	2.2	5.8
ααββ	4.6	9.0

Table S5. Geometric parameters compared between ROH– and η^2–bound geometries in the 1e^- reduced $RO^HP^HE^H$ state. Bond lengths are shown in Å.

Binding mode	ROH		η^2–ring		η^2–trans	
Valence isomer	αααββ	βααβ	αααββ	βααβ	αααββ	βααβ
Cluster bond lengths:						
Fe1 – S1	2.292	2.251	2.315	2.295	2.305	2.289
Fe1 – S2	2.285	2.268	2.281	2.280	2.281	2.294
Fe1 – S3	2.227	2.325	2.230	2.372	2.229	2.365
Fe2 – S1	2.332	2.343	2.343	2.323	2.346	2.326
Fe2 – S2	2.294	2.215	2.303	2.197	2.305	2.196
Fe2 – S4	2.274	2.391	2.269	2.368	2.275	2.364
Fe3 – S1	2.251	2.333	2.259	2.314	2.256	2.314
Fe3 – S3	2.322	2.255	2.329	2.266	2.321	2.262
Fe3 – S4	2.357	2.382	2.359	2.367	2.361	2.359
Fe4 – S2	2.292	2.326	2.278	2.311	2.282	2.315
Fe4 – S3	2.323	2.310	2.334	2.308	2.339	2.303
Fe4 – S4	2.351	2.296	2.336	2.249	2.336	2.249
Fe2 – S_{C13}	2.332	2.311	2.319	2.288	2.312	2.285
Fe3 – S_{C197}	2.289	2.324	2.296	2.357	2.284	2.339
Fe4 – S_{C96}	2.306	2.353	2.292	2.307	2.291	2.309
HMBPP bond lengths:						
Fe1 – O_{C4}	2.376	2.282	4.531	4.283	3.746	3.563
Fe1 – C_3	3.318	3.241	2.526	2.139	2.672	2.136
Fe1 – C_2	3.482	3.431	2.468	2.116	2.538	2.098
H-bond lengths:						
O_{C4} – O_{T167}	3.173	3.161	4.333	4.345	3.384	3.318
O_{T167} – O_{E126}	2.658	2.653	2.724	2.710	2.667	2.633
O_{E126} – O_{W1}	3.773	3.740	3.799	3.750	3.731	3.475
O_{W1} – O_{PPi}	2.842	2.841	2.994	3.005	2.963	3.012
O_{C4} – O_{E126}	4.155	4.155	3.590	3.644	3.170	3.134
O_{C4} – O_{PPi}	4.850	4.861	2.783	2.787	4.502	4.534
HMBPP angle						
C_2–C_3–C_4–O_{C4}	–98.8	–99.3	101.2	94.7	–150.6	–155.8

Table S6. NSPs computed for the lowest–energy, 1e^- reduced η^2–bound states omitted from Table 8 in the text.

	$RO^HP^-E^H$					
	αββα			βααβ		
	Ox (ROH)	Red(η^2–trans)	ΔNSP	Ox (ROH)	Red(η^2–trans)	ΔNSP
FE1	3.205	3.176	-0.030	-3.206	-2.886	0.320
FE2	-3.175	-2.986	0.189	3.174	3.219	0.045
FE3	-3.197	-2.894	0.303	3.195	3.322	0.127
FE4	3.222	3.292	0.070	-3.222	-3.199	0.023
Sum	0.055	0.588	0.533	-0.059	0.456	0.515
S1	-0.013	0.048	0.061	0.014	0.220	0.206
S2	0.086	0.167	0.082	-0.085	-0.040	0.045
S3	0.101	0.215	0.113	-0.101	-0.019	0.082
S4	-0.037	0.010	0.048	0.038	0.053	0.015
Sum	0.137	0.440	0.303	-0.133	0.215	0.349
C12	-0.233	-0.115	0.118	0.233	0.181	-0.053
C96	0.207	0.141	-0.066	-0.207	-0.143	0.064
C197	-0.185	-0.088	0.097	0.185	0.136	-0.049
Sum	-0.211	-0.062	0.149	0.212	0.174	-0.038
Total cluster	-0.019	0.966	0.985	0.019	0.845	0.826
O_{C4}	0.013	0.000	-0.012	-0.013	0.000	0.013
C_3	0.002	0.013	0.011	-0.002	0.057	0.059
C_2	0.000	-0.001	-0.001	0.000	0.108	0.108
Total HMBPP	0.019	0.020	0.001	-0.019	0.155	0.174
Cluster + HMBPP	-0.001	0.986	0.986	0.000	1.000	1.000

	$RO^{H}P^{H}E^{H}$					
	αββα			βααβ		
	Ox (ROH)	Red(η^2–ring)	ΔNSP	Ox (ROH)	Red(η^2–ring)	ΔNSP
FE1	3.208	3.180	-0.027	-3.207	-2.865	0.342
FE2	-3.181	-2.989	0.192	3.181	3.200	0.019
FE3	-3.193	-2.922	0.272	3.193	3.327	0.134
FE4	3.223	3.302	0.079	-3.223	-3.197	0.026
Sum	0.056	0.572	0.516	-0.056	0.466	0.522
S1	-0.015	0.039	0.054	0.015	0.216	0.201
S2	0.090	0.179	0.089	-0.090	-0.048	0.042
S3	0.102	0.219	0.117	-0.102	-0.028	0.074
S4	-0.040	0.017	0.058	0.040	0.047	0.006
Sum	0.137	0.454	0.317	-0.136	0.187	0.324
C12	-0.235	-0.109	0.126	0.235	0.190	-0.045
C96	0.213	0.153	-0.060	-0.212	-0.156	0.056
C197	-0.188	-0.100	0.088	0.188	0.143	-0.045
Sum	-0.210	-0.056	0.154	0.210	0.176	-0.034
Total cluster	-0.017	0.970	0.987	0.018	0.830	0.812
O_{C4}	0.012	0.005	-0.007	-0.012	0.002	0.014
C_3	0.003	0.010	0.007	-0.003	0.063	0.066
C_2	0.001	0.001	0.000	-0.001	0.115	0.116
Total HMBPP	0.017	0.018	0.001	-0.017	0.169	0.186
Cluster + HMBPP	0.000	0.988	0.988	0.001	0.998	0.997

	$RO^{H}P^{H}E^{H}$					
	αββα			βααβ		
	Ox (ROH)	Red(η^2–trans)	ΔNSP	Ox (ROH)	Red(η^2–trans)	ΔNSP
FE1	3.208	2.952	-0.255	-3.207	-2.882	0.325
FE2	-3.181	-2.364	0.817	3.181	3.222	0.041
FE3	-3.193	-2.928	0.266	3.193	3.329	0.136
FE4	3.223	3.236	0.014	-3.223	-3.216	0.007
Sum	0.056	0.898	0.841	-0.056	0.453	0.509
S1	-0.015	-0.037	-0.022	0.015	0.215	0.200
S2	0.090	0.159	0.069	-0.090	-0.046	0.044
S3	0.102	0.109	0.007	-0.102	-0.029	0.073
S4	-0.040	0.024	0.064	0.040	0.055	0.014
Sum	0.137	0.255	0.118	-0.136	0.194	0.330
C12	-0.235	-0.034	0.202	0.235	0.187	-0.048
C96	0.213	0.136	-0.076	-0.212	-0.152	0.061
C197	-0.188	-0.104	0.084	0.188	0.143	-0.045
Sum	-0.210	-0.001	0.209	0.210	0.177	-0.033
Total cluster	-0.017	1.151	1.169	0.018	0.824	0.807
O_{C4}	0.012	0.000	-0.011	-0.012	0.000	0.012
C_3	0.003	-0.072	-0.076	-0.003	0.068	0.071
C_2	0.001	-0.087	-0.088	-0.001	0.113	0.114
Total HMBPP	0.017	-0.154	-0.171	-0.017	0.174	0.191
Cluster + HMBPP	0.000	0.998	0.998	0.001	0.999	0.998

Table S7. ESP charge distributions computed for the lowest–energy, 1e^- reduced η^2–bound states omitted from Table 9 in the text.

	$RO^HP^-E^H$					
	αββα			βααβ		
	Ox	Red(η^2–trans)	Δq	Ox	Red(η^2–trans)	Δq
FE1	0.404	0.503	0.100	0.404	0.443	0.039
FE2	0.490	0.527	0.037	0.491	0.514	0.023
FE3	0.599	0.626	0.027	0.599	0.664	0.065
FE4	0.477	0.517	0.040	0.477	0.502	0.025
Sum	1.969	2.173	0.204	1.970	2.122	0.152
S1	-0.440	-0.596	-0.156	-0.440	-0.595	-0.155
S2	-0.302	-0.357	-0.055	-0.302	-0.299	0.003
S3	-0.412	-0.615	-0.203	-0.412	-0.580	-0.168
S4	-0.600	-0.734	-0.134	-0.600	-0.691	-0.091
Sum	-1.753	-2.301	-0.548	-1.754	-2.165	-0.411
C12	-0.267	-0.413	-0.146	-0.268	-0.373	-0.105
C96	-0.332	-0.439	-0.106	-0.332	-0.399	-0.067
C197	-0.393	-0.481	-0.088	-0.393	-0.445	-0.053
Sum	-0.993	-1.333	-0.340	-0.993	-1.217	-0.225
Total cluster	-0.777	-1.461	-0.685	-0.777	-1.260	-0.484
O_{C4}	-0.119	-0.472	-0.353	-0.119	-0.491	-0.372
C_3	-0.036	0.029	0.065	-0.035	0.006	0.042
C_2	-0.142	-0.103	0.039	-0.142	-0.108	0.034
Total HMBPP	-0.430	-0.724	-0.293	-0.430	-0.916	-0.486
Cluster + HMBPP	-1.207	-2.185	-0.978	-1.207	-2.177	-0.970

	$RO^{H}P^{H}E^{H}$					
	αββα			βαβα		
	Ox	Red(η^2–ring)	Δq	Ox	Red(η^2–ring)	Δq
FE1	0.395	0.360	-0.035	0.394	0.292	-0.103
FE2	0.505	0.554	0.049	0.505	0.538	0.033
FE3	0.582	0.620	0.038	0.582	0.661	0.079
FE4	0.468	0.539	0.071	0.468	0.509	0.041
Sum	1.949	2.073	0.124	1.949	1.999	0.050
S1	-0.452	-0.572	-0.120	-0.452	-0.578	-0.126
S2	-0.299	-0.322	-0.023	-0.299	-0.264	0.035
S3	-0.395	-0.601	-0.206	-0.394	-0.565	-0.171
S4	-0.578	-0.730	-0.152	-0.579	-0.673	-0.094
Sum	-1.724	-2.224	-0.500	-1.725	-2.080	-0.355
C12	-0.275	-0.426	-0.151	-0.275	-0.371	-0.096
C96	-0.318	-0.425	-0.107	-0.317	-0.386	-0.069
C197	-0.370	-0.475	-0.106	-0.370	-0.446	-0.076
Sum	-0.962	-1.326	-0.364	-0.963	-1.204	-0.241
Total cluster	-0.737	-1.477	-0.740	-0.738	-1.284	-0.547
O_{C4}	-0.159	-0.328	-0.169	-0.159	-0.349	-0.189
C_3	0.000	0.052	0.051	0.001	0.021	0.020
C_2	-0.187	-0.125	0.061	-0.187	-0.113	0.074
Total HMBPP	-0.121	-0.286	-0.165	-0.121	-0.435	-0.313
Cluster + HMBPP	-0.859	-1.764	-0.905	-0.859	-1.719	-0.860

	$RO^HP^HE^H$					
	αββα			βααβ		
	Ox	Red(η^2–trans)	Δq	Ox	Red(η^2–trans)	Δq
FE1	0.395	0.430	0.035	0.394	0.410	0.016
FE2	0.505	0.500	-0.004	0.505	0.511	0.006
FE3	0.582	0.612	0.030	0.582	0.626	0.044
FE4	0.468	0.513	0.045	0.468	0.491	0.023
Sum	1.949	2.055	0.105	1.949	2.038	0.089
S1	-0.452	-0.548	-0.096	-0.452	-0.586	-0.134
S2	-0.299	-0.326	-0.026	-0.299	-0.295	0.005
S3	-0.395	-0.576	-0.182	-0.394	-0.550	-0.156
S4	-0.578	-0.661	-0.082	-0.579	-0.651	-0.071
Sum	-1.724	-2.111	-0.386	-1.725	-2.082	-0.357
C12	-0.275	-0.409	-0.134	-0.275	-0.372	-0.097
C96	-0.318	-0.411	-0.093	-0.317	-0.377	-0.060
C197	-0.370	-0.466	-0.096	-0.370	-0.421	-0.051
Sum	-0.962	-1.285	-0.323	-0.963	-1.171	-0.208
Total cluster	-0.737	-1.341	-0.604	-0.738	-1.215	-0.477
O_{C4}	-0.159	-0.488	-0.329	-0.159	-0.487	-0.328
C_3	0.000	0.069	0.069	0.001	0.053	0.052
C_2	-0.187	-0.223	-0.036	-0.187	-0.203	-0.016
Total HMBPP	-0.121	-0.506	-0.385	-0.121	-0.603	-0.482
Cluster + HMBPP	-0.859	-1.848	-0.989	-0.859	-1.818	-0.959

Table S8. Relative energies (kcal mol^{-1}) of tight versus loose η^2–complexes in the 1e^- reduced state.

	DFT/COSMO $E_{"Loose"} - E_{"Tight"}$	DFT/SCRF $E_{"Loose"} - E_{"Tight"}$
$RO^HP^-E^H$ (η^2–ring)	7.8	8.8
$RO^HP^HE^H$ (η^2–ring)	13.5	11.2
$RO^HP^-E^H$ (η^2–trans)	9.0	7.0
$RO^HP^HE^H$ (η^2–trans)	10.2	8.8

Table S9. Relative energies (kcal mol^{-1}) of all valence isomers considered for 1e^- reduced η^2–bound states.

	Relative energies	
	DFT/COSMO	**DFT/SCRF**
$RO^-P^-E^H$ (RO^-)		
βαβα	39.8	21.1
βααβ	40.5	19.4
αββα	40.1	18.8
αααββ	39.8	20.6
$RO^-P^HE^H$ (RO^-)		
βαβα	29.5	19.8
βααβ	27.1	16.0
αββα	26.9	22.5
αααββ	29.9	18.6
$RO^HP^-E^-$ (ROH)		
βαβα	27.9	14.1
βααβ	27.9	10.8
αββα	30.5	9.8
αααββ	40.2	17.3
$RO^HP^HE^-$ (ROH)		
βαβα	17.0	11.7
βααβ	16.1	5.7
αββα	27.0	15.2
αααββ	26.5	15.8
$RO^HP^-E^H$ (ROH)		
βαβα	17.0	7.8
βααβ	15.6	6.0
αββα	17.6	7.7
αααββ	20.4	9.9
$RO^HP^HE^H$ (ROH)		
βαβα	11.2	11.6
βααβ	10.3	10.3
αββα	12.5	11.5
αααββ	14.9	14.7

	Relative energies	
	DFT/COSMO	**DFT/SCRF**
$RO^HP^-E^H$ (η^2–ring)		
βαβα	11.8	0.7
βααβ	10.9	**0.0**
αββα	19.7	8.8
αααββ	18.7	8.8
$RO^HP^HE^H$ (η^2–ring)		
βαβα	**0.0**	4.9
βααβ	2.4	2.3
αββα	13.5	13.7
αααββ	13.5	13.5
$RO^HP^-E^H$ (η^2–trans)		
βαβα	16.7	7.3
βααβ	17.2	7.2
αββα	26.1	14.6
αααββ	25.7	14.2
$RO^HP^HE^H$ (η^2–trans)		
βαβα	8.8	9.3
βααβ	9.9	10.1
αββα	21.7	21.1
αααββ	19.0	18.1

Table S10. Geometric parameters compared between ROH– and η^2–ring geometries in both the oxidized and 1e^- reduced $RO^HP^HE^H$ states. Bond lengths are shown in Å.

	OXIDIZED				REDUCED	
Binding mode	**ROH**	**ROH**	**η^2–ring**		**η^2–ring**	
Valence isomer	**ααββ**	**βααβ**	**ααββ**	**βααβ**	**ααββ**	**βααβ**
Cluster bond lengths:						
Fe1 – S1	2.292	2.251	2.288	2.196	2.315	2.295
Fe1 – S2	2.285	2.268	2.270	2.271	2.281	2.280
Fe1 – S3	2.227	2.325	2.221	2.295	2.230	2.372
Fe2 – S1	2.332	2.343	2.335	2.312	2.343	2.323
Fe2 – S2	2.294	2.215	2.304	2.195	2.303	2.197
Fe2 – S4	2.274	2.391	2.253	2.353	2.269	2.368
Fe3 – S1	2.251	2.333	2.231	2.300	2.259	2.314
Fe3 – S3	2.322	2.255	2.328	2.263	2.329	2.266
Fe3 – S4	2.357	2.382	2.353	2.352	2.359	2.367
Fe4 – S2	2.292	2.326	2.228	2.313	2.278	2.311
Fe4 – S3	2.323	2.310	2.323	2.332	2.334	2.308
Fe4 – S4	2.351	2.296	2.334	2.228	2.336	2.249
Fe2 – S_{C12}	2.332	2.311	2.260	2.239	2.319	2.288
Fe3 – S_{C197}	2.289	2.324	2.261	2.274	2.296	2.357
Fe4 – S_{C96}	2.306	2.353	2.281	2.277	2.292	2.307
HMBPP bond lengths:						
Fe1 – O_{C4}	2.376	2.282	4.536	4.540	4.531	4.283
Fe1 – C_3	3.318	3.241	2.601	2.638	2.526	2.139
Fe1 – C_2	3.482	3.431	2.529	2.561	2.468	2.116
H-bond lengths:						
O_{C4} – O_{T167}	3.173	3.161	4.324	4.297	4.333	4.345
O_{T167} – O_{E126}	2.658	2.653	2.705	2.712	2.724	2.710
O_{E126} – O_{W1}	3.773	3.740	3.717	3.704	3.799	3.750
O_{W1} – O_{PPi}	2.842	2.841	2.863	2.950	2.994	3.005
O_{C4} – O_{E126}	4.155	4.155	3.604	3.586	3.590	3.644
O_{C4} – O_{PPi}	4.850	4.861	2.727	2.759	2.783	2.787
HMBPP angle						
C_2–C_3–C_4–O_{C4}	–98.8	–99.3	99.4	100.3	101.2	94.7

Table S11. Comparison of NSPs computed for η^2–ring geometries in the oxidized and 1e^- reduced $RO^HP^HE^H$ states.

	$RO^HP^HE^H$					
	αααββ			βααβ		
	Ox (η^2–ring)	Red (η^2–ring)	ΔNSP	Ox (η^2–ring)	Red (η^2–ring)	ΔNSP
FE1	3.167	3.224	0.057	-3.122	-2.865	0.257
FE2	3.215	3.289	0.074	3.104	3.200	0.096
FE3	-3.188	-3.121	0.067	3.182	3.327	0.146
FE4	-3.194	-2.849	0.345	-3.202	-3.197	0.005
Sum	0.000	0.542	0.542	-0.038	0.466	0.504
S1	0.098	0.159	0.061	0.001	0.216	0.215
S2	0.129	0.276	0.147	-0.067	-0.048	0.019
S3	-0.022	0.022	0.044	-0.104	-0.028	0.076
S4	-0.073	-0.008	0.065	0.029	0.047	0.018
Sum	0.132	0.450	0.318	-0.140	0.187	0.328
C12	0.253	0.185	-0.068	0.244	0.190	-0.054
C96	-0.196	-0.086	0.110	-0.226	-0.156	0.069
C197	-0.212	-0.116	0.096	0.186	0.143	-0.043
Sum	-0.155	-0.017	0.137	0.205	0.176	-0.028
Total cluster	-0.022	0.975	0.997	0.026	0.830	0.803
O_{C4}	0.006	0.005	-0.001	-0.006	0.002	0.008
C_3	-0.006	-0.008	-0.002	-0.001	0.115	0.116
C_2	0.029	0.029	0.000	-0.015	0.063	0.078
Total HMBPP	0.025	0.021	-0.004	-0.023	0.169	0.191
Cluster + HMBPP	0.002	0.996	0.993	0.003	0.998	0.995

Table S12. Comparison of ESP charges computed for η^2–ring geometries in the oxidized and $1e^-$ reduced $RO^HP^HE^H$ states.

	$RO^HP^HE^H$					
	αααββ			βααβ		
	Ox (η^2–ring)	Red (η^2–ring)	Δq	Ox (η^2–ring)	Red (η^2–ring)	Δq
FE1	0.382	0.349	-0.034	0.375	0.292	-0.083
FE2	0.479	0.563	0.085	0.473	0.538	0.065
FE3	0.579	0.615	0.036	0.599	0.661	0.062
FE4	0.484	0.514	0.031	0.469	0.509	0.040
Sum	1.923	2.041	0.118	1.916	1.999	0.083
S1	-0.467	-0.583	-0.116	-0.455	-0.578	-0.122
S2	-0.282	-0.319	-0.037	-0.276	-0.264	0.011
S3	-0.449	-0.565	-0.116	-0.447	-0.565	-0.118
S4	-0.547	-0.735	-0.189	-0.543	-0.673	-0.130
Sum	-1.744	-2.202	-0.458	-1.721	-2.080	-0.359
C12	-0.257	-0.404	-0.147	-0.246	-0.371	-0.125
C96	-0.288	-0.469	-0.180	-0.291	-0.386	-0.095
C197	-0.321	-0.445	-0.124	-0.347	-0.446	-0.099
Sum	-0.866	-1.318	-0.452	-0.885	-1.204	-0.319
Total cluster	-0.687	-1.479	-0.792	-0.689	-1.284	-0.595
O_{C4}	-0.341	-0.330	0.011	-0.333	-0.349	-0.016
C_3	-0.069	-0.113	-0.044	-0.077	-0.113	-0.036
C_2	0.002	0.048	0.046	0.000	0.021	0.020
Total HMBPP	-0.141	-0.269	-0.128	-0.206	-0.435	-0.229
Cluster + HMBPP	-0.829	-1.748	-0.920	-0.895	-1.719	-0.824

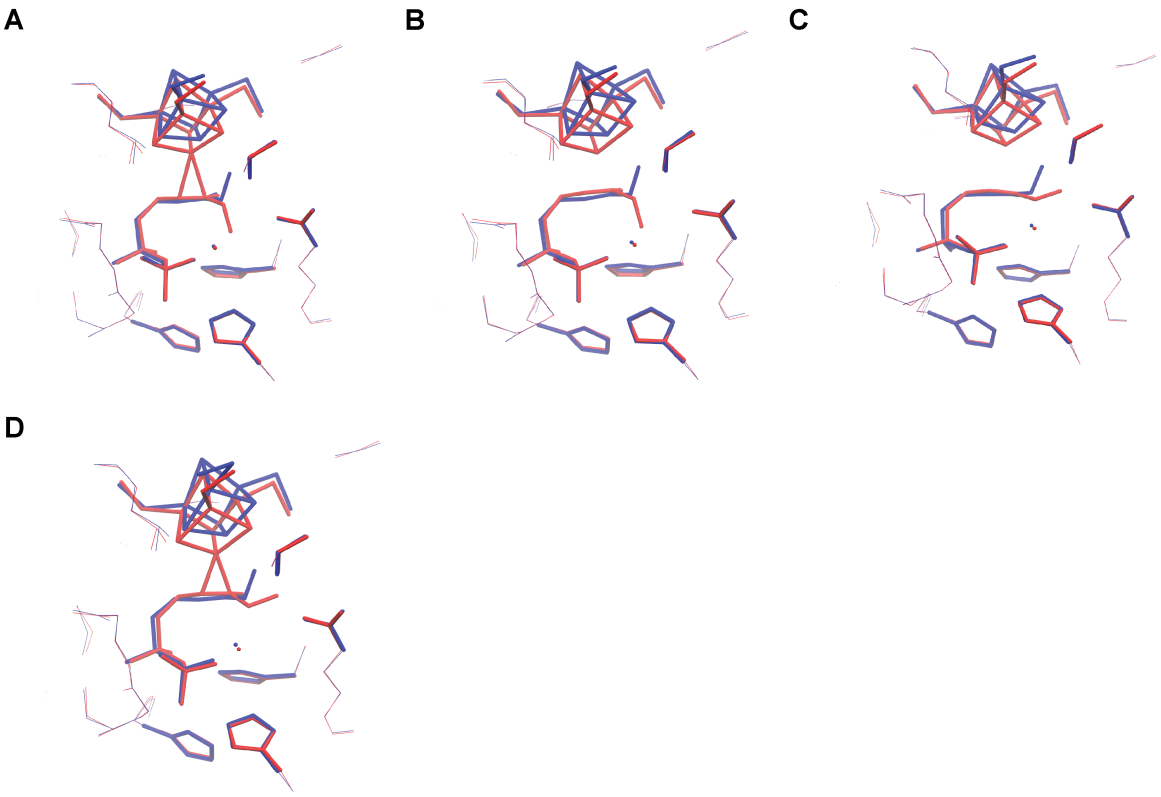

Fig. S1. Superposition of ROH– (blue) and η^2– (red) bound geometries in the 1e^- reduced state. (A) The $RO^HP\text{-}E^H$(ROH) βααβ and $RO^HP\text{-}E^H$(η^2–ring) βααβ states; (B) the $RO^HP\text{-}E^H$(ROH) αββα and $RO^HP\text{-}E^H$(η^2–ring) αββα states; (C) the $RO^HP\text{-}E^H$(ROH) αββα and $RO^HP\text{-}E^H$(η^2–trans) αββα states; (D) the $RO^HP\text{-}E^H$(ROH) βααβ and $RO^HP\text{-}E^H$(η^2–trans) βααβ states. While βαβα and ααββ states are omitted from this figure, their respective properties and geometries are similar to the βααβ and αββα shown above.