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Supporting Information

Substituent Effects in Iron Porphyrin Catalysts for the Hydrogen Evolution Reaction

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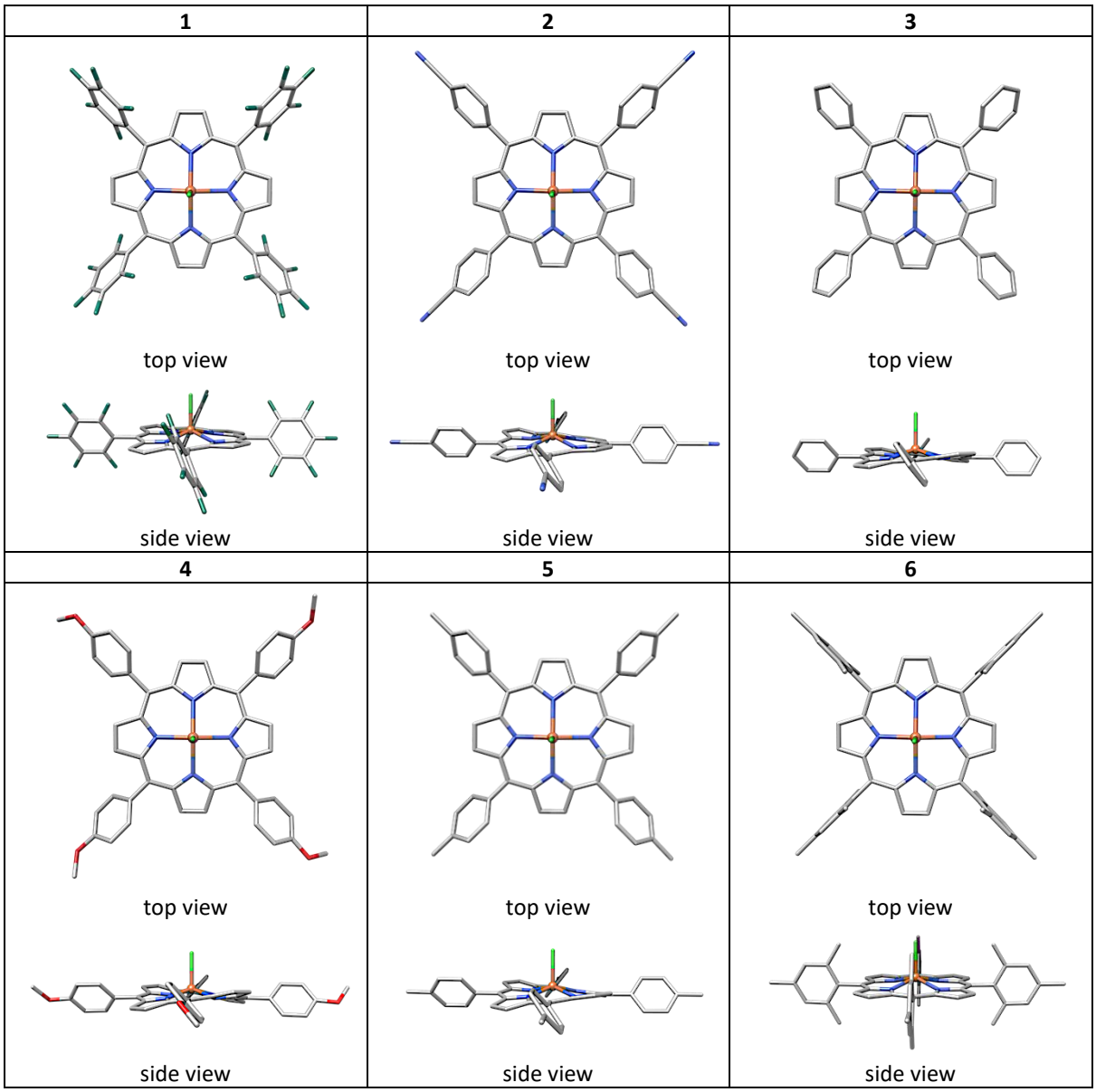


Figure S1: Optimized geometries of all Fe(III)-Cl complexes (1-6). Fe is depicted in orange, N in blue, Cl in light green, F in dark green, O in red, H in white and C in light grey. H atoms in CH groups are omitted for clarity.

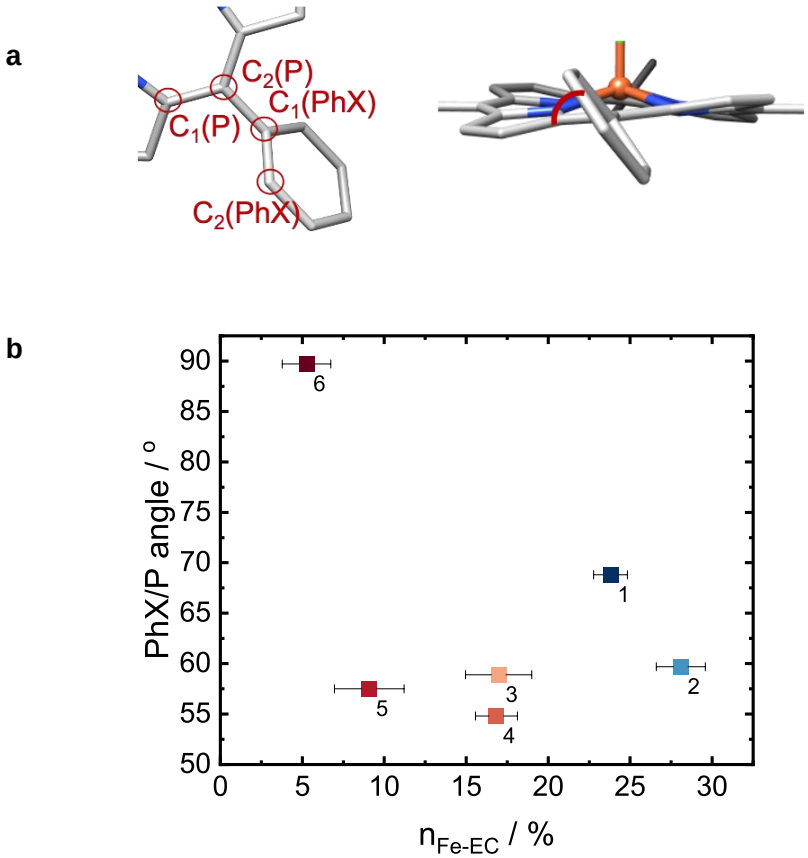


Figure S2: Phenyl ligand to porphyrin (PhX/P) angles a) Scheme of simplified PhX/P angle as the C_1(P)-C_2(P)-C_1(PhX)-C_2(PhX) dihedral, **b)** PhX/P angle plotted vs. electrochemical utilization of Fe.

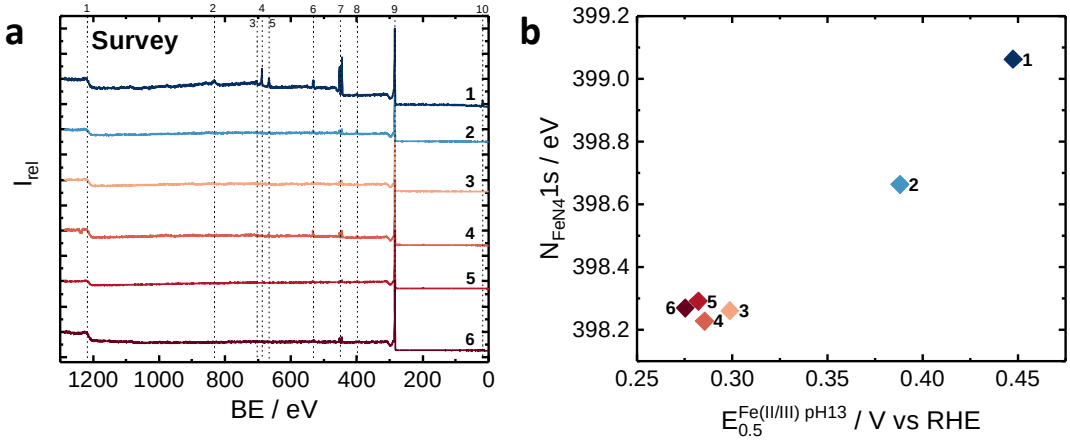


Figure S3: XPS analysis of porphyrins 1-6 impregnated on CB. a) Survey scan with the signals indicated with dashed lines and numbered on top of the graph 1 C-KVV, 2 F-KLL, 3 In3$p_{1/2}$, 4 F1s, 5 In3$p_{3/2}$, 6 O1s, 7 In3d, 8 N1s, 9 C1s, 10 In4d; b) correlation between the binding energy associated with the FeN_4 peak and the redox potential $E_{0.5}$ of Fe(II/III) in 0.1 M KOH. Bold numbers refer to the number of the porphyrin complex as indicated in the main manuscript.

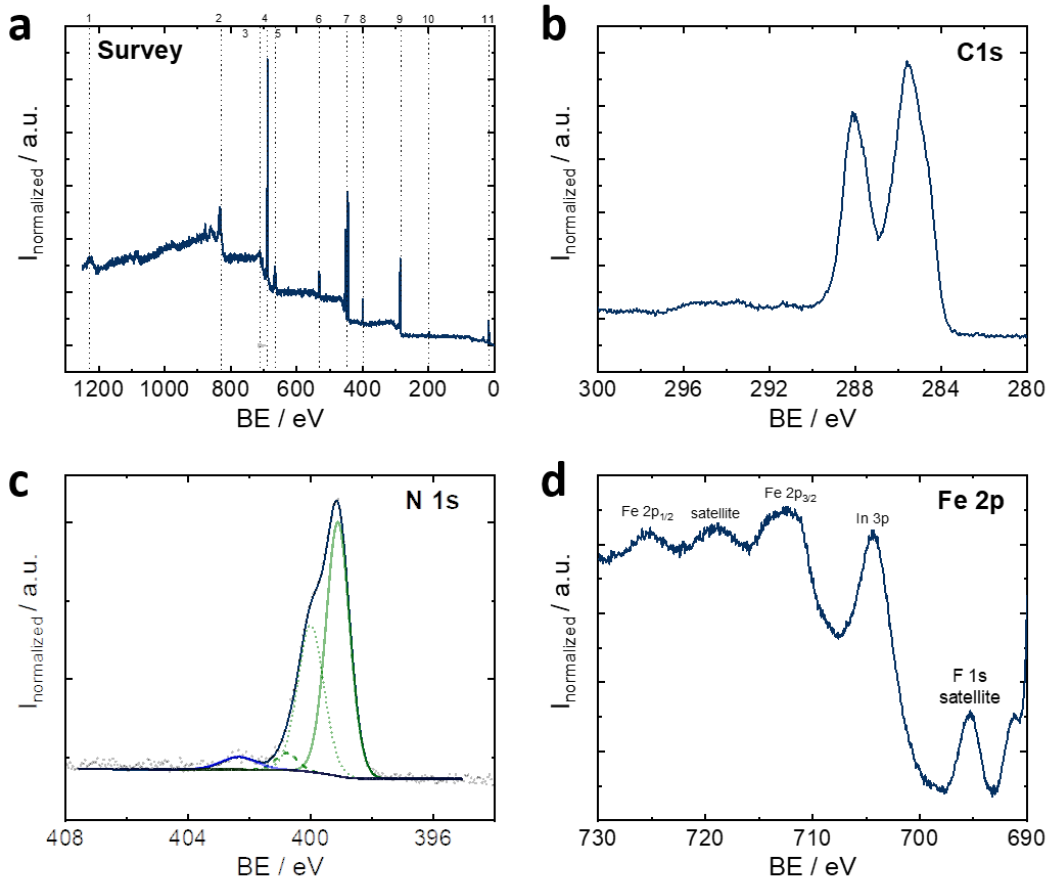


Figure S4: XPS analysis of porphyrin 1 drop casted from a DCM solution onto In foil. a) Survey scan with the signals 1 C-KVV, 2 F-KLL, 3 Fe2p, 4 F1s, 5 In3p3/2, 6 O1s, 7 In3d, 8 N1s, 9 C1s, 10 Cl2p, 11 In4d; b) HR-scan of C 1s region; c) HR-scan of N 1s region, with 4 component fit of the signal; d) HR-scan of Fe 2p region.

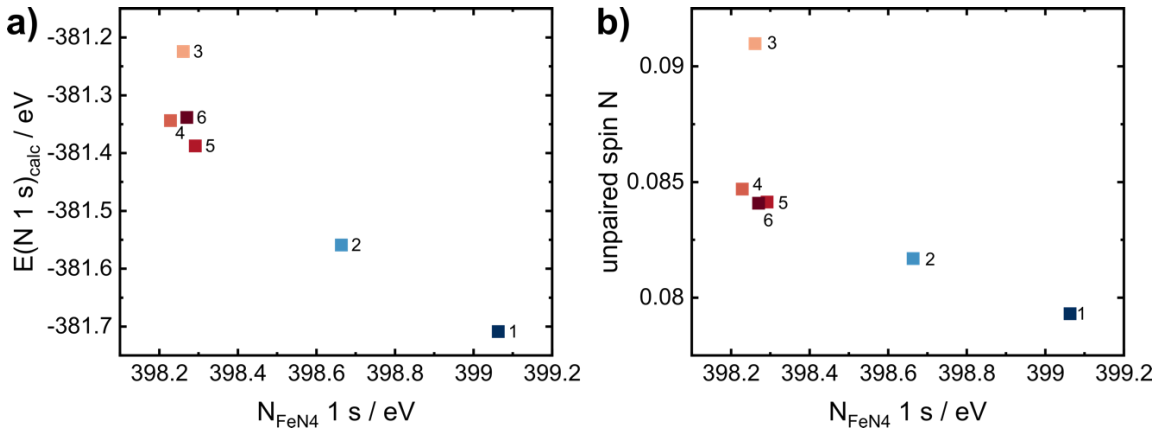


Figure S5: Comparison of N 1s binding energies measured by XPS with **a)** calculated mean N 1s orbital energies of Fe(III)-Cl and **b)** calculated mean Mulliken spin population on N as a measure of unpaired spin in the Fe(III)-Cl complexes.

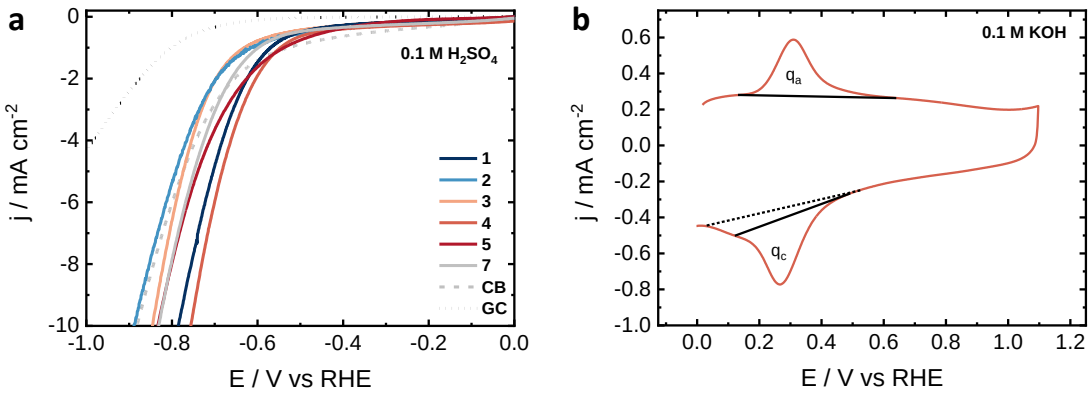


Figure S6: Supporting RDE and CV data a) HER activity of different porphyrins at pH 1, **b)** TPP(OMe)$_4$-FeCl peak integration at pH 13.

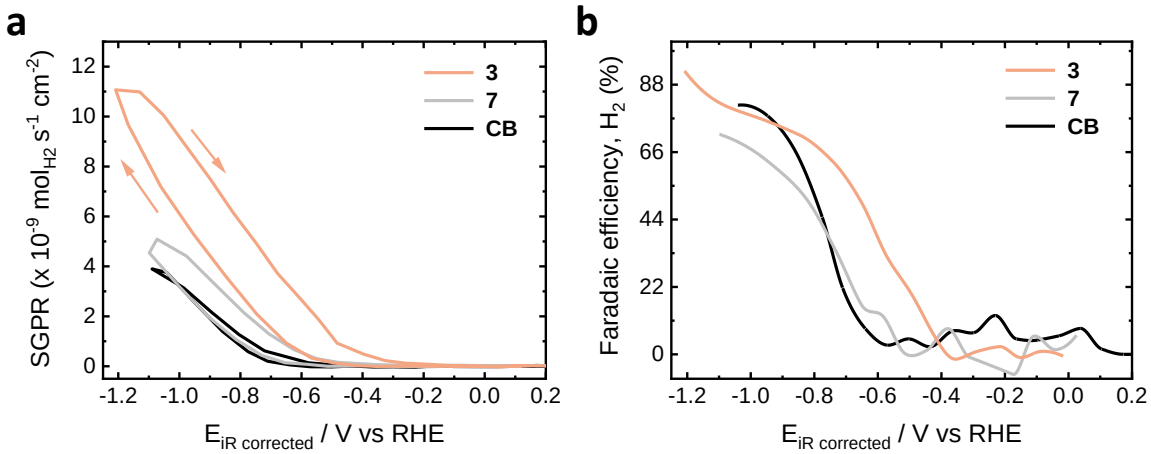


Figure S7: Differential electrochemical mass spectrometry (DEMS) **a**) The specific gas product rate (SGPR) of hydrogen for carbon supported iron porphyrin (**3**) and free base porphyrin (**7**) and the bare carbon black (**CB**) support and **b**) the corresponding transient faradaic efficiency of the investigated samples (calculation of transient faradaic efficiencies include capacitive currents, see section below).

To Figure S7:

For DEMS measurements the working electrode of a purpose build half-cell is coupled to a quadrupole mass spectrometer (ExQ Compact Gas Analyzer, Hiden Analytical) via a capillary inlet that serves as the reducing pressure step. The cell is built in a gas flow-by configuration where gas is passed through the back of the gas diffusion layer (GDL) through an intermediate porous Teflon membrane to avoid gas leakage. To promote the gas flow through the pipeline a syringe pump at 1.5 ml min^{-1} is coupled via a T-piece with an exhaust controlled with a bypass valve. A peristaltic pump is used to maintain the electrolyte flow at 8 ml min^{-1} that is being constantly purged with N_2. The gas analyzer has a 5 s of delay between the applied voltage and the mass current, which was compensated in the data treatment for an accurate product detection.

To obtain a direct correlation between the mass currents and the faradaic current (I_F) the hydrogen evolution reaction on Pt/C (Hispec 3000, Sigma Aldrich) was used as model reaction in 0.25 M H_2SO_4 electrolyte. By a protocol of consequent galvanostatic steps of 60 s the calibration constant is obtained through the linear relation between both values:

$$I_{MS,j} = \frac{K^*}{n_j} N_j I_{F,j}$$

Where $I_{MS,j}$ is the mass current for the species j (here 2 m/Z), $I_{F,j}$ the applied faradaic current, n_j the number of electrons involved in the production of, N_j the collection of the cell and K^* the calibration constant which contains all the settings from the experimental construction and the MS can also be referred as one value K^0.
This value is used for calculating the (transient) faradaic efficiency as follows:

$$FE_{j,gas}(\%) = \frac{I_{MS} * n_j}{I_{total} * K^0} x100$$

The mass current is correlated to the transient current response, as a consequence capacitive currents are included as well, which is lowering the obtained efficiencies.
Because the capillary has a constant intake of gases (of 4.3 ml min^{-1}) the specific gas product rate (SGPR) is calculated as follows:

$$SGPR\ (mol\ s^{-1}cm^{-2}) = \frac{\frac{P_j}{P_{total}} * V_{in}}{V_{mol} * A_{geo}}$$

Where P_j is the partial pressure of the species j and P_{total} the pressure in the vacuum gas chamber, V_{in} the intake volume from the capillary, V_{mol} the molar volume of an ideal gas (22.4 l mol^{-1} at standard pressure) and A_{geo} the geometric area of the catalyst layer.
The electrodes were prepared on GDLs (Freudenberg H23C6) by dropcasting a catalyst ink for a final loading of 0.32 mg cm^{-2} in an area of 0.45 cm^2. The ink formulation and preparation was as follows: for each measurement, 6 mg of a sample was mixed with 393 µL isopropanol, 56 µL water and 44 µL of Nafion 5wt% dispersion. The suspension is first homogenized in the vortex mixer for 1 min, then treated in the ultrasonic bath for 40 min (at room temperature), vortexed for another minute and sonicated for 15 min. The ink deposited was left to dry without heat being applied to the GDL.

To obtain the transient faradaic efficiencies, HER was tested in an electrolyte of 0.1 M KOH, using a glassy carbon counter electrode and a Hg|HgO|1 M NaOH reference electrode. The given potential is corrected for the electrolyte resistance.

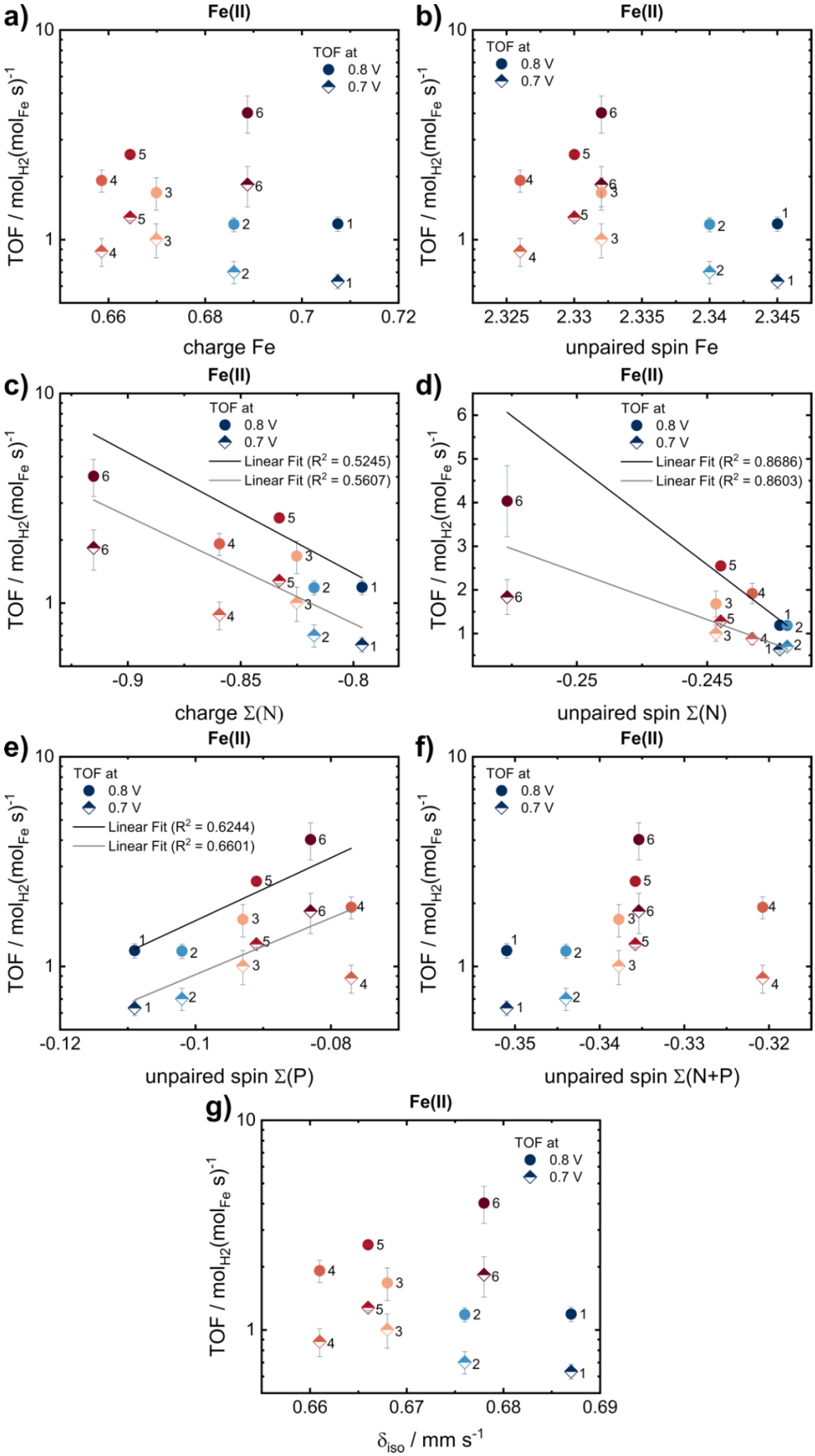


Figure S8: Properties of calculated Fe(II) vs. TOF. Mulliken charge on a) Fe and c) all N atoms, Mulliken spin population (b, d, e, f) as measure of unpaired spin on b) Fe, d) N (sum of all nitrogen atoms), e) P (sum of all porphin plane atoms without nitrogen atoms), f) P+N (sum of all porphin atoms with nitrogen atoms) and g) isomer shift. TOF values were calculated for overpotentials of 0.7 and 0.8 V.

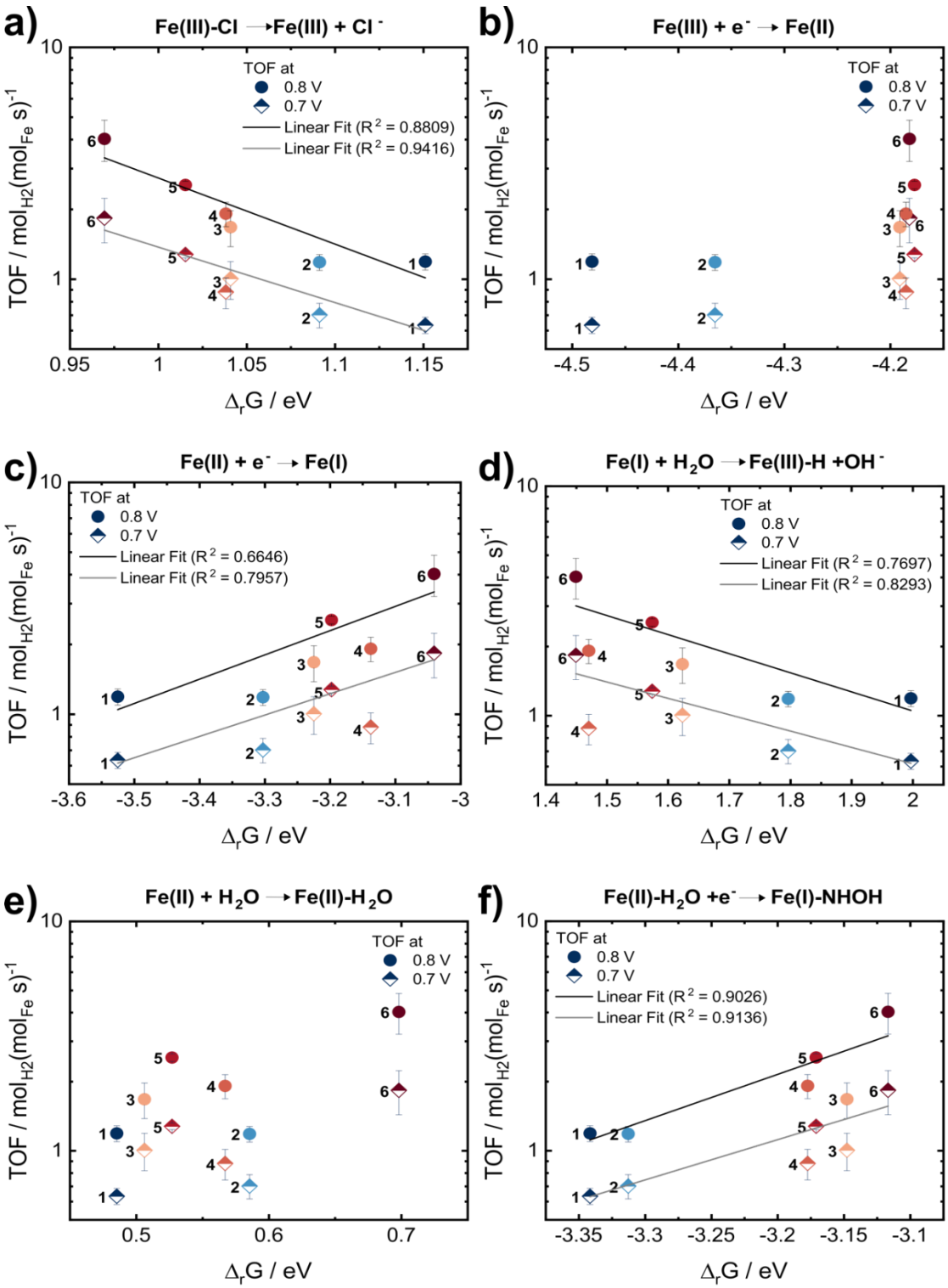
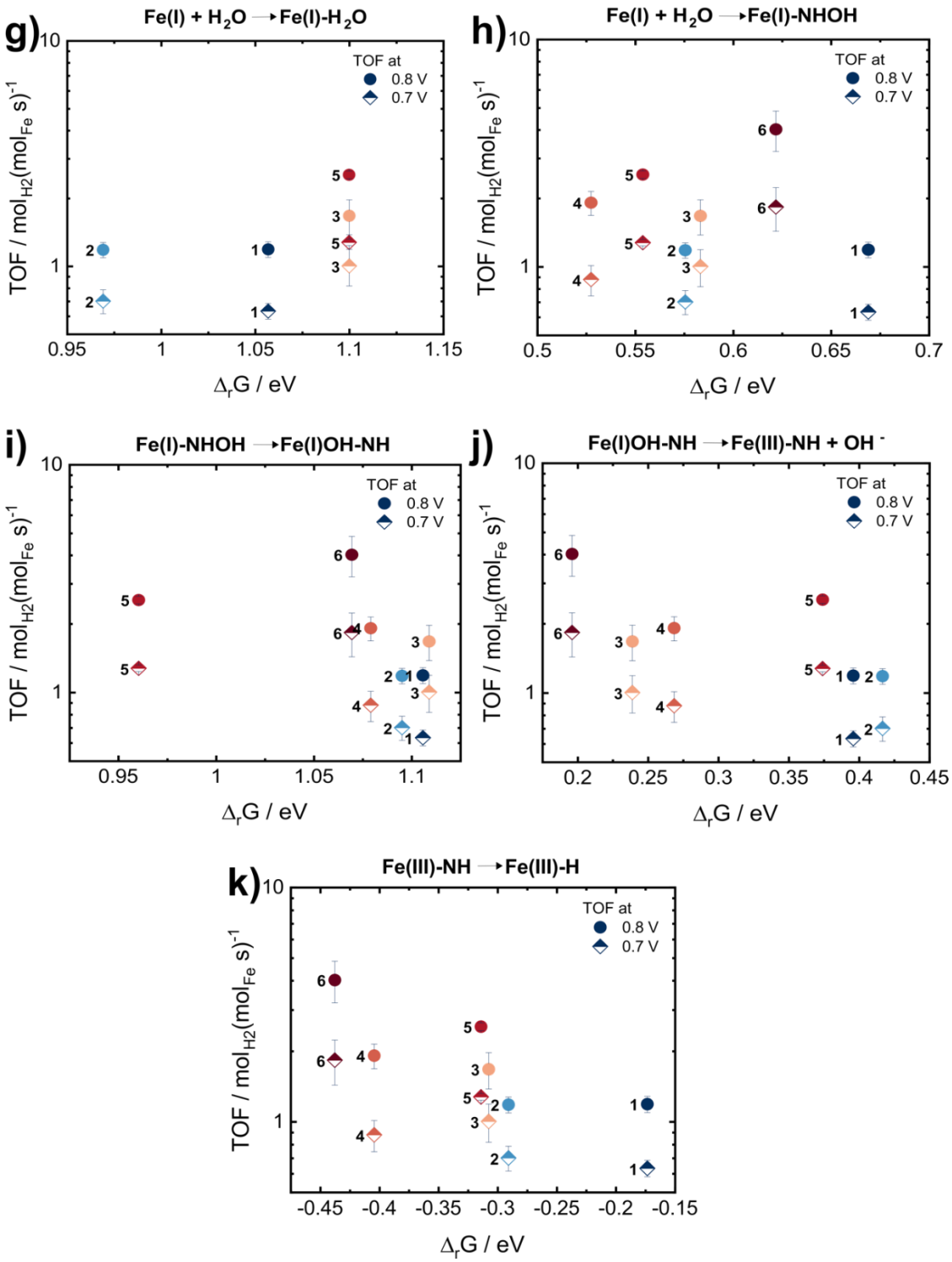


Figure S9: Gibbs free enthalpies of reaction for different reaction steps vs. TOF. Trendlines (linear regressions) were added as grey (η = 0.7 V) and black (η = 0.8 V) lines if R^2 exceeded 0.6.



Continued - Figure S9: Gibbs free enthalpies of reaction for different reaction steps vs. TOF. Trendlines (linear regressions) were added as grey (η = 0.7 V) and black (η = 0.8 V) lines if R^2 exceeded 0.6.

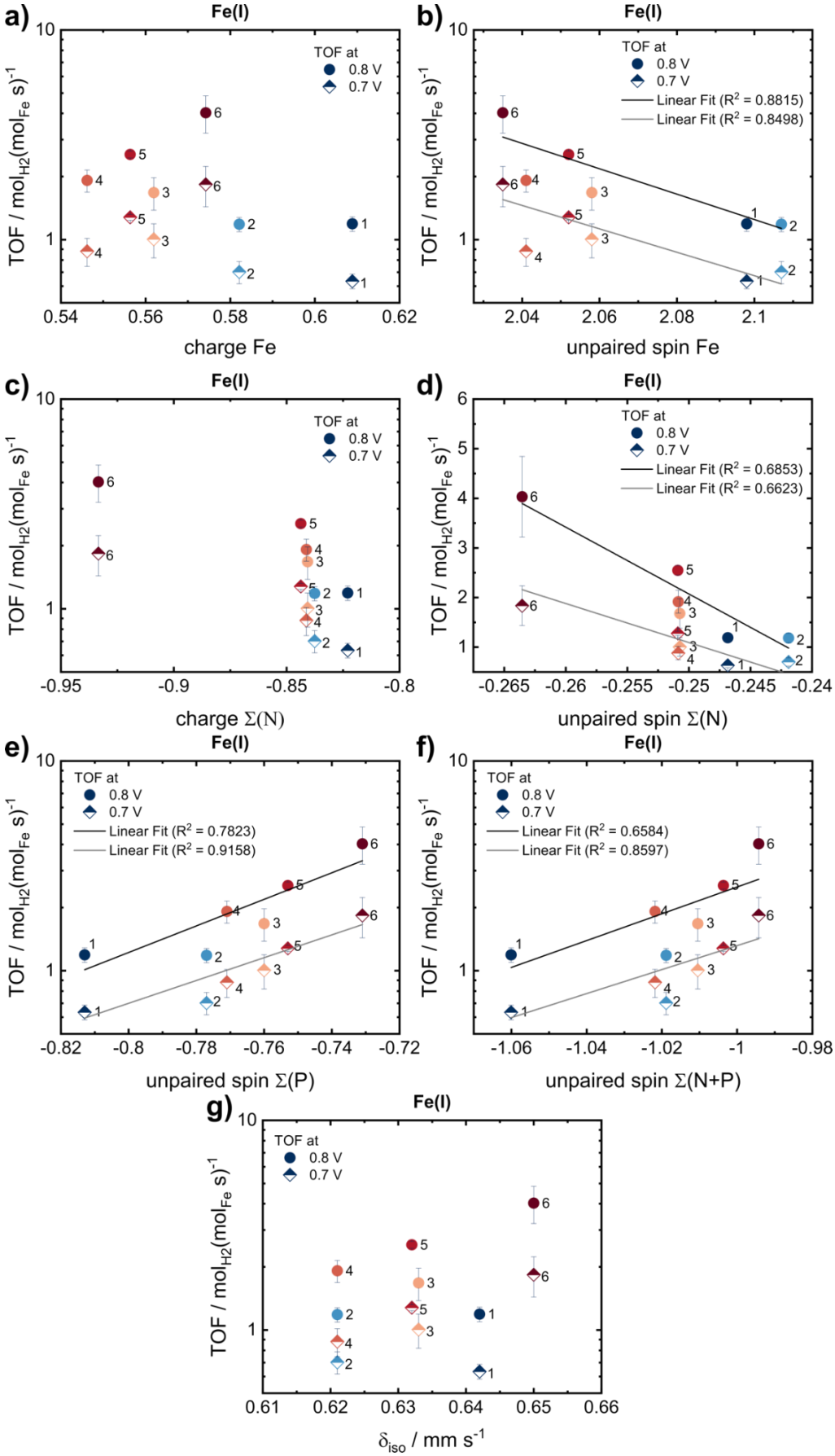


Figure S10: Properties of calculated Fe(I) vs. TOF. Mulliken charge on a) Fe and c) all N atoms, Mulliken spin population (b, d, e, f) as measure of unpaired spin on b) Fe, d) N (sum of all nitrogen atoms), e) P (sum of all porphin plane atoms without nitrogen atoms), f) P+N (sum of all porphin atoms with nitrogen atoms) and g) isomer shift. TOF values were calculated for overpotentials of 0.7 and 0.8 V.

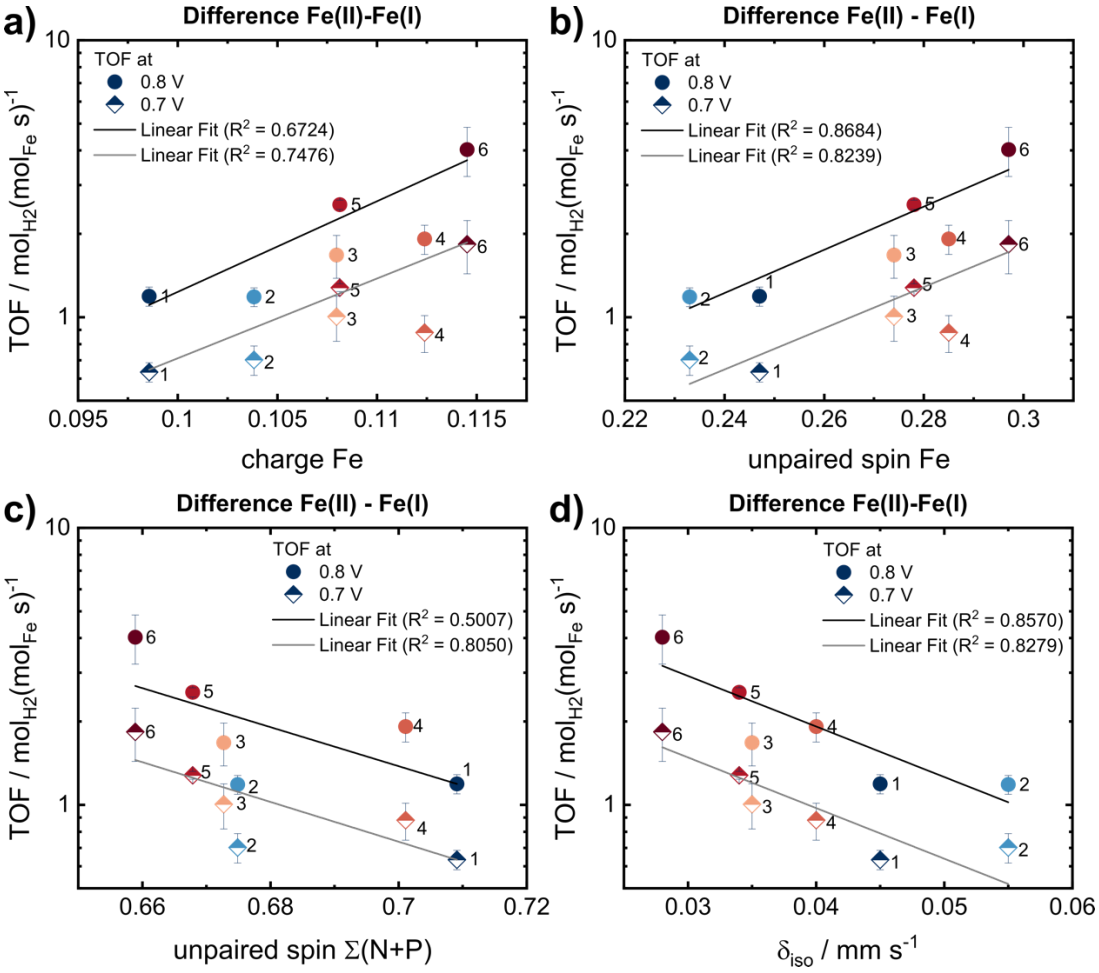


Figure S11: Difference values Fe(II) - Fe(I) for various properties vs. TOF. a) Correlation with charge on Fe. b), c) Correlation with Mulliken spin population as a measure of unpaired spin on Fe (b) and sum of N and all porphin plane atoms (c). d) Correlation with the calculated isomer shift.

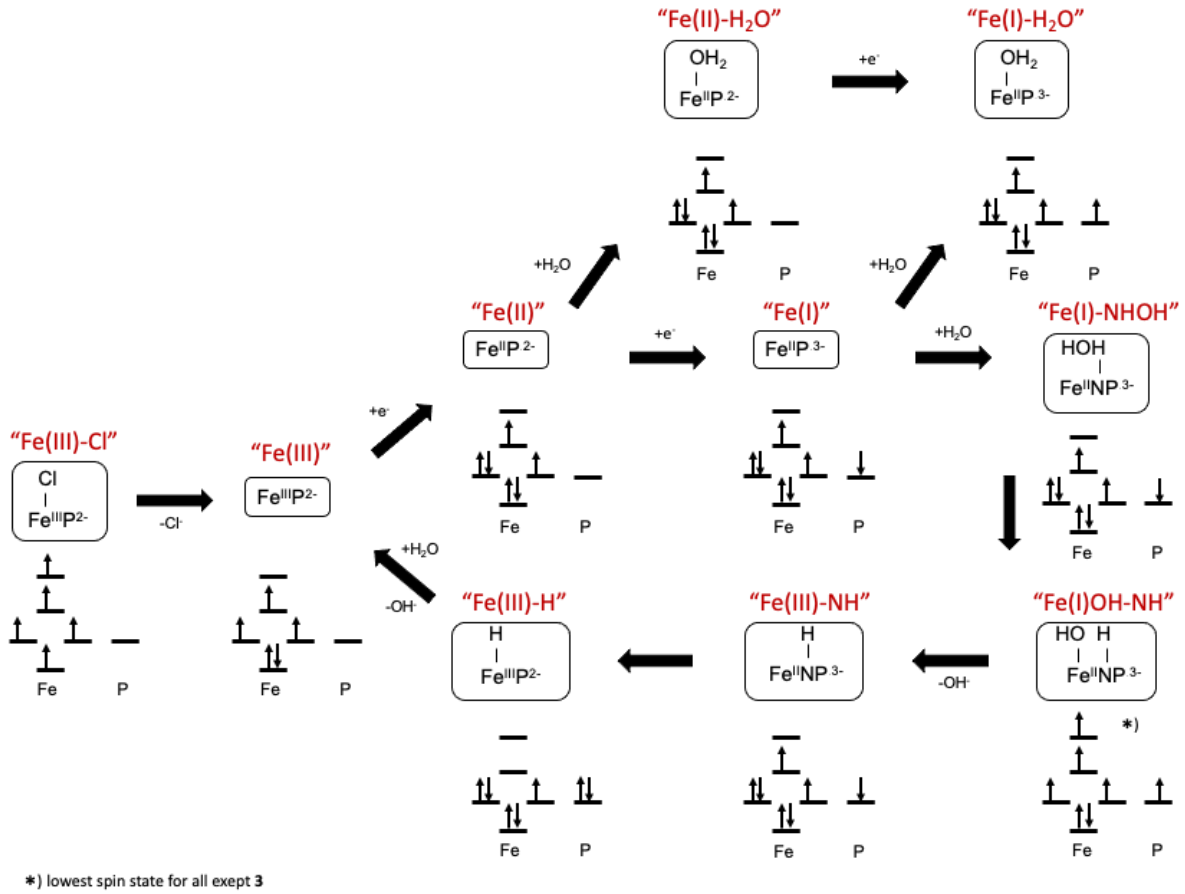


Figure S12: Orbital occupation scheme for intermediates of the HER cycle.

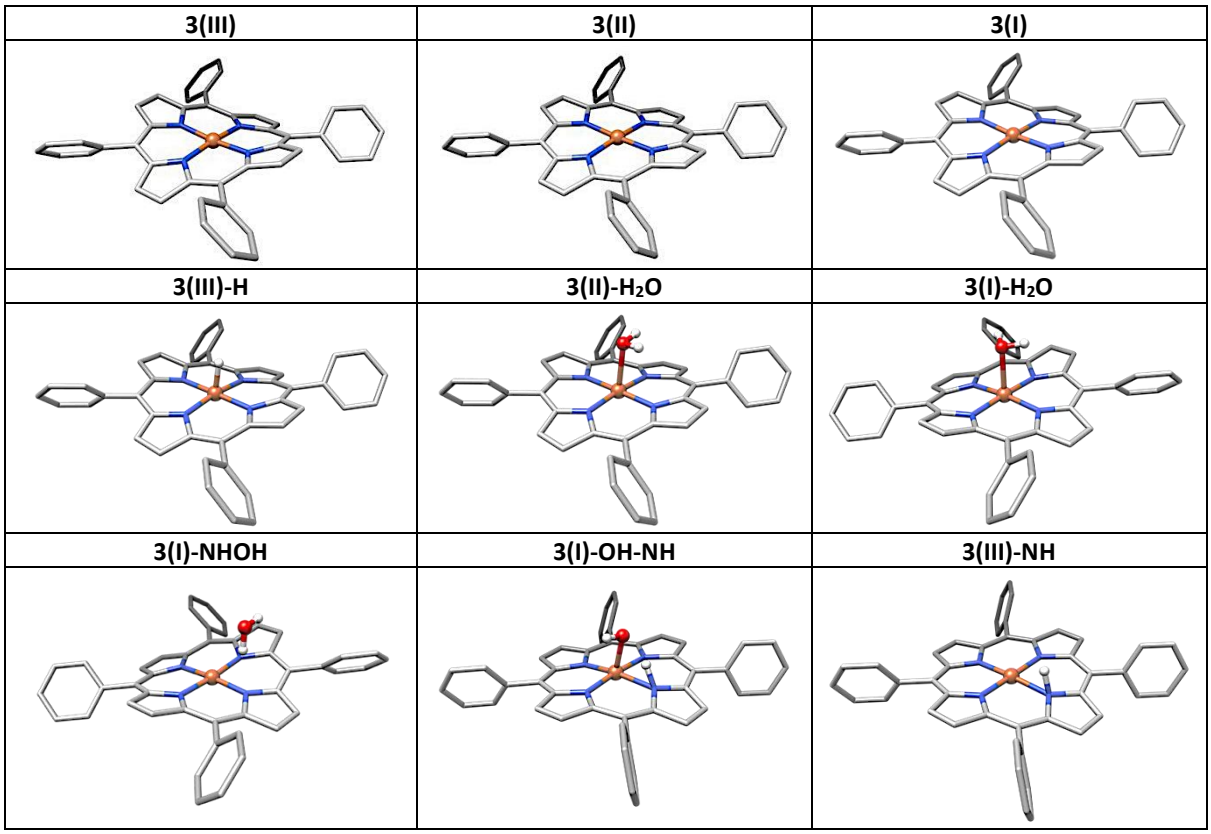


Figure S13: Structures of HER intermediates exemplarily shown for complex 3. The nomenclature for the labels gives the formal oxidation state of Fe in roman numbers (I-III) as well as axial ligands that are either coordinated to Fe (-H/-Cl/-H_2O) or to one of the porphyrinic N atoms (-NH/-NHOH). In the case of **3**(I)-OH-NH, OH is coordinated to Fe while H is coordinated to N. Fe is depicted in orange, N in blue, O in red, H in white and C in light grey. H atoms in CH groups are omitted for clarity.

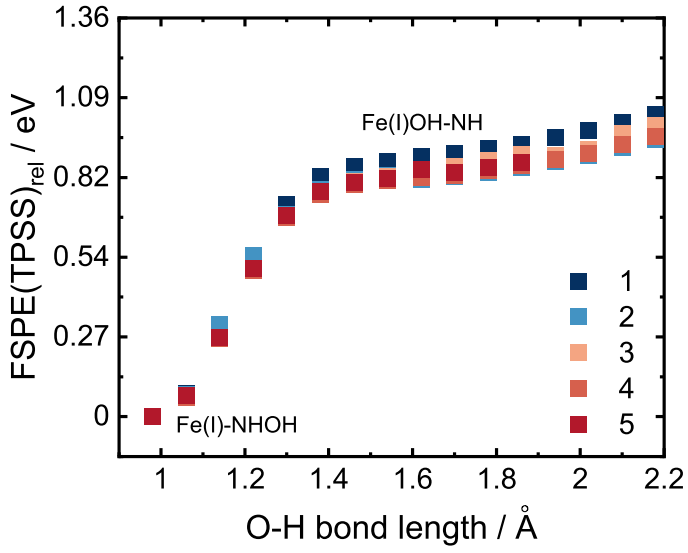


Figure S14: Relaxed surface scan for OH bond breaking step (reaction VIII in Table S6) for 1-5.

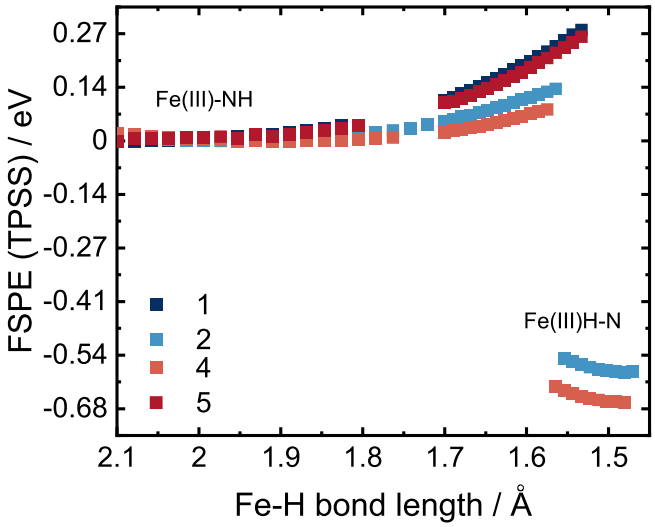


Figure S15: Relaxed surface scan for H migration (reaction X in Table S6) for 1, 2, 4 and 5; the scan terminated for **1** and **5** at 1.65 Å due to SCF failure**.**

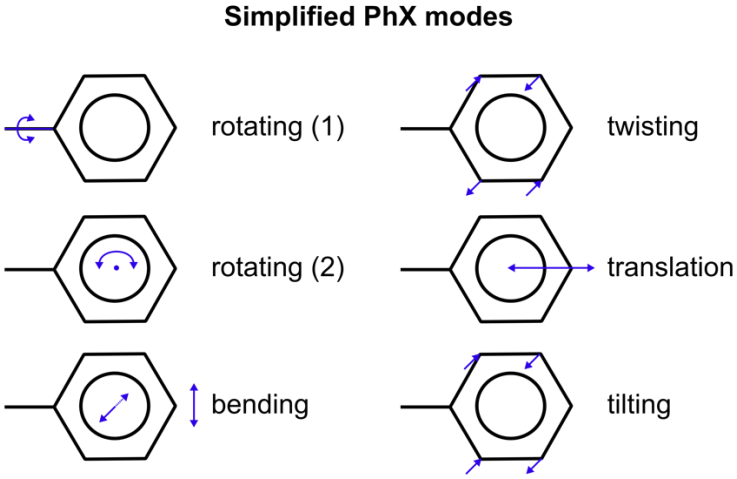


Figure S16: Scheme of simplified PhX vibrations for assignment of vibrational modes.

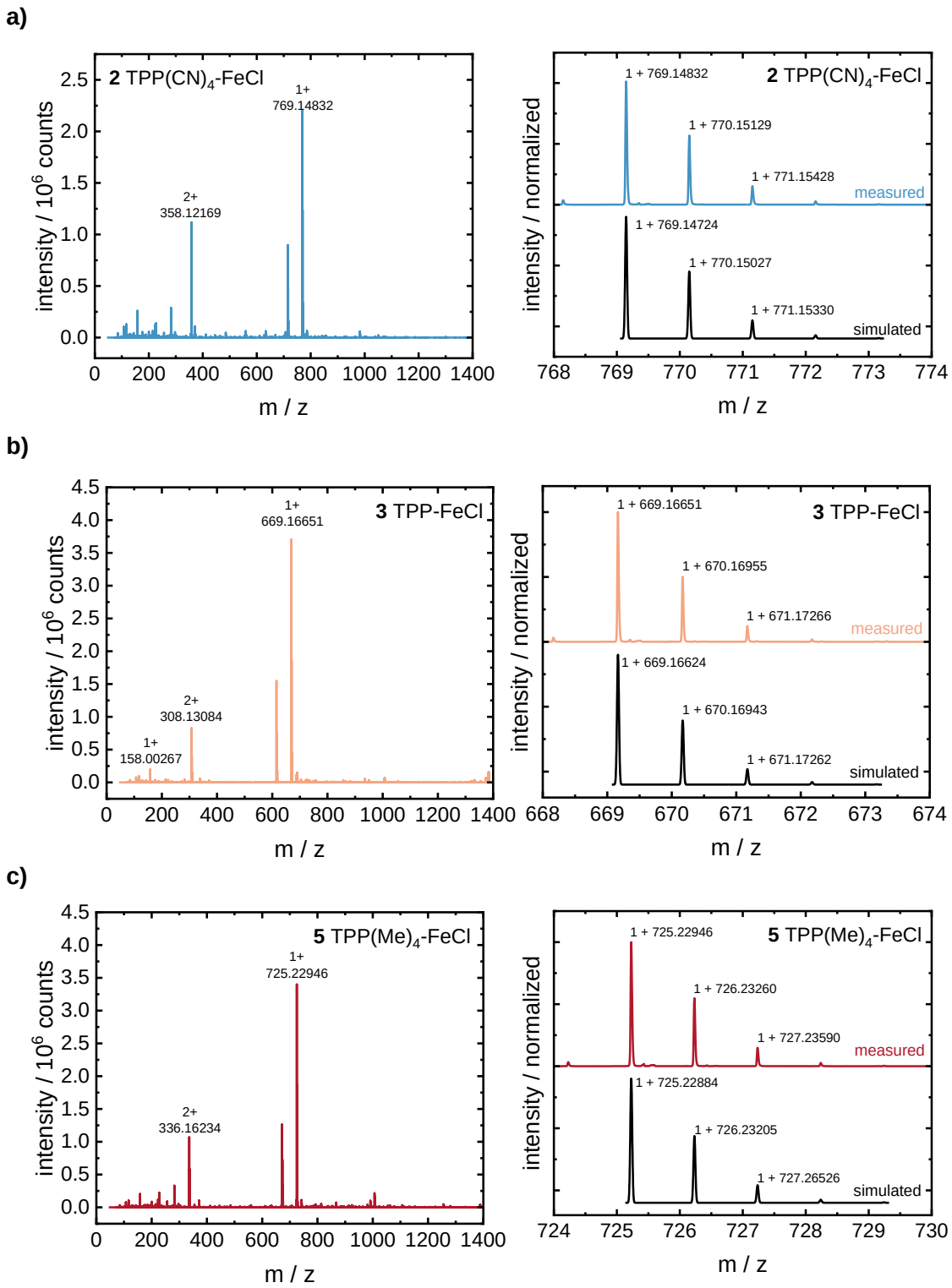
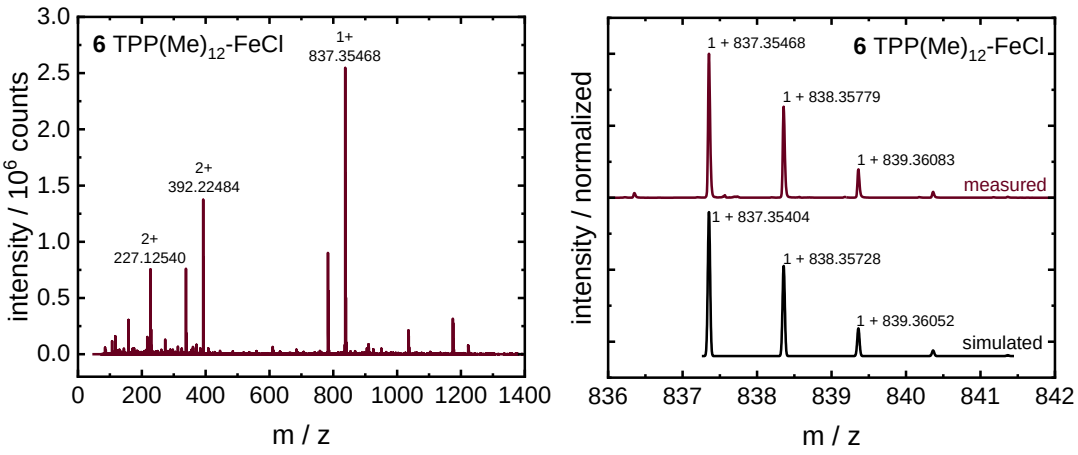


Figure S17: Mass spectra of the porphyrin complexes a) 2 $TPP(CN)_4$-$^{57}FeCl$, **b) 3** TPP-$^{57}FeCl$ and **c) 5** $TPP(CH)_4$-$^{57}FeCl$.

d)



Continued - Figure S17: Mass spectra of the porphyrin complexes d) 6 $TPP(CH)_{12}$-$^{57}FeCl$.

– Supplementary Tables –

Table S1: NRVS experimental frequencies and interpretation for complexes 2,3,5 and 6.

2		**3**		**5**		**6**		Mode description
pPDOS		pPDOS		pPDOS		pPDOS		
Frequency (cm^{-1})	Intensity (a.u.)	Frequency (cm^{-1})	Intensity (a.u.)	Frequency (cm^{-1})	Intensity (a.u.)	Frequency (cm^{-1})	Intensity (a.u.)	
26	0.26	26	0.13	23	0.26	27	0.11	lattice modes
		69	0.08					lattice modes
112	0.17	117	0.15	107	0.24	106	0.11	γ_9 (doming)
		195	0.06	172	0.06			
202	0.72	225	1.00	197	0.16	189	0.31	
233	0.83			215	0.83	222	0.15	
246	1.00	258	0.07	224	1.00	243	0.11	
				260	0.86	265	1.00	
300	0.77	291	0.72	298	0.29	313	0.04	
				350	0.25			
366	0.33	387	0.29	366	0.60	363	0.21	Fe-Cl stretch
402	0.12					373	0.18	
420	0.19	407	0.14	426	0.12	422	0.13	ν_{50}

Table S2: Predicted NRVS modes for complexes 2,3,5 and 6, simplified description and assignment. P designates the porphin plane, PhX the substituted aryl ring (see Figure S16 for assignment of phenyl vibrational modes) and oop an out-of-plane mode.

Complex **2**					
pPDOS		**Mode description**			**Assignment**
Frequency (cm-1)	**Intensity (a.u.)**	**P**	**PhX**	**Cl**	
6.3	0.979	oop wagging			
12.6	0.018	oop wagging			
18.8	0.120	in-plane	bending		
25.5	0.144	in-plane	bending		
26.8	0.347	doming/rocking	rotating (1)		
32.1	0.067	in-plane	bending		
33.1	0.010	oop tilting	rotating (1)		
36.0	0.013	oop tilting	rotating (1)	bending	
63.6	0.012	oop tilting	rotating (1)	bending	
84.8	0.231	oop	CN bending	bending	
91.5	0.210	oop	CN bending rotating (1)	bending	
94.1	0.226	oop doming	rotating (1)		γ_9 (doming)
117.9	0.028	oop tilting	bending		
120.5	0.019	oop tilting	bending		
121.1	0.062	oop doming	bending		γ_9 (doming)
125.2	0.019	oop	bending		
127.9	0.034	oop	bending		
172.8	0.014	oop twisting	rotating (2) CN bending		
191.9	0.030	asym. in-plane stretch	translation		
198.2	0.215	in-plane translation	translation		
201.5	0.280	in-plane translation	translation	bending	
208.1	0.078	oop doming	rotating (1)		γ_6 (inverse doming)
226.0	0.299	asym. oop	rotating (2) CN bending	bending	
235.0	0.030	asym. oop	rotating (2) CN bending	bending	
244.1	0.389	asym. in-plane Fe-N stretch + oop			
245.0	0.135	asym. in-plane Fe-N stretch + oop			
245.9	0.164	asym. in-plane Fe-N stretch + oop		bending	
259.6	0.011	oop inverse doming	rotating (2)		γ_6 (inverse doming)
296.8	0.139	asym. in-plane Fe-N stretch	tilting		
302.8	0.126	asym. in-plane Fe-N stretch	tilting		
335.3	0.329			stretching	Fe-Cl stretch
341.6	0.012	oop twisting	rotating (2)		
384.7	0.010	sym. in-plane Fe-N stretch			ν_8 (breathing)
425.1	0.013	in-plane	twisting		ν_{50}
426.2	0.011	in-plane	twisting		ν_{50}

Complex **3**					
pPDOS		**Mode description**			**Assignment**
Frequency (cm^{-1})	**Intensity (a.u.)**	**P**	**PhX**	**Cl**	
30.2	0.222	oop wagging	rotating (1)		
33.9	0.165	oop wagging	rotating (1)		
47.0	0.042	oop wagging	rotating (1)		
53.7	0.061	in plane	bending		
56.7	0.061	in plane	bending		
58.6	0.007	oop	rotating (1)		
79.1	0.014	oop tilting	rotating (1)	bending	
84.0	0.023	oop tilting	rotating (1)	bending	
95.8	0.033	oop tilting	rotating (2)		
104.0	0.557	oop doming			γ_9 (doming)
116.5	0.008	oop tilting	rotating (2)		
153.4	0.008	oop twisting	rotating (2)		
191.1	0.028	asym. in-plane stretch	translation		
198.5	0.036	asym. in-plane stretch	translation		
203.8	0.009	sym. in-plane stretch	translation		
218.5	0.210	asym. in-plane Fe-N stretch	translation tilting	bending	
221.3	0.511	asym. in-plane Fe-N stretch	translation tilting	bending	
221.7	0.058	oop	translation tilting	bending	
224.3	0.183	asym. in plane stretch + oop	translation	bending	
228.6	0.146	asym. in plane stretch + oop	tilting	bending	
236.7	0.027	oop doming	tilting		γ_6 (inverse doming)
240.7	0.094	Asym. oop	rotating (2)	bending	
265.9	0.009	oop doming	rotating (2)		γ_6 (inverse doming)
286.6	0.181	asym. in-plane Fe-N stretch	tilting		
292.5	0.023	oop twisting			
293.5	0.118	asym. in-plane Fe-N stretch		bending	
298.0	0.006	in-plane rotating	tilting		
324.5	0.017	oop twisting	rotating (2)		
328.5	0.274			stretching	Fe-Cl stretch
391.8	0.009	sym. in-plane stretch			ν_8 (breathing)
409.2	0.013	asym. in-plane Fe-N stretch	twisting		ν_{50}
411.6	0.013	asym. in-plane Fe-N stretch	twisting		ν_{50}
432.5	0.007	in-plane	twisting		
442.6	0.006	in-plane	twisting		
447.5	0.006	in-plane	stretching		

Complex **5**					
pPDOS		**Mode description**			**Assignment**
Frequency (cm-1)	**Intensity (a.u.)**	**P**	**PhX**	**Cl**	
13.2	0.241		bending		
21.8	0.457	oop wagging	Rotating (1)		
22.9	0.331	oop wagging	CH_3 rotating		
25.4	0.126	oop wagging	rotating (1)		
37.2	0.028	oop tilting	rotating (1) bending	bending	
38.9	0.024	oop tilting	rotating (1) bending	bending	
48.6	0.014	in-plane rotating	bending CH_3 bending		
62.5	0.012	oop tilting	rotating (1)	bending	
76.6	0.007		CH_3 rotating		
78.2	0.007		CH_3 rotating		
92.5	0.484	oop doming	rotating (2)		γ_9 (doming)
93.9	0.312	oop doming	rotating (2)		γ_9 (doming)
102.9	0.053	oop tilting	rotating (1)		
114.3	0.007	asym. in-plane stretch	translation		
144.9	0.011	oop	bending		
148.2	0.007	oop	bending		
156.7	0.027	oop tilting	bending		
159.4	0.033	oop	bending		
161.7	0.029	in-plane + oop	tilting		
184.5	0.032	asym. in-plane stretch + oop	translation		
189.4	0.060	asym. in-plane stretch + oop	translation		
198.5	0.010	oop doming	rotating (2)		γ_6 (inverse doming)
207.5	0.084	asym. in-plane stretch + oop	translation	bending	
210.2	0.330	asym. in plane stretch + oop	translation	bending	
213.7	0.635	asym. in-plane stretch + oop		bending	
225.6	0.202	asym. in-plane stretch + oop		bending	
232.9	0.036	oop doming	rotating (2)		γ_6 (inverse doming)
253.4	0.016	oop doming	rotating (2)		γ_6 (inverse doming)
260.3	0.458	asym. in-plane Fe-N stretch + oop			
269.1	0.301	asym. in-plane Fe-N stretch + oop	tilting		
292.5	0.027	oop twisting	CH_3 bending		
296.1	0.017	oop twisting	CH_3 bending		
328.4	0.402			stretching	Fe-Cl stretch
335.9	0.015		tilting	stretching	Fe-Cl stretch
342.7	0.046	asym. in-plane Fe-N stretch	tilting		
345.9	0.040	asym. in-plane Fe-N stretch	tilting		
389.7	0.013	sym. in-plane Fe-N stretch			ν_8 (breathing)
419.5	0.008	in-plane	twisting		ν_{50}
420.3	0.010	in-plane	twisting		ν_{50}
431.2	0.007	in-plane	twisting		

Complex **6**					
pPDOS		**Mode description**			**Assignment**
Frequency (cm^{-1})	**Intensity (a.u.)**	**P**	**PhX**	**Cl**	
40.6	0.074		bending		
42.1	0.037	oop wagging	rotating (1)		
71.0	0.016	oop wagging	rotating (2)		
74.9	0.040	oop tilting	rotating (2)	bending	
78.7	0.020		CH_3 rotating		
81.8	0.014	oop tilting	CH_3 rotating	bending	
89.9	0.465	oop doming	bending		γ_9 (doming)
100.9	0.019	(in-plane)	tilting		
104.9	0.269	asym. in-plane stretch + oop	translation		
106.5	0.102	(in-plane)	tilting	(bending)	
106.8	0.045	(in-plane)	tilting	(bending)	
160.9	0.045	oop doming	rotating (2) CH_3 rotating		γ_6 (inverse doming)
176.1	0.014	(in-plane)	CH_3 rotating		
182.0	0.173	asym. in-plane stretch	translation CH_3 rotating		
184.1	0.231	asym. in-plane stretch	translation CH_3 rotating		
185.5	0.008	(asym. in-plane stretch)	CH_3 rotating		
186.9	0.013	(asym. in-plane stretch)	CH_3 rotating		
188.7	0.042	(asym. in-plane stretch)	CH_3 rotating		
189.9	0.011	(asym. in-plane stretch)	CH_3 rotating		
198.0	0.010	asym. in-plane stretch + oop	tilting CH_3 rotating		
199.5	0.011	(asym. in-plane stretch + oop)	tilting		
200.7	0.010	(asym. in-plane stretch + oop)	tilting		
213.6	0.052	oop tilting	rotating (2)	bending	
216.8	0.123	oop tilting	rotating (2)	bending	
233.3	0.069	oop doming	rotating (2)		γ_6 (inverse doming)
257.9	0.574	asym. in-plane stretch	translation tilting	bending	
263.9	0.557	asym. in-plane stretch	translation tilting	bending	
302.7	0.015	oop twisting	CH_3 bending		
303.6	0.017	oop twisting	CH_3 bending		
333.5	0.353			stretching	Fe-Cl stretch
364.0	0.032	asym. in-plane Fe-N stretch	tilting		
366.4	0.032	asym. in-plane Fe-N stretch	tilting		
397.6	0.013	sym. in-plane Fe-N stretch			ν_8 (breathing)
423.9	0.021	in-plane	stretching		ν_{50}
427.3	0.024	in-plane	stretching		ν_{50}

Table S3: Overview of experimentally obtained values: redox potentials in DCM, HOMO/LUMO energies, redox potentials in KOH and H_2SO_4 and turnover frequencies in KOH.

Parameter	Unit	1	2	3	4	5	6
Abbreviation		$TPP(F)_{20}$-FeCl	$TPP(CN)_4$-FeCl	TPP-FeCl	$TPP(OMe)_4$-FeCl	$TPP(Me)_4$-FeCl	$TPP(Me)_{12}$-FeCl
$E_{0.5}$ ($P^{0/+}$ in DCM)	V vs Fc/Fc^+	-	0.833	0.666	0.526	0.585	0.603
$E_{0.5}$ ($P^{0/+}$ in DCM)	V vs RHE	-	1.574	1.407	1.266	1.326	1.344
$E_{0.5}$ ($Fe^{II/III}$ in DCM)	V vs Fc/Fc^+	-0.582	-0.682	-0.791	-0.812	-0.811	-
$E_{0.5}$ ($Fe^{II/III}$ in DCM)	V vs RHE	0.159	0.059	-0.051	-0.071	-0.071	-
$E_{0.5}$ ($Fe^{I/II}$ in DCM)	V vs Fc/Fc^+	-1.263	-1.443	-1.618	-1.571	-1.567	-
$E_{0.5}$ ($Fe^{I/II}$ in DCM)	V vs RHE	-0.522	-0.702	-0.877	-0.831	-0.827	-
E (LUMO)	eV	4.34	4.23	4.15	4.14	4.12	4.01
E (HOMO)	eV	5.62	5.65	5.39	5.26	5.30	5.33
E (band gap)	eV	1.28	1.41	1.25	1.13	1.19	1.32
$E_{0.5}$ ($Fe^{II/III}$ in 0.1 M KOH)	V vs RHE	0.448	0.388	0.299	0.285	0.282	0.275
$E_{0.5}$ ($Fe^{II/III}$ in 0.1 M H_2SO_4)	V vs RHE	0.341	0.296	0.187	0.153	0.143	0.139
$TOF_{0.7\,V}$ (in 0.1 M KOH)	s^{-1}	0.634	0.702	1.00	0.880	1.28	1.84
$TOF_{0.8\,V}$ (in 0.1 M KOH)	s^{-1}	1.19	1.18	1.68	1.92	2.55	4.03
$n_{Fe\text{-}EC}$	nmol cm^{-2}	58.30	78.56	50.16	46.59	25.99	14.18
$n_{Fe\text{-}theo.}$	nmol cm^{-2}	244.91	279.72	295.49	276.63	286.23	269.56
Contacting efficiency	%	23.8	28.1	17.0	16.8	9.1	5.3
XPS N 1s	eV	399.06	398.66	398.26	398.23	398.29	398.27

Table S4: Overview of all calculated structures sorted by substituent 1-6. Name, charge C, multiplicity M, electronic energies obtained with TPSS and OLYP in Eh, relative electronic energy E_{rel} in kcal mol^{-1}, Mulliken spin population (MSP) on Fe and, if applicable, identification of any negative frequencies.

Name	C	M	Comment	FSPE(TPSS)	FSPE(OLYP)	E_{rel}(OLYP)	MSP(Fe)
1(III)-Cl	0	2	-5.11 cm^{-1} a)	-5621.8151	-5621.9507	14.4	1.17
	0	4	-3.37 cm^{-1} a)	-5621.8254	-5621.9724	0.8	2.72
	0	6	-10.04 cm^{-1} a)	-5621.8097	-5621.9737	0.0	4.12
1(III)	1	2	----	-5161.3206	-5161.4807	38.1	0.62
	1	4	----	-5161.3710	-5161.5415	0.0	2.86
	1	6	----	-5161.3109	-5161.4809	38.0	2.92
1(II)	0	1	b)	-5161.5054	-5161.6550	33.3	0.00
	0	3	-2.45 cm^{-1} a) c)	-5161.5496	-5161.7081	0.0	2.35
	0	5	b)	-5161.5269	-5161.6870	13.2	3.81
1(I)	-1	2	----	-5161.6843	-5161.8337	0.0	2.10
	-1	4	-13.40 cm^{-1} a) c)	-5161.6668	-5161.8161	11.0	2.40
1(III)-H	0	2	-2.75 cm^{-1} a)	-5162.1283	-5162.2705	0.0	1.24
	0	4	-29.14 cm^{-1} d), -5.46 cm^{-1} a)	-5162.0840	-5162.2143	35.3	2.21
	0	6	no geometry found				
1(II)-H_2O	0	1	-5.64 cm^{-1} a) c)	-5238.0255	-5238.1332	15.6	0.00
	0	3	----	-5238.0389	-5238.1580	0.0	2.35
	0	5	----	-5238.0172	-5238.1192	24.4	2.93
1(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	-3.38 cm^{-1} d)	-5238.1545	-5238.2626	9.8	2.38
	-1	6	-15.27 cm^{-1} e), -11.96 cm^{-1} a) e) c)	-5238.1349	-5238.2501	17.7	3.79
1(I)-FeOH-NH	-1	2	-9.16 cm^{-1} a) d)	-5238.1268	-5238.2368	26.0	2.22
	-1	4	no geometry found				
	-1	6	----	-5238.1163	-5238.2340	27.8	3.67
1(I)-NHOH	-1	2	----	-5238.1641	-5238.2783	0.0	2.07
	-1	4	no geometry found				
1(III)-NH	0	2	-11.14 cm^{-1} a) d)	-5162.1134	-5162.2657	3.0	1.98
	0	4	-11.98 cm^{-1} a) d)	-5162.108	-5162.2589	7.3	2.47
	0	6	no geometry found				

a) porphyrin plane bending
b) geometry with many negative frequencies, not further evaluated but shown for completeness.
c) PhX rotation
d) PhX bending
e) H_2O bending

Name	C	M	Comment	FSPE(TPSS)	FSPE(OLYP)	E_{rel}(OLYP)	MSP(Fe)
2(III)-Cl	0	2	----	-4005.2205	-4005.9056	14.2	1.22
	0	4	----	-4005.2313	-4005.9272	0.6	2.74
	0	6	-7.56 cm^{-1} a)	-4005.2150	-4005.9281	0.0	4.11
2(III)	1	2	b)	-3544.7351	-3545.4437	35.0	0.64
	1	4	-6.94 cm^{-1} a)	-3544.7805	-3545.4995	0.0	2.86
	1	6	b)	-3544.7492	no SCF convergence		
2(II)	0	1	-6.59 cm^{-1} a)	-3544.9067	-3545.6058	33.5	0.00
	0	3	----	-3544.9515	-3545.6591	0.0	2.34
	0	5	----	-3544.9288	-3545.6211	23.9	2.87
2(I)	-1	2	----	-3545.0800	-3545.7793	0.0	2.11
	-1	4	-5.06 cm^{-1} a)	-3545.0643	-3545.7640	9.6	2.40
2(III)-H	0	2	-6.64 cm^{-1} a)	-3545.5315	-3546.2229	0.0	1.23
	0	4	-----	-3545.4871	-3546.1799	27.0	1.94
	0	6	-7.68 cm^{-1} a)	-3545.4210	-3546.1133	68.8	2.04
2(II)-H_2O	0	1	-6.99 cm^{-1} a) f)	-3621.4259	-3622.0832	16.0	0.00
	0	3	-5.94 cm^{-1} a) d)	-3621.4403	-3622.1086	0.0	2.35
	0	5	-3.84 cm^{-1} a) d)	-3621.4199	-3622.0700	24.2	2.99
2(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	-12.74 cm^{-1} a) d)	-3621.5523	-3622.2114	9.1	2.38
	-1	6	no geometry found				
2(I)-FeOH-NH	-1	2	----	-3621.5196	-3622.1820	27.6	2.20
	-1	4	no geometry found, H_2O detached				
	-1	6	-23.15 cm^{-1} a) g)	-3621.5150	-3622.1841	26.2	3.67
2(I)-NHOH	-1	2	----	-3621.5611	-3622.2259	0.0	2.08
	-1	4	----	-3621.5522	-3622.2134	7.8	2.34
2(III)-NH	0	2	-11.46 cm^{-1} c)	-3545.5097	-3546.2133	6.0	1.89
	0	4	-10.62 cm^{-1} d)	-3545.4971	-3546.2075	9.7	2.44
	0	6	b)	-3545.4745	-3546.1802	26.8	3.75

a) porphyrin plane bending
b) geometry with many negative frequencies, not further evaluated but shown for completeness.
c) PhX rotation
d) PhX bending
f) H_2O rotating
g) OH bending

Name	C	M	Comment	FSPE(TPSS)	FSPE(OLYP)	E_{rel}(OLYP)	MSP(Fe)
3(III)-Cl	0	2	-3.09 cm^{-1} a)	-3636.1758	-3636.8572	14.1	1.20
	0	4	----	-3636.1866	-3636.8759	2.4	2.67
	0	6	----	-3636.1700	-3636.8797	0.0	4.07
3(III)	1	2	b)	-3175.6978	-3176.4353	15.7	2.24
	1	4	-15.29 cm^{-1} a)	-3175.7382	-3176.4603	0.0	2.86
	1	6	-13.77 cm^{-1} a)	-3175.7086	-3176.4037	35.5	2.96
3(II)	0	1	-5.94 cm^{-1} a)	-3175.8594	-3176.5624	33.5	0.00
	0	3	----	-3175.9045	-3176.6158	0.0	2.33
	0	5	b)	-3175.8813	-3176.5648	32.0	2.87
3(I)	-1	2	----	-3176.0274	-3176.7308	0.0	2.06
	-1	4	----	-3176.0077	-3176.7126	11.4	2.40
3(III)-H	0	2	----	-3176.4854	-3177.1803	0.0	1.22
	0	4	-21.81 cm^{-1} a)	-3176.4576	-3177.1224	36.3	2.24
	0	6	b)	-3176.3972	-3177.0517	80.7	2.32
3(II)-H_2O	0	1	----	-3252.3771	-3253.0388	16.1	0.00
	0	3	----	-3252.3926	-3253.0644	0.0	2.33
	0	5	----	-3252.3716	-3253.0234	25.7	2.99
3(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	-60.74 cm^{-1} f)	-3252.4894	-3253.1580	12.5	2.42
	-1	6	no geometry found				
3(I)-FeOH-NH	-1	2	----	-3252.4685	-3253.1367	25.9	2.17
	-1	4	no geometry found, H_2O detached				
	-1	6	----	-3252.4427	-3253.1099	42.8	2.88
3(I)-NHOH	-1	2	----	-3252.5086	-3253.1780	0.0	2.02
	-1	4	----	-3252.4969	-3253.1595	11.6	2.38
3(III)-NH	0	2	----	-3176.4623	-3177.1701	6.4	1.85
	0	4	----	-3176.4527	-3177.1652	9.5	2.39
	0	6	----	-3176.4296	-3177.1503	18.8	3.79

a) porphyrin plane bending
b) geometry with many negative frequencies, not further evaluated but shown for completeness.
f) H_2O rotating

Name	C	M	Comment	FSPE(TPSS)	FSPE(OLYP)	E_{rel}(OLYP)	MSP(Fe)
4(III)-Cl	0	2	----	-4094.3842	-4094.9851	13.5	1.30
	0	4	-13.85 cm^{-1} a)	-4094.3950	-4095.0065	0.1	2.75
	0	6	-10.79 cm^{-1} a)	-4094.3782	-4095.0066	0.0	4.10
4(III)	1	2	-18.18 cm^{-1} d)	-3633.9168	no SCF convergence		
	1	4	-40.32 cm^{-1} h)	-3633.9493	-3634.5808	0.0	2.71
	1	6	b)	-3633.9215	-3634.5164	40.4	3.10
4(II)	0	1	----	-3634.0676	-3634.6775	35.7	0.00
	0	3	-23.29 cm^{-1} a) d)	-3634.1115	-3634.7345	0.0	2.33
	0	5	-22.22 cm^{-1} a) d)	-3634.0709	-3634.6942	25.3	2.62
4(I)	-1	2	-9.48 cm^{-1} a)	-3634.2324	-3634.8485	0.0	2.04
	-1	4	-23.90 cm^{-1} a)	-3634.2209	-3634.8293	12.0	2.39
4(III)-H	0	2	----	-3634.6928	-3635.2999	0.0	1.22
	0	4	-63.11 cm^{-1} a)	-3634.6450	-3635.2424	36.1	2.27
	0	6	b)	-3634.6476	-3635.2015	61.8	3.32
4(II)-H_2O	0	1	-17.63 cm^{-1} a) d)	-3710.5844	-3711.1579	16.0	0.00
	0	3	-15.10 cm^{-1} a) d) -9.63 cm^{-1} a) d)	-3710.5995	-3711.1834	0.0	2.33
	0	5	no geometry found				
4(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	no geometry found, H_2O detached				
	-1	6	no geometry found				
4(I)-FeOH-NH	-1	2	-13.40 cm^{-1} a) d)	-3710.6730	-3711.2535	26.5	2.16
	-1	4	no geometry found				
	-1	6	----	-3710.6592	-3711.2521	27.4	3.90
4(I)-NHOH	-1	2	----	-3710.7141	-3711.2957	0.0	2.01
	-1	4	-28.09 cm^{-1} d)	-3710.7023	-3711.2765	12.1	2.38
4(III)-NH	0	2	----	-3634.6679	-3635.2871	8.1	1.82
	0	4	----	-3634.6541	-3635.2811	11.8	2.41
	0	6	no geometry found				

a) porphyrin plane bending
b) geometry with many negative frequencies, not further evaluated but shown for completeness.
d) PhX bending
h) CH_3OH bending

Name	C	M	Comment	FSPE(TPSS)	FSPE(OLYP)	E_{rel}(OLYP)	MSP(Fe)
5(III)-Cl	0	2	-43.33 cm^{-1} i), -40.16 cm^{-1} i), -34.38 cm^{-1} i)	-3793.3758	-3794.1021	13.8	1.27
	0	4	----	-3793.3863	-3794.1235	0.4	2.75
	0	6	-29.43 cm^{-1} i)	-3793.3699	-3794.1241	0.0	4.11
5(III)	1	2	-32.15; cm^{-1} i), -1.58 cm^{-1} a)	-3332.9030	no SCF convergence		
	1	4	i) j)	-3332.9389	-3333.6989	0.0	2.87
	1	6	-45.08 cm^{-1} i)	-3332.9102	-3333.6438	34.6	2.96
5(II)	0	1	b)	-3333.0586	-3333.7999	33.3	0.00
	0	3	-40.94 cm^{-1} i), -38.50 cm^{-1} i), -34.57 cm^{-1} i)	-3333.1039	-3333.8530	0.0	2.33
	0	5	b)	-3333.0626	-3333.8121	25.7	2.66
5(I)	-1	2	-14.68 cm^{-1} i)	-3333.2258	-3333.9671	0.0	2.05
	-1	4	-24.36 cm^{-1} i)	-3333.2049	-3333.9474	12.3	2.38
5(III)-H	0	2	-29.23 cm^{-1} i)	-3333.6850	-3334.4178	0.0	1.22
	0	4	-166.62 cm^{-1} a), -11.21 cm^{-1} i)	-3333.6374	-3334.3724	28.5	1.95
	0	6	----	-3333.5974	-3334.3479	43.8	3.81
5(II)-H_2O	0	1	-33.12 cm^{-1} i), -30.09 , cm^{-1} i), -28.61 cm^{-1} i)	-3409.5768	-3410.2760	16.1	0.00
	0	3	-20.03 cm^{-1} i)	-3409.5919	-3410.3017	0.0	2.33
	0	5	-31.64 cm^{-1} i), -25.57 cm^{-1} i)	-3409.5708	-3410.2602	26.0	3.00
5(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	-27.51 cm^{-1} i)	-3409.6875	-3410.3940	12.9	2.42
	-1	6	-24.92 cm^{-1} i), -2.57 cm^{-1} a) d) e)	-3409.6721	-3410.3814	20.8	3.79
5(I)-FeOH-NH	-1	2	----	-3409.6728	-3410.3742	25.3	2.18
	-1	4	no geometry found, H_2O detached				
	-1	6	----	-3409.6613	-3410.3755	24.4	3.88
5(I)-NHOH	-1	2	----	-3409.7072	-3410.4145	0.0	2.02
	-1	4	-58.89 cm^{-1} i)	-3409.6954	-3410.3957	11.8	2.37
5(III)-NH	0	2	-33.63, cm^{-1} i), -29.45 cm^{-1} a) c), -19.31 cm^{-1} i)	-3333.6685	-3334.4105	4.6	1.94
	0	4	-40.64 cm^{-1} i)	-3333.6540	-3334.3992	11.7	2.38
	0	6	no geometry found				

a) porphyrin plane bending
b) geometry with many negative frequencies, not further evaluated but shown for completeness.
c) PhX rotation
d) PhX bending
e) H_2O bending
i) CH_3 rotation
j) geometry with many negative frequencies

Name	C	M	Comment	FSPE(TPSS)	FSPE(OLYP)	Erel(OLYP)	MSP(Fe)
6(III)-Cl	0	2	-26.67 cm^{-1} d)	-4107.7838	-4108.5493	14.8	1.20
	0	4	-33.32 cm^{-1} d)	-4107.7936	-4108.5713	1.1	2.73
	0	6	-13.42 cm^{-1} i)	-4107.7778	-4108.5730	0.0	4.12
6(III)	1	2	-33.54 cm^{-1} i)	-3647.3315	-3648.0902	35.9	0.64
	1	4	----	-3647.3450	-3648.1473	0.0	2.87
	1	6	no geometry found				
6(II)	0	1	no geometry found				
	0	3	-30.52 cm^{-1} i)	-3647.5124	-3648.3029	0.0	2.33
	0	5	----	-3647.4883	-3648.2506	32.8	2.95
6(I)	-1	2	-12.82 cm^{-1} i)	-3647.6329	-3648.4141	0.0	2.04
	-1	4	-18.85 cm^{-1} d) i)	-3647.6111	-3648.3941	12.6	2.39
6(III)-H	0	2	----	-3648.0936	-3648.8676	0.0	1.24
	0	4	-39.89 cm^{-1} i), -1.81 cm^{-1} a)	-3648.0652	-3648.8085	37.1	2.25
	0	6	-26.94 cm^{-1} c), -21.65 cm^{-1} i)	-3648.0475	-3648.7929	46.9	4.03
6(II)-H_2O	0	1	-27.16 cm^{-1} c)	-3723.9844	-3724.7235	15.3	0.00
	0	3	-6.13 cm^{-1} a) d) f)	-3723.9996	-3724.7479	0.0	2.33
	0	5	-8.33 cm^{-1} a) c)	-3723.9760	-3724.7055	26.6	2.92
6(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	no geometry found, H_2O detached				
	-1	6	b)	-3724.0746	no SCF convergence		
6(I)-FeOH-NH	-1	2	no geometry found, H_2O detached				
	-1	4	no geometry found, H_2O detached				
	-1	6	----	-3724.0630	-3724.8151	27.9	3.85
6(I)-NHOH	-1	2		-3724.1150	-3724.8596	0.0	2.00
	-1	4	-19.36 cm^{-1} c)	-3724.1013	-3724.8403	12.1	2.34
6(III)-NH	0	2	----	-3648.0744	-3648.8550	7.9	1.86
	0	4	----	-3648.0677	-3648.8471	12.9	2.31
	0	6	b)	-3648.0352	no SCF convergence		

a) porphyrin plane bending
b) geometry with many negative frequencies, not further evaluated, only shown for completeness.
c) PhX rotation
d) PhX bending
f) H_2O rotating
i) CH_3 rotation

Table S5: Mulliken spin populations of OLYP single point calculations for all calculated structures sorted by substituent 1-6. Charge C, multiplicity M, axial ligand L (sum over all atoms if there is more than one atom), nitrogen atoms N (sum), P porphin (sum of all atoms in porphin plane) and substituted aryl rest PhX (sum).

Name	C	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
1(III)-Cl	0	2	1.17	0.02	-0.18	-0.01	0.01
	0	4	2.72	0.29	-0.20	0.18	0.01
	0	6	4.12	0.30	0.32	0.26	0.01
1(III)	1	2	0.62		0.08	0.24	0.06
	1	4	2.86		-0.18	0.29	0.03
	1	6	2.92		0.23	1.69	0.16
1(II)	0	1	0.00		0.00	0.00	0.00
	0	3	2.35		-0.24	-0.11	0.01
	0	5	3.81		-0.06	0.24	0.01
1(I)	-1	2	2.10		-0.25	-0.81	-0.04
	-1	4	2.40		-0.13	0.63	0.10
1(III)-H	0	2	1.24		-0.14	0.02	-0.01
	0	4	2.21		-0.14	1.08	0.04
	0	6	no geometry found				
1(II)-H_2O	0	1	0.00	0.00	0.00	0.00	0.00
	0	3	2.35	0.04	-0.23	-0.12	-0.04
	0	5	2.93	0.06	-0.11	1.08	0.04
1(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	2.38	0.03	-0.13	0.57	0.15
	-1	6	3.79	0.03	0.07	0.97	0.13
1(I)-FeOH-NH	-1	2	2.22	0.11	-0.23	-1.05	-0.04
	-1	4	no geometry found				
	-1	6	3.67	0.14	0.05	1.04	0.11
1(I)-NHOH	-1	2	2.07	0.00	-0.24	-0.80	-0.04
	-1	4	no geometry found				
1(III)-NH	0	2	1.98	-0.01	-0.21	-0.72	-0.04
	0	4	2.47	0.00	-0.18	0.73	-0.02
	0	6	no geometry found				

Name	C	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
2(III)-Cl	0	2	1.22	0.02	-0.20	-0.04	0.00
	0	4	2.74	0.27	-0.19	0.18	0.01
	0	6	4.11	0.28	0.33	0.27	0.02
2(III)	1	2	0.64		0.06	0.23	0.07
	1	4	2.86		-0.17	0.28	0.03
	1	6	no SCF convergence				
2(II)	0	1	0.00		0.00	0.00	0.00
	0	3	2.34		-0.24	-0.10	0.00
	0	5	2.87		-0.08	1.00	0.21
2(I)	-1	2	2.11		-0.24	-0.78	-0.09
	-1	4	2.40		-0.15	0.49	0.26
2(III)-H	0	2	1.23	-0.10	-0.14	0.02	0.00
	0	4	1.94	-0.13	-0.04	1.07	0.16
	0	6	2.04	-0.14	-0.01	2.74	0.37
2(II)-H_2O	0	1	0.00	0.00	0.00	0.00	0.00
	0	3	2.35	0.03	-0.23	-0.18	0.03
	0	5	2.99	0.00	0.00	0.00	0.00
2(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	2.38	0.03	-0.16	0.43	0.31
	-1	6	no geometry found				
2(I)-FeOH-NH	-1	2	2.20	0.11	-0.23	-0.99	-0.09
	-1	4	no geometry found, H_2O detached				
	-1	6	3.67	0.14	0.03	0.92	0.25
2(I)-NHOH	-1	2	2.08	0.00	-0.23	-0.77	-0.09
	-1	4	2.34	0.00	-0.17	0.52	0.31
2(III)-NH	0	2	1.89	-0.02	-0.20	-0.62	-0.05
	0	4	2.44	0.00	-0.19	0.70	0.06
	0	6	3.75	0.00	0.08	1.01	0.16

Name	C	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
3(III)-Cl	0	2	1.20	0.03	-0.17	-0.06	0.00
	0	4	2.67	0.35	-0.16	0.13	0.01
	0	6	4.07	0.34	0.36	0.21	0.02
3(III)	1	2	2.24		-0.44	-0.63	-0.17
	1	4	2.86		-0.17	0.28	0.03
	1	6	2.96		0.18	1.57	0.29
3(II)	0	1	0.00		0.00	0.00	0.00
	0	3	2.33		-0.24	-0.09	0.01
	0	5	2.87		-0.10	1.15	0.08
3(I)	-1	2	2.06		-0.25	-0.76	-0.05
	-1	4	2.40		-0.12	0.67	0.05
3(III)-H	0	2	1.22	-0.10	-0.14	0.02	0.00
	0	4	2.24	-0.16	-0.16	1.02	0.06
	0	6	2.32	-0.14	-0.06	2.67	0.21
3(II)-H_2O	0	1	0.00	0.00	0.00	0.00	0.00
	0	3	2.33	0.03	-0.23	-0.10	-0.04
	0	5	2.99	0.05	-0.11	0.95	0.11
3(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	2.42	0.03	-0.10	0.53	0.12
	-1	6	no geometry found				
3(I)-FeOH-NH	-1	2	2.17	0.10	-0.23	-1.00	-0.03
	-1	4	no geometry found, H_2O detached				
	-1	6	2.88	0.20	-0.02	1.79	0.16
3(I)-NHOH	-1	2	2.02	0.00	-0.24	-0.74	-0.04
	-1	4	2.38	0.00	-0.13	0.63	0.12
3(III)-NH	0	2	1.85	-0.03	-0.20	-0.59	-0.03
	0	4	2.39	0.00	-0.18	0.78	0.02
	0	6	3.79	0.00	0.09	1.08	0.05

Name	C	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
4(III)-Cl	0	2	1.30	0.02	-0.23	-0.06	-0.03
	0	4	2.75	0.25	-0.18	0.18	0.00
	0	6	4.10	0.26	0.34	0.29	0.01
4(III)	1	2			0.00	0.00	0.00
	1	4	2.71		-0.14	0.34	0.08
	1	6	3.10		0.07	1.46	0.37
4(II)	0	1	0.00		0.00	0.00	0.00
	0	3	2.33		-0.24	-0.08	0.00
	0	5	2.62		0.03	1.22	0.13
4(I)	-1	2	2.04		-0.25	-0.77	-0.02
	-1	4	2.39		-0.13	0.69	0.05
4(III)-H	0	2	1.22	-0.10	-0.14	0.02	0.00
	0	4	2.27	-0.13	-0.17	1.02	0.02
	0	6	3.32	-0.24	0.19	1.47	0.26
4(II)-H_2O	0	1	0.00	0.00	0.00	0.00	0.00
	0	3	2.33	0.03	-0.23	-0.13	0.00
	0	5	no geometry found				
4(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	no geometry found, H_2O detached				
	-1	6	no geometry found				
4(I)-FeOH-NH	-1	2	2.16	0.10	-0.23	-1.02	-0.01
	-1	4	no geometry found				
	-1	6	3.90	0.15	0.14	0.78	0.02
4(I)-NHOH	-1	2	2.01	0.00	-0.24	-0.75	-0.02
	-1	4	2.38	0.00	-0.13	0.69	0.05
4(III)-NH	0	2	1.82	-0.03	-0.20	-0.58	-0.01
	0	4	2.41	0.00	-0.18	0.76	0.01
	0	6	no geometry found				

Name	C	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
5(III)-Cl	0	2	1.27	0.02	-0.22	-0.06	0.00
	0	4	2.75	0.25	-0.19	0.18	0.01
	0	6	4.11	0.26	0.34	0.28	0.02
5(III)	1	2	no SCF convergence				
	1	4	2.87		-0.17	0.28	0.03
	1	6	2.96		0.16	1.52	0.35
5(II)	0	1	0.00		0.00	0.00	0.00
	0	3	2.33		-0.24	-0.09	0.01
	0	5	2.66		0.02	1.19	0.13
5(I)	-1	2	2.05		-0.25	-0.75	-0.05
	-1	4	2.38		-0.13	0.69	0.06
5(III)-H	0	2	1.22	-0.10	-0.14	0.02	0.00
	0	4	1.95	-0.13	-0.02	1.11	0.09
	0	6	3.81	0.03	0.12	0.98	0.05
5(II)-H_2O	0	1	0.00	0.00	0.00	0.00	0.00
	0	3	2.33	0.03	-0.23	-0.16	0.03
	0	5	3.00	0.05	-0.10	0.94	0.11
5(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	2.42	0.03	-0.10	0.54	0.11
	-1	6	3.79	0.03	0.10	0.95	0.13
5(I)-FeOH-NH	-1	2	2.18	0.10	-0.24	-0.97	-0.07
	-1	4	no geometry found, H_2O detached				
	-1	6	3.88	0.14	0.17	0.71	0.09
5(I)-NHOH	-1	2	2.02	0.00	-0.24	-0.74	-0.04
	-1	4	2.37	0.00	-0.13	0.63	0.12
5(III)-NH	0	2	1.94	-0.01	-0.22	-0.67	-0.04
	0	4	2.38	0.01	-0.15	0.65	0.11
	0	6	no geometry found				

Name	C	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
6(III)-Cl	0	2	1.20	0.03	-0.22	-0.02	0.01
	0	4	2.73	0.27	-0.19	0.19	0.00
	0	6	4.12	0.27	0.34	0.27	0.01
6(III)	1	2	0.64		-0.01	0.36	0.01
	1	4	2.87		-0.19	0.29	0.03
	1	6	no geometry found				
6(II)	0	1	no geometry found				
	0	3	2.33		-0.25	-0.08	0.00
	0	5	2.95		-0.10	1.05	0.10
6(I)	-1	2	2.04		-0.26	-0.73	-0.04
	-1	4	2.39		-0.12	0.72	0.01
6(III)-H	0	2	1.24	-0.10	-0.15	0.03	-0.01
	0	4	2.25	-0.16	-0.16	0.97	0.09
	0	6	4.03	-0.01	0.12	0.75	0.12
6(II)-H_2O	0	1	0.00	0.00	0.00	0.00	0.00
	0	3	2.33	0.03	-0.24	-0.08	-0.04
	0	5	2.92	0.05	-0.08	1.08	0.03
6(I)-H_2O	-1	2	no geometry found, H_2O detached				
	-1	4	no geometry found, H_2O detached				
	-1	6	no SCF convergence				
6(I)-FeOH-NH	-1	2	no geometry found, H_2O detached				
	-1	4	no geometry found, H_2O detached				
	-1	6	3.85	0.13	0.18	0.82	0.02
6(I)-NHOH	-1	2	2.00	0.00	-0.25	-0.71	-0.04
	-1	4	2.34	0.01	-0.12	0.82	-0.04
6(III)-NH	0	2	1.86	-0.02	-0.21	-0.60	-0.03
	0	4	2.31	0.00	-0.18	0.84	0.03
	0	6	no SCF convergence				

Table S6: Gibbs free enthalpies of reactions I-X. Corrected Gibbs enthalpies of formation of reactants and products Δ*G* in Eh and Gibbs free enthalpy of reaction $\Delta_r G$ in eV.

Fe(III)-Cl → Fe(III) + Cl^-						
Complex	**Δ*G*(Fe(III)-Cl) / Eh**	**Δ*G*(Fe(III)) / Eh**	**Δ*G*(Cl^-) / Eh**			**$\Delta_r G$ / eV**
1	-5621.6348	-5161.2004	-460.3921			1.1510
2	-4005.4197	-3544.9875	-460.3921			1.0911
3	-3636.3644	-3175.9340	-460.3921			1.0408
4	-4094.3673	-3633.9370	-460.3921			1.0382
5	-3793.5015	-3333.0721	-460.3921			1.0153
6	-4107.7511	-3647.3234	-460.3921			0.9695
Fe(III) + e^- → Fe(II)						
Complex	**Δ*G*(Fe(III)) / Eh**	**Δ*G*(Fe(II)) / Eh**	**$\Delta_r G$ / eV**	**FSPE(OLYP) Fe(III) / Eh**	**FSPE(OLYP) Fe(II) / Eh**	**ΔFSPE(OLYP) / eV**
1	-5161.2004	-5161.3651	-4.4814	-5161.5415	-5161.7081	-4.5331
2	-3544.9875	-3545.1479	-4.3655	-3545.4995	-3545.6591	-4.3440
3	-3175.9340	-3176.0881	-4.1911	-3176.4603	-3176.6158	-4.2315
4	-3633.9370	-3634.0908	-4.1853	-3634.5808	-3634.7345	-4.1811
5	-3333.0721	-3333.2256	-4.1773	-3333.6989	-3333.8530	-4.1931
6	-3647.3234	-3647.4771	-4.1821	-3648.1473	-3648.3029	-4.2336
Fe(II) + e^- → Fe(I)						
Complex	**Δ*G*(Fe(II)) / Eh**	**Δ*G*(Fe(I)) / Eh**	**$\Delta_r G$ / eV**	**FSPE(OLYP) Fe(II) / Eh**	**FSPE(OLYP) Fe(I) / Eh**	**ΔFSPE(OLYP) / eV**
1	-5161.3651	-5161.4947	-3.5253	-5161.7081	-5161.8337	-3.4176
2	-3545.1479	-3545.2693	-3.3028	-3545.6591	-3545.7793	-3.2708
3	-3176.0881	-3176.2066	-3.2249	-3176.6158	-3176.7308	-3.1296
4	-3634.0908	-3634.2062	-3.1379	-3634.7345	-3634.8485	-3.1015
5	-3333.2256	-3333.3431	-3.1980	-3333.8530	-3333.9671	-3.1051
6	-3647.4771	-3647.5888	-3.0406	-3648.3029	-3648.4141	-3.0249
	Fe(I) + H_2O → Fe(III)-H + OH^-					
Complex	**Δ*G*(Fe(I)) / Eh**	**Δ*G*(H_2O) / Eh**	**Δ*G*(Fe(III)-H) / Eh**	**Δ*G*(OH^-) / Eh**	**$\Delta_r G$ / eV**	
1	-5161.4947	-76.4491	-5161.9208	-75.9496	1.9968	
2	-3545.2693	-76.4491	-3545.7028	-75.9496	1.7961	
3	-3176.2066	-76.4491	-3176.6464	-75.9496	1.6233	
4	-3634.2062	-76.4491	-3634.6516	-75.9496	1.4703	
5	-3333.3431	-76.4491	-3333.7848	-75.9496	1.5739	
6	-3647.5888	-76.4491	-3648.0351	-75.9496	1.4491	

Fe(II) + H_2O → Fe(II)-H_2O				
Complex	**Δ*G*(Fe(II)) / Eh**	**Δ*G*(H_2O) / Eh**	**Δ*G*(Fe(II)-H_2O) / Eh**	**$\Delta_r G$ / eV**
1	-5161.3651	-76.4491	-5237.7964	0.4852
2	-3545.1479	-76.4491	-3621.5756	0.5854
3	-3176.0881	-76.4491	-3252.5186	0.5062
4	-3634.0908	-76.4491	-3710.5192	0.5670
5	-3333.2256	-76.4491	-3409.6554	0.5269
6	-3647.4771	-76.4491	-3723.9006	0.6980
Fe(I) + H_2O → Fe(I)-H_2O				
Complex	**Δ*G*(Fe(I)) / Eh**	**Δ*G*(H_2O) / Eh**	**Δ*G*(Fe(I)-H_2O) / Eh**	**$\Delta_r G$ / eV**
1	-5161.4947	-76.4491	-5237.9050	1.0568
2	-3545.2693	-76.4491	-3621.6828	0.9690
3	-3176.2066	-76.4491	-3252.6153	1.0999
4	-3634.2062	-76.4491	------	------
5	-3333.3431	-76.4491	-3409.7519	1.0998
6	-3647.5888	-76.4491	------	------
Fe(I) + H_2O → Fe(I)-NHOH				
Complex	**Δ*G*(Fe(I)) / Eh**	**Δ*G*(H_2O) / Eh**	**Δ*G*(Fe(I)-NHOH) / Eh**	**$\Delta_r G$ / eV**
1	-5161.4947	-76.4491	-5237.9192	0.6689
2	-3545.2693	-76.4491	-3621.6973	0.5754
3	-3176.2066	-76.4491	-3252.6343	0.5832
4	-3634.2062	-76.4491	-3710.6359	0.5273
5	-3333.3431	-76.4491	-3409.7719	0.5538
6	-3647.5888	-76.4491	-3724.0151	0.6217
Fe(I)-NHOH → Fe(I)OH-NH (M=6)				
Complex	**Δ*G*(Fe(I)-NHOH) / Eh**	**Δ*G*(Fe(I)OH-NH) / Eh**		**$\Delta_r G$ / eV**
1	-5237.9192	-5237.8786		1.1057
2	-3621.6973	-3621.6571		1.0950
3	-3252.6343	-3252.5935		1.1089
4	-3710.6359	-3710.5963		1.0790
5	-3409.7719	-3409.7366		0.9603
6	-3724.0151	-3723.9758		1.0693
Fe(I)OH-NH → Fe(III)-NH + OH^-				
Complex	**Δ*G*(Fe(I)OH-NH) / Eh**	**Δ*G*(Fe(III)-NH) / Eh**	**Δ*G*(OH^-) / Eh**	**$\Delta_r G$ / eV**
1	-5237.8786	-5161.9144	-75.9496	0.3958
2	-3621.6571	-3545.6921	-75.9496	0.4166
3	-3252.5935	-3176.6351	-75.9496	0.2388
4	-3710.5963	-3634.6368	-75.9496	0.2685
5	-3409.7366	-3333.7733	-75.9496	0.3740
6	-3723.9758	-3648.0190	-75.9496	0.1959

Fe(III)-NH → Fe(III)-H			
Complex	**Δ*G*(Fe(III)-NH) / Eh**	**Δ*G*(Fe(III)-NH) / Eh**	**$\Delta_r G$ / eV**
1	-5161.9144	-5161.9208	-0.1736
2	-3545.6921	-3545.7028	-0.2909
3	-3176.6351	-3176.6464	-0.3077
4	-3634.6368	-3634.6516	-0.4045
5	-3333.7733	-3333.7848	-0.3142
6	-3648.0190	-3648.0351	-0.4379

Table S7: Selected bond lengths in Å for lowest lying spin states sorted by intermediate.

Name	M	FeN_1	FeN_2	FeN_3	FeN_4	ø(FeN)	Fe-L
1(III)Cl	6	2.090	2.091	2.090	2.091	2.091	2.223
2(III)-Cl	6	2.091	2.093	2.091	2.093	2.092	2.235
3(III)-Cl	6	2.091	2.092	2.091	2.092	2.092	2.242
4(III)-Cl	6	2.090	2.093	2.091	2.094	2.092	2.246
5(III)-Cl	6	2.091	2.093	2.091	2.093	2.092	2.243
6(III)-Cl	6	2.090	2.089	2.090	2.090	2.090	2.238
1(III)	4	1.965	1.965	1.964	1.964	1.965	
2(III)	4	1.960	1.960	1.960	1.960	1.960	
3(III)	4	1.959	1.958	1.959	1.959	1.959	
4(III)	4	1.955	1.956	1.956	1.956	1.956	
5(III)	4	1.959	1.958	1.958	1.958	1.958	
6(III)	4	1.964	1.964	1.964	1.964	1.964	
1(II)	3	1.991	1.987	1.991	1.987	1.989	
2(II)	3	1.988	1.983	1.988	1.983	1.986	
3(II)	3	1.987	1.982	1.987	1.982	1.985	
4(II)	3	1.979	1.984	1.979	1.984	1.982	
5(II)	3	1.986	1.981	1.986	1.981	1.984	
6(II)	3	1.991	1.987	1.991	1.986	1.989	
1(I)	2	1.981	1.979	1.985	1.988	1.983	
2(I)	2	1.975	1.975	1.974	1.975	1.975	
3(I)	2	1.977	1.977	1.977	1.977	1.977	
4(I)	2	1.971	1.972	1.972	1.972	1.972	
5(I)	2	1.976	1.976	1.976	1.976	1.976	
6(I)	2	1.982	1.981	1.982	1.981	1.982	
1(III)-H	2	1.984	1.983	1.979	1.978	1.981	1.481
2(III)-H	2	1.980	1.979	1.976	1.974	1.977	1.484
3(III)-H	2	1.979	1.975	1.974	1.973	1.975	1.486
4(III)-H	2	1.971	1.974	1.976	1.969	1.973	1.487
5(III)-H	2	1.981	1.976	1.973	1.971	1.975	1.486
6(III)-H	2	1.977	1.977	1.982	1.982	1.980	1.487
1(II)-H_2O	3	2.002	2.003	1.997	1.998	2.000	2.270
2(II)-H_2O	3	1.998	1.994	1.994	2.000	1.997	2.294
3(II)-H_2O	3	1.998	2.000	1.992	1.993	1.996	2.319
4(II)-H_2O	3	1.989	1.989	1.997	1.994	1.992	2.323
5(II)-H_2O	3	1.991	1.998	1.996	1.991	1.994	2.321
6(II)-H_2O	3	1.990	1.990	1.998	1.998	1.994	2.352
1(I)-H_2O	4	2.002	2.014	2.014	2.004	2.009	2.361
2(I)-H_2O	4	2.001	1.996	1.992	2.005	1.999	2.355
3(I)-H_2O	4	2.002	2.014	2.002	2.004	2.006	2.286
4(I)-H_2O	4	no geometry found, H_2O detached					
5(I)-H_2O	4	2.002	2.014	2.001	2.004	2.005	2.290
6(I)-H_2O	4	no geometry found, H_2O detached					

Name	M	FeN_1	FeN_2	FeN_3	FeN_4	ø(FeN)	N-H	O-H	Fe-O
1(I)-NHOH	2	1.979	1.985	1.996	1.981	1.985	2.034	0.987/ 0.977	3.031
2(I)-NHOH	2	1.983	1.973	1.971	1.973	1.975	1.985	0.990/ 0.976	3.375
3(I)-NHOH	2	1.968	1.970	1.981	1.970	1.972	1.977	0.991/ 0.976	3.353
4(I)-NHOH	2	1.967	1.966	1.967	1.978	1.970	1.972	0.992/ 0.976	3.348
5(I)-NHOH	2	1.967	1.969	1.980	1.969	1.971	1.975	0.992/ 0.976	3.355
6(I)-NHOH	2	1.989	1.977	1.974	1.976	1.979	1.992	0.991/ 0.976	3.208
1(I)-FeOH-NH	2	1.983	**2.184**	1.980	1.940	2.022	1.091	1.582/ 0.976	2.003
2(I)-FeOH-NH	2	1.985	1.946	1.989	**2.184**	2.026	1.093	1.583/ 0.976	2.012
3(I)-FeOH-NH	2	1.986	**2.179**	1.982	1.938	2.021	1.090	1.592/ 0.976	2.032
4(I)-FeOH-NH	2	**2.179**	1.982	1.939	1.989	2.022	1.092	1.585/ 0.976	2.034
5(I)-FeOH-NH	2	1.924	1.972	**2.159**	1.972	2.007	1.083	1.608/ 0.976	2.041
6(I)-FeOH-NH	2	no geometry found							
1(I)-FeOH-NH	6	2.071	**2.353**	2.077	2.037	2.135	1.057	1.732/ 0.976	1.961
2(I)-FeOH-NH	6	2.083	2.040	2.077	**2.362**	2.141	1.050	1.777/ 0.976	1.959
3(I)-FeOH-NH	6	1.985	**2.283**	1.980	1.971	2.055	1.039	1.934/ 0.977	1.917
4(I)-FeOH-NH	6	**2.327**	2.084	2.025	2.084	2.130	1.053	1.846/ 0.975	1.972
5(I)-FeOH-NH	6	2.006	2.059	**2.412**	2.091	2.142	1.050	1.786/ 0.975	1.978
6(I)-FeOH-NH	6	**2.436**	2.082	2.003	2.061	2.146	1.048	1.804/ 0.975	1.967
1(III)-NH	2	1.963	**2.095**	1.963	1.951	1.993	1.050		
2(III)-NH	2	**2.077**	1.953	1.942	1.953	1.981	1.064		
3(III)-NH	2	1.952	1.952	**2.078**	1.952	1.984	1.067		
4(III)-NH	2	1.969	1.952	1.969	**2.096**	1.997	1.075		
5(III)-NH	2	**2.098**	1.973	1.956	1.974	2.000	1.046		
6(III)-NH	2	1.969	**2.094**	1.969	1.952	1.996	1.059		

Table S8: Selected bond angles (°) for lowest lying spin states sorted by intermediate.

		N-Fe-N (adjacent)					N-Fe-N (opposite)			N-Fe-L				
Name	**M**	**N_1N_2**	**N_1N_4**	**N_2N_3**	**N_3N_4**	**ø**	**N_1N_3**	**N_2N_4**	**Ø**	**N_1**	**N_2**	**N_3**	**N_4**	**Ø**
1(III)Cl	6	87.1	87.1	87.0	87.1	87.0	153.6	153.9	153.8	103.2	103.1	103.2	103.1	103.1
2(III)-Cl	6	87.0	87.0	87.0	87.0	87.0	153.7	153.6	153.7	103.1	103.3	103.1	103.1	103.2
3(III)-Cl	6	87.0	87.0	87.0	87.0	87.0	153.2	153.7	153.4	103.4	103.2	103.4	103.1	103.3
4(III)-Cl	6	87.0	86.8	86.9	87.0	86.9	152.6	153.6	153.1	103.6	103.1	103.7	103.3	103.4
5(III)-Cl	6	86.9	87.0	87.0	86.9	86.9	153.0	153.6	153.3	103.5	103.2	103.5	103.2	103.3
6(III)-Cl	6	86.8	86.8	86.8	86.8	86.8	152.9	152.8	152.8	103.6	103.6	103.5	103.6	103.6
1(III)	4	90.1	90.1	90.1	90.2	90.1	174.4	174.3	174.4					
2(III)	4	90.2	90.2	90.2	90.2	90.2	173.9	173.8	173.8					
3(III)	4	90.2	90.1	90.2	90.2	90.2	173.9	173.7	173.8					
4(III)	4	89.6	90.3	90.2	89.5	89.9	174.1	175.9	175.0					
5(III)	4	90.2	90.2	90.2	90.2	90.2	174.0	173.7	173.9					
6(III)	4	90.2	90.1	90.1	90.2	90.2	174.1	174.0	174.1					
1(II)	3	90.0	90.0	90.0	90.0	90.0	177.4	177.9	177.6					
2(II)	3	90.1	90.1	90.1	90.0	90.1	175.8	177.0	176.4					
3(II)	3	90.1	90.1	90.1	90.1	90.1	175.4	176.7	176.0					
4(II)	3	90.1	90.1	90.1	90.1	90.1	176.4	174.7	175.5					
5(II)	3	90.1	90.1	90.1	90.1	90.1	175.2	176.5	175.8					
6(II)	3	90.0	90.0	90.0	90.0	90.0	179.4	179.3	179.3					
1(I)	2	90.4	89.9	90.2	89.7	90.0	176.7	176.6	176.7					
2(I)	2	90.1	90.1	90.2	90.2	90.1	174.2	174.2	174.2					
3(I)	2	90.3	90.0	90.0	90.3	90.1	174.5	174.5	174.5					
4(I)	2	90.2	90.2	90.2	90.2	90.2	173.8	173.7	173.8					
5(I)	2	90.3	90.0	90.0	90.3	90.1	174.3	174.3	174.3					
6(I)	2	90.0	90.0	90.0	90.0	90.0	177.5	177.5	177.5					
1(III)-H	2	90.3	89.5	89.6	90.5	89.9	172.4	178.2	175.3	88.2	86.8	99.3	95.0	92.3
2(III)-H	2	90.2	89.5	89.6	90.4	89.9	170.9	178.5	174.7	88.8	87.1	100.3	94.4	92.6
3(III)-H	2	90.3	89.5	89.6	90.4	89.9	170.1	178.5	174.3	88.8	87.4	101.1	94.1	92.8
4(III)-H	2	89.6	90.4	90.1	89.6	89.9	169.5	178.5	174.0	101.3	87.6	89.2	93.8	93.0
5(III)-H	2	90.1	89.4	89.7	90.5	89.9	169.8	178.6	174.2	89.0	87.4	101.3	93.9	92.9
6(III)-H	2	90.4	89.5	89.5	90.1	89.9	174.5	174.6	174.6	97.8	97.6	87.7	87.7	92.7
1(II)-H_2O	3	90.5	89.3	89.3	90.6	89.9	173.8	176.9	175.3	90.1	89.0	96.1	94.2	
2(II)-H_2O	3	89.2	90.5	90.6	89.3	89.9	173.2	177.4	175.3	90.2	94.7	96.6	87.9	
3(II)-H_2O	3	90.5	89.3	89.4	90.6	89.9	173.1	178.0	175.5	88.8	87.3	98.1	94.7	
4(II)-H_2O	3	90.7	89.3	89.4	90.5	89.9	178.4	172.5	175.5	86.7	89.6	94.8	97.8	
5(II)-H_2O	3	89.3	90.7	90.5	89.3	89.9	172.8	178.1	175.4	97.5	87.1	89.6	94.8	
6(II)-H_2O	3	90.7	89.3	89.3	90.5	89.9	175.8	175.8	175.8	98.2	98.3	86.0	85.9	
1(I)-H_2O	4	89.8	90.3	90.0	89.7	89.9	174.7	177.5	176.1	84.9	96.8	100.3	85.7	
2(I)-H_2O	4	89.8	89.9	90.1	89.9	89.9	173.0	177.8	175.4	85.7	87.2	96.4	99.8	
3(I)-H_2O	4	89.8	90.0	89.8	90.0	89.9	172.2	176.8	174.5	93.7	95.3	94.1	88.0	
4(I)-H_2O	4	no geometry found, H_2O detached												
5(I)-H_2O	4	89.8	90.0	89.8	90.0	89.9	172.1	176.9	174.5	87.8	93.7	95.3	94.2	
6(I)-H_2O	**4**	no geometry found, H_2O detached												

		N-Fe-N (adjacent)					N-Fe-N (opposite)							
Name	**M**	**N_1N_2**	**N_1N_4**	**N_2N_3**	**N_3N_4**	**ø**	**N_1N_3**	**N_2N_4**	**Ø**	**Fe-N-H_1**	**N-H_1-O**	**Fe-O-H_1**	**Fe-O-H_2**	**N-Fe-O**
1(I)-NHOH	2	90.3	90.1	89.7	90.1	90.1	176.1	176.3	176.2	75.4	165.9	46.9	80.8	69.9
2(I)-NHOH	2	90.2	89.9	90.2	90.5	90.2	173.8	173.7	173.7	82.1	171.6	33.5	90.0	60.9
3(I)-NHOH	2	90.4	90.2	89.9	90.2	90.2	173.4	173.5	173.5	81.2	170.4	32.6	93.0	61.1
4(I)-NHOH	2	90.3	90.2	90.4	90.0	90.2	173.1	173.0	173.1	81.1	170.0	32.5	92.3	61.1
5(I)-NHOH	2	90.4	90.2	89.9	90.2	90.2	173.3	173.3	173.3	81.2	170.1	32.4	92.6	61.0
6(I)-NHOH	2	89.9	90.0	90.3	90.1	90.1	175.5	175.6	175.6	78.0	170.1	38.2	92.1	64.9
1(I)-FeOH-NH	2	87.8	91.9	88.2	91.8	89.9	175.4	172.2	173.8	65.6	151.4	66.6	104.0	76.4
2(I)-FeOH-NH	2	91.9	88.1	91.8	87.7	89.9	174.6	172.4	173.5	64.6	153.2	65.5	103.3	76.7
3(I)-FeOH-NH	2	87.7	91.9	88.1	91.8	89.9	174.8	171.8	173.3	64.8	153.7	64.8	102.8	76.7
4(I)-FeOH-NH	2	88.3	87.5	91.8	91.8	89.9	172.5	174.3	173.4	64.5	154.2	64.7	102.6	76.5
5(I)-FeOH-NH	2	91.8	91.8	88.0	88.3	90.0	169.9	176.3	173.1	66.9	151.2	65.2	102.8	76.8
6(I)-FeOH-NH	2	no geometry found												
1(I)-FeOH-NH	6	86.7	91.0	86.6	91.0	88.8	161.4	164.8	163.1	62.5	151.8	68.5	108.6	77.2
2(I)-FeOH-NH	6	90.9	86.7	91.0	86.7	88.8	161.7	164.4	163.1	63.1	150.3	68.5	108.1	78.1
3(I)-FeOH-NH	6	86.3	91.5	86.8	91.6	89.0	166.2	162.6	164.4	70.8	137.6	68.8	107.0	82.8
4(I)-FeOH-NH	6	85.2	84.9	92.3	91.0	88.3	162.0	157.7	159.9	61.7	151.7	64.8	107.6	81.4
5(I)-FeOH-NH	6	93.5	92.7	84.6	83.8	88.6	166.0	155.7	160.8	60.8	153.8	67.9	108.8	77.5
6(I)-FeOH-NH	6	83.3	83.7	92.6	92.5	88.0	161.6	153.3	157.4	57.9	156.9	66.7	107.9	78.1
1(III)-NH	2	88.7	91.5	88.7	91.5	90.1	173.8	176.2	175.0	73.0				
2(III)-NH	2	88.9	88.9	91.4	91.4	90.2	174.3	173.4	173.8	66.3				
3(III)-NH	2	91.3	91.3	88.9	88.9	90.1	176.2	172.5	174.4	65.1				
4(III)-NH	2	91.4	88.7	91.4	88.7	90.1	175.2	176.0	175.6	63.0				
5(III)-NH	2	88.8	88.6	91.3	91.3	90.0	179.2	177.4	178.3	75.7				
6(III)-NH	2	88.7	91.4	88.7	91.4	90.1	175.5	176.2	175.9	68.3				

Table S9: Selected dihedral angles for lowest lying spin states by intermediates in °. Smallest dihedral angle C_1(P)-C_2(P)-C_1(PhX)-C_2(PhX) (see Figure S5) for each of four PhX groups per complex is reported.

Name	M	PhX_1	PhX_2	PhX_3	PhX_4	ø
1(III)Cl	**6**	69.7	68.3	68.2	68.9	68.8
2(III)-Cl	**6**	59.7	59.7	59.8	59.6	59.7
3(III)-Cl	**6**	58.9	58.9	59.0	58.8	58.9
4(III)-Cl	**6**	54.7	54.8	55.0	54.5	54.8
5(III)-Cl	**6**	57.5	57.4	57.5	57.4	57.5
6(III)-Cl	**6**	90.0	89.6	89.9	89.5	89.7
1(III)	**4**	67.2	67.7	67.9	66.8	67.4
2(III)	**4**	56.6	56.7	56.6	56.5	56.6
3(III)	**4**	55.7	55.8	55.7	55.6	55.7
4(III)	**4**	39.6	49.0	47.3	48.9	46.2
5(III)	**4**	54.5	54.2	54.2	54.4	54.3
6(III)	**4**	83.9	83.8	83.6	83.9	83.8
1(II)	**3**	70.6	69.9	69.3	70.3	70.0
2(II)	**3**	59.5	59.8	59.6	59.6	59.6
3(II)	**3**	59.6	59.9	59.7	59.8	59.7
4(II)	**3**	44.0	56.7	56.7	56.6	53.5
5(II)	**3**	58.6	58.6	58.5	58.7	58.6
6(II)	**3**	88.9	88.7	89.1	88.9	88.9
1(I)	**2**	69.7	69.4	69.0	69.8	69.5
2(I)	**2**	56.5	56.6	56.5	56.4	56.5
3(I)	**2**	59.8	58.9	59.9	58.8	59.3
4(I)	**2**	44.5	57.8	57.9	57.7	54.5
5(I)	**2**	59.0	58.3	59.0	58.1	58.6
6(I)	**2**	86.6	86.6	86.6	86.5	86.6
1(III)-H	**2**	70.4	69.3	70.1	70.5	70.1
2(III)-H	**2**	60.6	60.1	60.7	60.4	60.4
3(III)-H	**2**	60.1	59.6	60.3	60.1	60.0
4(III)-H	**2**	55.0	55.1	55.5	55.6	55.3
5(III)-H	**2**	58.7	58.4	59.1	58.7	58.8
6(III)-H	**2**	89.0	88.8	88.9	89.0	88.9

Name	M	PhX_1	PhX_2	PhX_3	PhX_4	ø
1(II)-H_2O	**3**	69.7	69.8	69.2	71.1	70.0
2(II)-H_2O	**3**	60.6	60.8	60.9	59.1	60.3
3(II)-H_2O	**3**	60.0	60.8	59.7	60.8	60.3
4(II)-H_2O	**3**	57.8	57.8	58.2	56.5	57.6
5(II)-H_2O	**3**	59.6	59.5	59.7	58.7	59.4
6(II)-H_2O	**3**	88.7	90.8	88.2	88.9	89.2
1(I)-H_2O	**4**	70.2	65.1	68.8	65.3	67.4
2(I)-H_2O	**4**	55.9	50.6	56.4	51.0	53.4
3(I)-H_2O	**4**	56.5	56.5	56.0	56.3	56.3
4(I)-H_2O	**4**	no geometry found, H_2O detached				
5(I)-H_2O	**4**	56.1	55.9	55.9	55.6	55.9
6(I)-H_2O	**4**	no geometry found, H_2O detached				
1(I)-NHOH	**2**	69.4	68.1	70.2	68.2	69.0
2(I)-NHOH	**2**	53.7	57.1	54.0	56.6	55.3
3(I)-NHOH	**2**	58.0	58.7	58.1	58.8	58.4
4(I)-NHOH	**2**	56.7	56.7	57.2	56.8	56.9
5(I)-NHOH	**2**	58.0	58.4	58.1	57.6	58.0
6(I)-NHOH	**2**	86.6	84.4	84.1	84.7	84.9
1(I)-FeOH-NH	**2**	70.9	67.2	66.9	72.0	69.3
2(I)-FeOH-NH	**2**	70.7	61.8	61.5	71.0	66.3
3(I)-FeOH-NH	**2**	65.4	76.9	77.5	65.3	71.3
4(I)-FeOH-NH	**2**	73.6	63.7	63.8	72.2	68.3
5(I)-FeOH-NH	**2**	57.5	57.7	53.9	53.7	55.7
6(I)-FeOH-NH	**2**	no geometry found				
1(I)-FeOH-NH	**6**	69.5	68.6	63.4	63.0	66.1
2(I)-FeOH-NH	**6**	49.3	48.7	62.2	61.9	55.5
3(I)-FeOH-NH	**6**	67.8	67.9	50.7	50.7	59.3
4(I)-FeOH-NH	**6**	70.0	59.6	60.3	71.5	65.3
5(I)-FeOH-NH	**6**	53.5	50.8	49.8	49.3	50.8
6(I)-FeOH-NH	**6**	73.8	72.6	80.8	78.6	76.5
1(III)-NH	**2**	72.576	72.498	65.066	64.776	68.7
2(III)-NH	**2**	71.681	71.292	64.89	64.606	68.1
3(III)-NH	**2**	66.363	66.472	74.083	73.835	70.2
4(III)-NH	**2**	68.853	63.224	62.795	69.094	66.0
5(III)-NH	**2**	50.775	55.667	55.925	50.684	53.3
6(III)-NH	**2**	81.708	77.489	77.294	81.479	79.5

Table S10: Mulliken spin populations for lowest lying spin state sorted by intermediate. Multiplicity M, axial ligand L (sum if more than one atom), nitrogen atoms N (sum), P porphin (sum of all atoms in porphin plane) and substituted aryl rest PhX (sum).

	M	Fe	Σ(L)	Σ(N)	Σ(P)	Σ(PhX)
1(III)Cl	6	4.119	0.296	0.317	0.256	0.012
2(III)-Cl	6	4.114	0.277	0.327	0.266	0.017
3(III)-Cl	6	4.069	0.344	0.364	0.208	0.015
4(III)-Cl	6	4.102	0.255	0.339	0.293	0.011
5(III)-Cl	6	4.107	0.261	0.337	0.278	0.017
6(III)-Cl	6	4.116	0.270	0.336	0.270	0.007
1(III)	4	2.861		-0.179	0.289	0.029
2(III)	4	2.860		-0.174	0.284	0.029
3(III)	4	2.863		-0.174	0.280	0.030
4(III)	4	2.714		-0.138	0.342	0.083
5(III)	4	2.866		-0.173	0.276	0.031
6(III)	4	2.869		-0.188	0.292	0.026
1(II)	3	2.345		-0.242	-0.109	0.006
2(II)	3	2.340		-0.242	-0.102	0.004
3(II)	3	2.332		-0.245	-0.093	0.006
4(II)	3	2.326		-0.243	-0.077	-0.005
5(II)	3	2.330		-0.244	-0.091	0.006
6(II)	3	2.332		-0.253	-0.083	0.003
1(I)	2	2.098		-0.247	-0.813	-0.038
2(I)	2	2.107		-0.242	-0.777	-0.088
3(I)	2	2.058		-0.251	-0.760	-0.048
4(I)	2	2.041		-0.251	-0.771	-0.019
5(I)	2	2.052		-0.251	-0.753	-0.049
6(I)	2	2.035		-0.264	-0.731	-0.041
1(III)-H	2	1.239	-0.102	-0.145	0.018	-0.011
2(III)-H	2	1.227	-0.099	-0.142	0.017	-0.004
3(III)-H	2	1.220	-0.097	-0.142	0.019	-0.001
4(III)-H	2	1.216	-0.096	-0.140	0.022	-0.003
5(III)-H	2	1.218	-0.096	-0.141	0.018	0.001
6(III)-H	2	1.238	-0.101	-0.151	0.030	-0.015
1(II)-H_2O	3	2.354	0.036	-0.231	-0.120	-0.038
2(II)-H_2O	3	2.348	0.033	-0.231	-0.176	0.026
3(II)-H_2O	3	2.334	0.031	-0.232	-0.098	-0.035
4(II)-H_2O	3	2.331	0.031	-0.230	-0.128	-0.003
5(II)-H_2O	3	2.333	0.031	-0.232	-0.160	0.028
6(II)-H_2O	3	2.327	0.029	-0.238	-0.078	-0.040
1(I)-H_2O	4	2.380	0.030	-0.127	0.571	0.146
2(I)-H_2O	4	2.381	0.029	-0.157	0.433	0.315
3(I)-H_2O	4	2.418	0.032	-0.099	0.533	0.117
4(I)-H_2O	4	no geometry found, H_2O detached				
5(I)-H_2O	4	2.416	0.031	-0.097	0.535	0.114
6(I)-H_2O	4	no geometry found, H_2O detached				

Name	M	Fe	O	H_1	H_2	N_1	N_2	N_3	N_4	Σ(P)	Σ(PhX)
1(I)-FeOH-NH	2	2.218	0.101	0.006	0.001	-0.058	**-0.033**	-0.055	-0.086	-1.053	-0.041
2(I)-FeOH-NH	2	2.201	0.100	0.005	0.001	-0.054	-0.085	-0.057	**-0.030**	-0.995	-0.086
3(I)-FeOH-NH	2	2.166	0.092	0.005	0.001	-0.058	**-0.030**	-0.056	-0.089	-0.996	-0.035
4(I)-FeOH-NH	2	2.161	0.091	0.005	0.001	**-0.029**	-0.055	-0.090	-0.058	-1.015	-0.010
5(I)-FeOH-NH	2	2.180	0.090	0.006	0.001	-0.086	-0.059	**-0.035**	-0.056	-0.968	-0.072
6(I)-FeOH-NH	2	no geometry found									
1(I)-FeOH-NH	6	3.668	0.127	0.005	0.004	0.055	**-0.042**	0.06	-0.020	1.037	0.106
2(I)-FeOH-NH	6	3.665	0.127	0.005	0.004	0.047	-0.018	0.042	**-0.042**	0.921	0.249
3(I)-FeOH-NH	6	2.876	0.187	0.006	0.003	-0.005	**-0.013**	-0.007	0.003	1.789	0.162
4(I)-FeOH-NH	6	3.904	0.143	0.003	0.003	**0.029**	0.003	0.096	0.015	0.782	0.022
5(I)-FeOH-NH	6	3.883	0.134	0.004	0.003	0.092	0.031	0.035	**0.013**	0.712	0.094
6(I)-FeOH-NH	6	3.851	0.131	0.002	0.002	**-0.006**	0.085	0.000	0.099	0.818	0.019
1(I)-NHOH	2	2.067	0.008	-0.003	0.000	-0.062	-0.061	**-0.053**	-0.063	-0.797	-0.037
2(I)-NHOH	2	2.085	0.004	-0.004	0.000	**-0.052**	-0.060	-0.059	-0.061	-0.766	-0.087
3(I)-NHOH	2	2.023	0.004	-0.004	0.000	-0.061	-0.063	**-0.054**	-0.062	-0.742	-0.041
4(I)-NHOH	2	2.011	0.004	-0.003	0.000	-0.062	-0.061	-0.063	**-0.054**	-0.755	-0.017
5(I)-NHOH	2	2.017	0.004	-0.004	0.000	-0.061	-0.063	**-0.054**	-0.062	-0.736	-0.041
6(I)-NHOH	2	2.003	0.005	-0.004	-0.001	**-0.055**	-0.066	-0.065	-0.066	-0.713	-0.038
1(III)-NH	2	1.977		-0.013		-0.064	**-0.027**	-0.064	-0.051	-0.721	-0.038
2(III)-NH	2	1.889		-0.025		-0.063	-0.053	-0.063	**-0.021**	-0.619	-0.046
3(III)-NH	2	1.849		-0.028		-0.063	**-0.021**	-0.063	-0.055	-0.592	-0.027
4(III)-NH	2	1.821		-0.033		**-0.020**	-0.063	-0.056	-0.064	-0.578	-0.008
5(III)-NH	2	1.937		-0.012		-0.052	-0.066	**-0.033**	-0.066	-0.672	-0.036
6(III)-NH	2	1.863		-0.022		**-0.025**	-0.064	-0.056	-0.064	-0.596	-0.035

Table S11: Calculated Mössbauer parameter for lowest lying spin state sorted by intermediate. Multiplicity M, final single point energy for B3LYP density functional FSPE(B3LYP) in Eh, Mulliken spin population (MSP) at iron ion, electron density at iron nucleus $\rho(0)$ in au^{-3}, isomer shift δ_{iso} in mm s^{-1} and quadrupole splitting ΔE_Q in mm s^{-1}.

Name	M	FSPE(B3LYP)	MSP(Fe)	$\rho(0)$ / au^{-3}	δ_{iso} / mm s^{-1}	ΔE_Q / mm s^{-1}
1(III)Cl	6	-5621.0794	4.23	11816.705	0.487	0.396
2(III)-Cl	6	-4005.1873	4.22	11816.680	0.499	0.405
3(III)-Cl	6	-3636.0948	4.26	11816.753	0.463	0.806
4(III)-Cl	6	-4094.3033	4.21	11816.649	0.515	0.402
5(III)-Cl	6	-3793.4560	4.21	11816.659	0.510	0.394
6(III)-Cl	6	-4107.9206	4.22	11816.672	0.503	0.345
1(III)	4	-5160.6972	3.01	11816.980	0.351	4.901
2(III)	4	-3544.8085	3.01	11817.001	0.340	4.953
3(III)	4	-3175.8512	3.01	11817.010	0.336	4.981
4(III)	4	-3633.9248	2.98	11817.055	0.313	4.513
5(III)	4	-3333.0802	3.01	11817.009	0.336	4.996
6(III)	4	-3647.5440	3.01	11817.003	0.340	4.933
1(II)	3	-5160.8771	2.19	11816.302	0.687	-3.307
2(II)	3	-3544.9814	2.19	11816.324	0.676	-3.338
3(II)	3	-3176.0202	2.19	11816.339	0.668	-3.356
4(II)	3	-3634.0947	2.19	11816.354	0.661	-3.375
5(II)	3	-3333.2478	2.19	11816.344	0.666	-3.363
6(II)	3	-3647.7131	2.20	11816.320	0.678	-3.351
1(I)	2	-5160.9923	2.16	11816.392	0.642	2.425
2(I)	2	-3545.0895	2.15	11816.434	0.621	2.491
3(I)	2	-3176.1234	2.12	11816.409	0.633	2.390
4(I)	2	-3634.1967	2.11	11816.434	0.621	2.422
5(I)	2	-3333.3501	2.11	11816.413	0.632	2.391
6(I)	2	-3647.8138	2.10	11816.376	0.650	2.319
1(III)-H	2	-5161.4372	1.21	11817.166	0.259	-2.436
2(III)-H	2	-3545.5428	1.21	11817.177	0.253	-2.467
3(III)-H	2	-3176.5823	1.20	11817.182	0.251	-2.480
4(III)-H	2	-3634.6573	1.20	11817.193	0.245	-2.509
5(III)-H	2	-3333.8101	1.20	11817.185	0.249	-2.499
6(III)-H	2	-3648.2756	1.22	11817.165	0.259	-2.353
1(II)-H_2O	3	-5237.3306	2.16	11816.173	0.751	-1.414
2(II)-H_2O	3	-3621.4344	2.16	11816.191	0.742	-1.399
3(II)-H_2O	3	-3252.4727	2.15	11816.205	0.735	-1.400
4(II)-H_2O	3	-3710.5472	2.15	11816.219	0.727	-1.405
5(II)-H_2O	3	-3409.7003	2.15	11816.212	0.731	-1.401
6(II)-H_2O	3	-3724.1638	2.16	11816.224	0.725	-1.391

1(I)-H_2O	4	-5237.4426	2.19	11816.183	0.746	-1.306
2(I)-H_2O	4	-3621.5406	2.18	11816.219	0.728	-1.329
3(I)-H_2O	4	-3252.5690	2.21	11816.175	0.749	-2.717
4(I)-H_2O	4		no geometry found, H_2O detached			
5(I)-H_2O	4	-3409.7954	2.21	11816.178	0.748	-2.731
6(I)-H_2O	4		no geometry found, H_2O detached			
1(I)-FeOH-NH	2	-5237.4012	0.12	11816.161	0.757	-1.846
2(I)-FeOH-NH	2	-3621.4987	0.12	11816.132	0.771	-1.840
3(I)-FeOH-NH	2	-3252.5343	0.13	11816.141	0.766	-1.903
4(I)-FeOH-NH	2	-3710.6072	0.13	11816.134	0.770	-1.896
5(I)-FeOH-NH	2	-3409.7632	0.13	11816.186	0.744	-2.012
6(I)-FeOH-NH	2		no geometry found			
1(I)-FeOH-NH	6	-5237.4196	3.78	11815.766	0.952	4.099
2(I)-FeOH-NH	6	-3621.5202	3.77	11815.758	0.956	4.073
3(I)-FeOH-NH	6	-3252.5150	2.94	11816.759	0.460	2.406
4(I)-FeOH-NH	6	-3710.6233	3.80	11815.734	0.968	4.191
5(I)-FeOH-NH	6	-3409.7814	3.80	11815.789	0.941	4.122
6(I)-FeOH-NH	6	-3724.2400	3.78	11815.811	0.930	4.194
1(I)-NHOH	2	-5237.4389	2.12	11816.373	0.652	2.314
2(I)-NHOH	2	-3621.5373	2.12	11816.424	0.626	2.428
3(I)-NHOH	2	-3252.5721	2.08	11816.423	0.627	2.360
4(I)-NHOH	2	-3710.6455	2.07	11816.434	0.621	2.369
5(I)-NHOH	2	-3409.7990	2.07	11816.426	0.625	2.358
6(I)-NHOH	2	-3724.2632	2.06	11816.383	0.647	2.271
1(III)-NH	2	-5161.4353	1.98	11816.513	0.582	0.666
2(III)-NH	2	-3545.5228	1.99	11816.162	0.756	-3.050
3(III)-NH	2	-3176.5697	1.97	11816.494	0.591	0.823
4(III)-NH	2	-3634.6340	1.90	11816.137	0.768	-2.731
5(III)-NH	2	-3333.8063	1.94	11816.598	0.540	-0.767
6(III)-NH	2	-3648.2543	1.90	11816.245	0.715	-2.336

Table S12: Gibbs free enthalpies for lowest lying spin state sorted by intermediate. Final single point energies (FSPE) for TPSS and OLYP density functionals in Eh, standard enthalpy (Δ*H*), entropy (Δ*S*) and Gibbs free enthalpy (Δ*G*) of formation in Eh, corrected Gibbs free enthalpy of formation (ΔG_{corr}) in Eh, Gibbs enthalpy of reaction relative to fourfold coordinated Fe(III) species in Eh and in eV.

Name	M	FSPE(TPSS)	FSPE(OLYP)	Δ*H*	Δ*S*	Δ*G*	ΔG_{corr}	$\Delta G - \Delta G_{Fe(III)}$ / Eh	$\Delta G - \Delta G_{Fe(III)}$ / eV
1(III)Cl	6	-5621.8097	-5621.9737	-5621.3269	0.1440	-5621.4709	-5621.6348	-0.0423	-1.15
2(III)-Cl	6	-4005.2150	-4005.9281	-4004.5856	0.1210	-4004.7066	-4005.4197	-0.0401	-1.09
3(III)-Cl	6	-3636.1700	-3636.886	-3635.5404	0.1075	-3635.6479	-3636.3644	-0.0382	-1.04
4(III)-Cl	6	-4094.3782	-4095.0066	-4093.6122	0.1266	-4093.7389	-4094.3673	-0.0382	-1.04
5(III)-Cl	6	-3793.3699	-3794.1241	-3792.6257	0.1215	-3792.7472	-3793.5015	-0.0373	-1.02
6(III)-Cl	6	-4107.7778	-4108.5730	-4106.8051	0.1509	-4106.9559	-4107.7511	-0.0356	-0.97
1(III)	4	-5161.3710	-5161.5415	-5160.8889	0.1410	-5161.0299	-5161.2004	0.0000	0.00
2(III)	4	-3544.7805	-3545.4995	-3544.1531	0.1155	-3544.2686	-3544.9875	0.0000	0.00
3(III)	4	-3175.7382	-3176.4603	-3175.1119	0.1001	-3175.2120	-3175.9340	0.0000	0.00
4(III)	4	-3633.9493	-3634.5808	-3633.1842	0.1213	-3633.3055	-3633.9370	0.0000	0.00
5(III)	4	-3332.9389	-3333.6989	-3332.2009	0.1112	-3332.3120	-3333.0721	0.0000	0.00
6(III)	4	-3647.3450	-3648.1473	-3646.3734	0.1477	-3646.5211	-3647.3234	0.0000	0.00
1(II)	3	-5161.5496	-5161.7081	-5161.0687	0.1379	-5161.2067	-5161.3651	-0.1647	-4.48
2(II)	3	-3544.9515	-3545.6591	-3544.3231	0.1172	-3544.4403	-3545.1479	-0.1604	-4.37
3(II)	3	-3175.9045	-3176.6158	-3175.2760	0.1008	-3175.3768	-3176.0881	-0.1540	-4.19
4(II)	3	-3634.1115	-3634.7345	-3633.3475	0.1203	-3633.4679	-3634.0908	-0.1538	-4.19
5(II)	3	-3333.1039	-3333.8530	-3332.3646	0.1118	-3332.4765	-3333.2256	-0.1535	-4.18
6(II)	3	-3647.5124	-3648.3029	-3646.5418	0.1448	-3646.6865	-3647.4771	-0.1537	-4.18
1(I)	2	-5161.6843	-5161.8337	-5161.2042	0.1411	-5161.3453	-5161.4947	-0.2942	-8.01
2(I)	2	-3545.0800	-3545.7793	-3544.4534	0.1166	-3544.5700	-3545.2693	-0.2818	-7.67
3(I)	2	-3176.0274	-3176.7308	-3175.4020	0.1012	-3175.5031	-3176.2066	-0.2725	-7.42
4(I)	2	-3634.2324	-3634.8485	-3633.4702	0.1199	-3633.5901	-3634.2062	-0.2691	-7.32
5(I)	2	-3333.2258	-3333.9671	-3332.4867	0.1151	-3332.6018	-3333.3431	-0.2710	-7.38
6(I)	2	-3647.6329	-3648.4141	-3646.6641	0.1436	-3646.8077	-3647.5888	-0.2654	-7.22
1(III)-H	2	-5162.1283	-5162.2705	-5161.6402	0.1384	-5161.7786	-5161.9208	-0.2209	-6.01
2(III)-H	2	-3545.5315	-3546.2229	-3544.8966	0.1148	-3545.0114	-3545.7028	-0.2158	-5.87
3(III)-H	2	-3176.4854	-3177.1803	-3175.8502	0.1013	-3175.9515	-3176.6464	-0.2129	-5.79
4(III)-H	2	-3634.6928	-3635.2999	-3633.9206	0.1238	-3634.0445	-3634.6516	-0.2151	-5.85
5(III)-H	2	-3333.6850	-3334.4178	-3332.9365	0.1155	-3333.0520	-3333.7848	-0.2132	-5.80
6(III)-H	2	-3648.0936	-3648.8676	-3647.1147	0.1463	-3647.2611	-3648.0351	-0.2122	-5.77
1(II)-H_2O	3	-5238.0389	-5238.1580	-5237.5308	0.1465	-5237.6773	-5237.7964	-0.1469	-4.00
2(II)-H_2O	3	-3621.4403	-3622.1086	-3620.7861	0.1210	-3620.9072	-3621.5756	-0.1389	-3.78
3(II)-H_2O	3	-3252.3926	-3253.0644	-3251.7386	0.1082	-3251.8468	-3252.5186	-0.1354	-3.68
4(II)-H_2O	3	-3710.5995	-3711.1834	-3709.8113	0.1239	-3709.9352	-3710.5192	-0.1330	-3.62
5(II)-H_2O	3	-3409.5919	-3410.3017	-3408.8240	0.1216	-3408.9456	-3409.6554	-0.1342	-3.65
6(II)-H_2O	3	-3723.9996	-3724.7479	-3723.0026	0.1497	-3723.1523	-3723.9006	-0.1280	-3.48

1(I)-H_2O	4	-5238.1545	-5238.2626	-5237.6511	0.1457	-5237.7968	-5237.9050	-0.2554	-6.95
2(I)-H_2O	4	-3621.5523	-3622.2114	-3620.9019	0.1218	-3621.0238	-3621.6828	-0.2462	-6.70
3(I)-H_2O	4	-3252.4894	-3253.1580	-3251.8392	0.1075	-3251.9467	-3252.6153	-0.2321	-6.32
4(I)-H_2O	4								
5(I)-H_2O	4	-3409.6875	-3410.3940	-3408.9226	0.1228	-3409.0453	-3409.7519	-0.2306	-6.28
6(I)-H_2O	4								
1(I)-FeOH-NH	2	-5238.1268	-5238.2368	-5237.6233	0.1410	-5237.7643	-5237.8742	-0.2247	-6.11
2(I)-FeOH-NH	2	-3621.5196	-3622.1820	-3620.8684	0.1213	-3620.9897	-3621.6521	-0.2154	-5.86
3(I)-FeOH-NH	2	-3252.4685	-3253.1367	-3251.8184	0.1068	-3251.9253	-3252.5935	-0.2104	-5.72
4(I)-FeOH-NH	2	-3710.6730	-3711.2535	-3709.8860	0.1255	-3710.0115	-3710.5920	-0.2058	-5.60
5(I)-FeOH-NH	2	-3409.6728	-3410.3742	-3408.9079	0.1210	-3409.0289	-3409.7303	-0.2091	-5.69
6(I)-FeOH-NH	2								
1(I)-FeOH-NH	6	-5238.1163	-5238.2340	-5237.6131	0.1477	-5237.7608	-5237.8786	-0.2290	-6.23
2(I)-FeOH-NH	6	-3621.5150	-3622.1841	-3620.8658	0.1221	-3620.9879	-3621.6571	-0.2204	-6.00
3(I)-FeOH-NH	6	-3252.4427	-3253.1099	-3251.7924	0.1075	-3251.8999	-3252.5671	-0.1840	-5.01
4(I)-FeOH-NH	6	-3710.6592	-3711.2535	-3709.8719	0.1301	-3710.0020	-3710.5963	-0.2101	-5.72
5(I)-FeOH-NH	6	-3409.6613	-3410.3755	-3408.8980	0.1244	-3409.0224	-3409.7366	-0.2154	-5.86
6(I)-FeOH-NH	6	-3724.0630	-3724.8151	-3723.0701	0.1535	-3723.2237	-3723.9758	-0.2033	-5.53
1(I)-NHOH	2	-5238.1641	-5238.2783	-5237.6592	0.1458	-5237.8050	-5237.9192	-0.2697	-7.34
2(I)-NHOH	2	-3621.5611	-3622.2259	-3620.9085	0.1240	-3621.0326	-3621.6973	-0.2607	-7.09
3(I)-NHOH	2	-3252.5086	-3253.1780	-3251.8571	0.1078	-3251.9649	-3252.6343	-0.2511	-6.83
4(I)-NHOH	2	-3710.7141	-3711.2957	-3709.9252	0.1291	-3710.0543	-3710.6359	-0.2497	-6.80
5(I)-NHOH	2	-3409.7072	-3410.4145	-3408.9411	0.1236	-3409.0647	-3409.7719	-0.2507	-6.82
6(I)-NHOH	2	-3724.1150	-3724.8596	-3723.1190	0.1516	-3723.2706	-3724.0151	-0.2426	-6.60
1(III)-NH	2	-5162.1134	-5162.2657	-5161.6232	0.1389	-5161.7621	-5161.9144	-0.2145	-5.84
2(III)-NH	2	-3545.5097	-3546.2133	-3544.8728	0.1157	-3544.9886	-3545.6921	-0.2051	-5.58
3(III)-NH	2	-3176.4623	-3177.1701	-3175.8250	0.1024	-3175.9274	-3176.6351	-0.2016	-5.49
4(III)-NH	2	-3634.6679	-3635.2871	-3633.8933	0.1243	-3634.0177	-3634.6368	-0.2002	-5.45
5(III)-NH	2	-3333.6685	-3334.4105	-3332.9194	0.1119	-3333.0313	-3333.7733	-0.2016	-5.49
6(III)-NH	2	-3648.0744	-3648.8550	-3647.0931	0.1453	-3647.2384	-3648.0190	-0.1961	-5.34

Table S13: Comparison of predicted and experimental Mössbauer parameters for Fe(III)Cl complexes 1, 3 and 4.

	calc. (this work)			**exp.**			
Complex	**$\rho(0)$**	**δ_{iso}**	**ΔE_Q**	**δ_{iso}**	**ΔE_Q**	**T**	**Ref.**
1	11816.7047	0.487	0.396	0.38	0.85	4.2 K	**[1,2]**
3	11816.7530	0.463	0.806	0.41	0.46	4.2 K	**[2,3]**
4	11816.6488	0.515	0.402	0.37	1.03	4.2 K	**[1,2]**

SI references

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