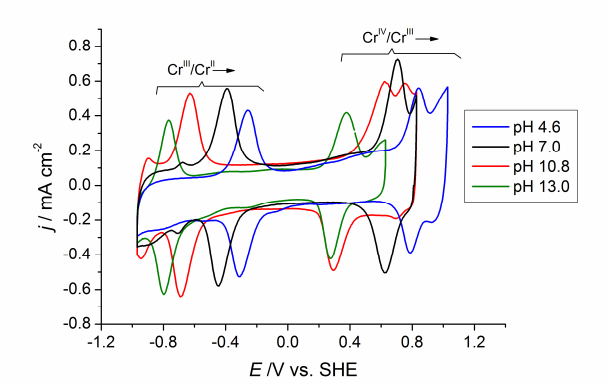
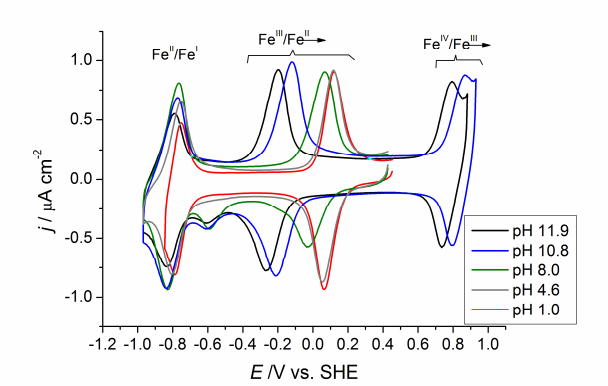


S1. Cyclic voltammograms of a pyrolitic graphite electrode with adsorbed Cr protoporphyrin IX, in 0.1 M acetate pH 4.6 (—), 0.1 M phosphate pH 7.0 (—), 0.1 M phosphate pH 10.8 (—) and 0.1 M sodium hydroxide, pH 13.0 (—). Voltammograms were measured at a scan rate of 2 V/s.



S2. Cyclic voltammograms of a DDAB film with incorporated Fe protoporphyrin IX on a pyrolitic graphite electrode, in 0.1 M HCl pH 1.0 (—), 0.1 M acetate pH 4.6 (—), 0.1 M phosphate pH 8.0 (—), 0.1 M phosphate, pH 10.8 (—) and 0.1 M phosphate, pH 11.9 (—). Voltammograms were measured at a scan rate of 2 V/s.

S3. The calculated formation energies of the different metal porphyrins, for different spin states and different oxidation states (in eV). The corresponding symmetry is also given. The energies of the optimized geometries were calculated with the OPBE functional.

$[M^{I}]^{-}$

S	Cr		Mn		Fe		Co		Ni	
0			-203.79[a]	D_{4h}			-206.50	D_{4h}		
½	-205.28[a]	D_{2h}			-206.43[a]	D_{4h}			-205.564[a]	D_{4h}
1			-205.15	D_{4h}			-205.97	D_{2h}		
3/2	-206.73	D_{2h}			-206.20[a]	D_{4h}			-204.409	D_{2h}
2			[b]				-205.22	D_{2h}		
5/2	-206.50	D_{2h}			-205.71	D_{2h}				

$[M^{II}]$

S	Cr		Mn		Fe		Co		Ni	
0					-203.99	D_{2h}			-204.11	D_{4h}
½			-201.97[a]	D_{4h}			-204.80	D_{4h}		
1	-203.84[a]	D_{2h}			-204.75	D_{2h}			-203.21	D_{4h}
3/2			-203.55[a]	D_{2h}			-203.95	D_{4h}		
2	-205.33	D_{4h}			-204.40	D_{2h}				
5/2			-203.55	D_{4h}						

$[M^{III}\text{-OH}]$

S	Cr		Mn		Fe		Co		Ni	
0			-209.93[a]	C_s			-211.38	C_s		
½	-211.72[a]	C_s			-211.68	C_s			-209.84	C_s
1			-210.48	C_s			-211.30	C_s		
3/2	-212.72	C_s			-211.82	C_s			-209.77	C_s
2			[b]				-211.19	C_s		
5/2	-210.82	C_s			-212.09	C_s			[b]	

$[M^{IV}\text{-O}]$

S	Cr		Mn		Fe		Co		Ni	
0	-209.48	C_{4v}			[b]				-205.03	C_{2v}
½			-207.20	C_{2v}			-206.74	C_{4v}		
1	-209.35	C_{2v}			-208.57	C_{4v}			-205.19	C_{2v}
3/2			-207.40	C_{4v}			-207.51	C_{4v}		
2	-207.70	C_{4v}			-208.15	C_{4v}			-205.80	C_{4v}
5/2			-205.44	C_{2v}			[b]			

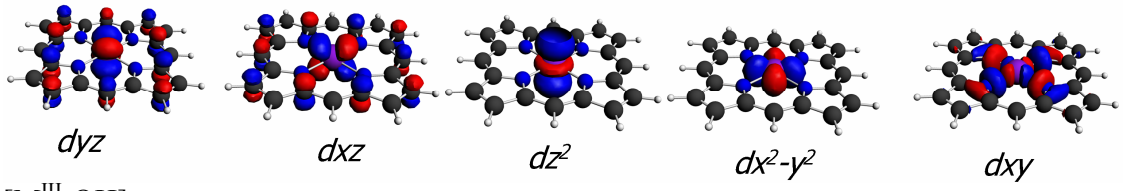
[a] Spin contaminated value (Wittbrodt et al., J. Chem. Phys. 1995, 99, 3465). Energies have not been corrected for this spin contamination. However, correction would not affect the designation of ground state spin states. Only in the case of $[M^{I}]^{-}$ there would be some influence of spin contamination on the ground state energies.

[b] SCF does not converge.

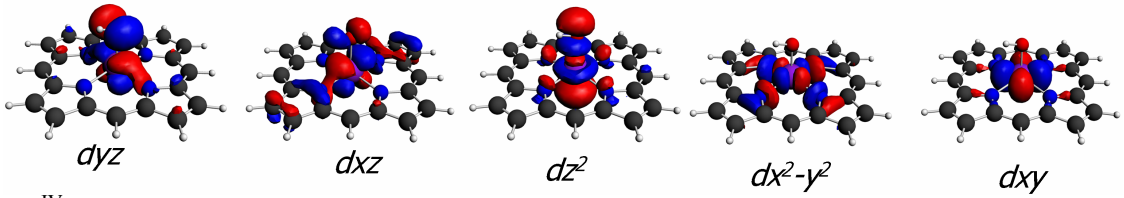
S4. Occupations of metalloporphyrin orbitals that have mainly metal d-orbital character for the different metalloporphyrins in different oxidation states. The total number of d electrons and the spin states are also given. Representations of these orbitals and the names of the corresponding d-orbitals are shown below the table.

Oxidation state	Metal	*dyz*	*dxz*	dz^2	dx^2-y^2	*dxy*	nr. of d electrons	Spin
$[M^{I}]^-$	Cr	2	1	1	1	0	5	3/2
	Mn	2	2	1	1	0	6	1
	Fe	2	2	1	2	0	7	1/2
	Co	2	2	2	2	0	8	0
	Ni	2	2	2	2	1	9	1/2
$[M^{II}]$	Cr	1	1	1	1	0	4	2
	Mn	1	1	1	1	1	5	5/2
	Fe	2	1	1	2	0	6	1
	Co	2	2	1	2	0	7	1/2
	Ni	2	2	2	2	0	8	0
$[M^{III}$-OH]	Cr	1	1	0	0	1	3	3/2
	Mn	1	1	0	0	2	4	1
	Fe	1	1	1	1	1	5	5/2
	Co	2	2	0	0	2	6	0
	Ni	2	2	1	0	2	7	1/2
$[M^{IV}$-O]	Cr	0	0	0	0	2	2	0
	Mn	1	1	0	0	1	3	3/2
	Fe	1	1	0	0	2	4	1
	Co	1	1	0	1	2	5	3/2
	Ni	1	1	1	1	2	6	2

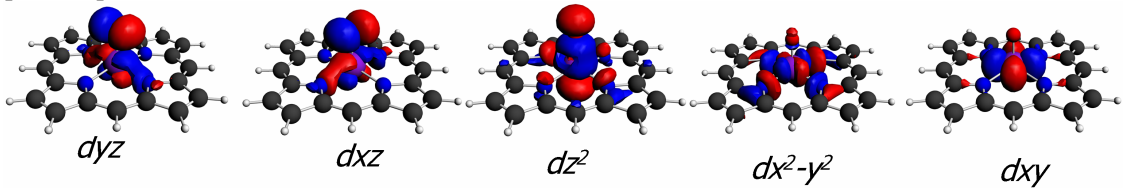
$[M^{I}]^-$ and $[M^{II}]$



$[M^{III}$-OH]



$[M^{IV}$-O]



S5. The calculated formation energies of the different metal porphyrins, for different spin states and different oxidation states (in eV). The corresponding symmetry is also given. The energies were calculated with the B3LYP functional.

$[M^{I}]^{-}$

S	Cr	Mn	Fe	Co	Ni
0		-214.32[a]		-219.36	
½	-216.68[a]		-218.11[a]		-217.82
1		-215.80[a]		-219.55	
3/2	-218.01[a]		-218.03[a]		-217.72
2		[b]			
5/2	-217.81		-218.12		

$[M^{II}]$

S	Cr	Mn	Fe	Co	Ni
0			-215.04		-216.87
½		-212.63[a]		-218.34	
1	-215.38[a]		-216.95		-216.50
3/2		-214.30		-217.81	
2	-216.64		-216.84		
5/2		-214.60			

$[M^{III}\text{-OH}]$

S	Cr	Mn	Fe	Co	Ni
0		-221.58[a]		-225.68	
½	-224.23[a]		-224.67		-223.54
1		-222.57		-225.57	
3/2	-225.10		-224.95		-223.53
2		[b]		-225.63	
5/2	-223.00		-225.22		[b]

$[M^{IV}\text{-O}]$

S	Cr	Mn	Fe	Co	Ni
0	-221.41		[b]		-217.69
½		-218.64		-220.49[a]	
1	-221.17		-221.02		-218.76
3/2		-218.84		-221.32	
2	-219.10		-220.73		-219.07
5/2		-216.88		[b]	

[a] Spin contaminated value (Wittbrodt et al., J. Chem. Phys. 1995, 99, 3465). Energies have not been corrected for this spin contamination. However, correction would not affect the designation of ground state spin states. Only in the case of $[M^{I}]^{-}$ there would be some influence of spin contamination on the ground state energies.

[b] SCF does not converge.