Understanding the role of nitrogen-doping and surface topology in the binding of Fe(III)/Fe(II) to biobased carbon electrodes

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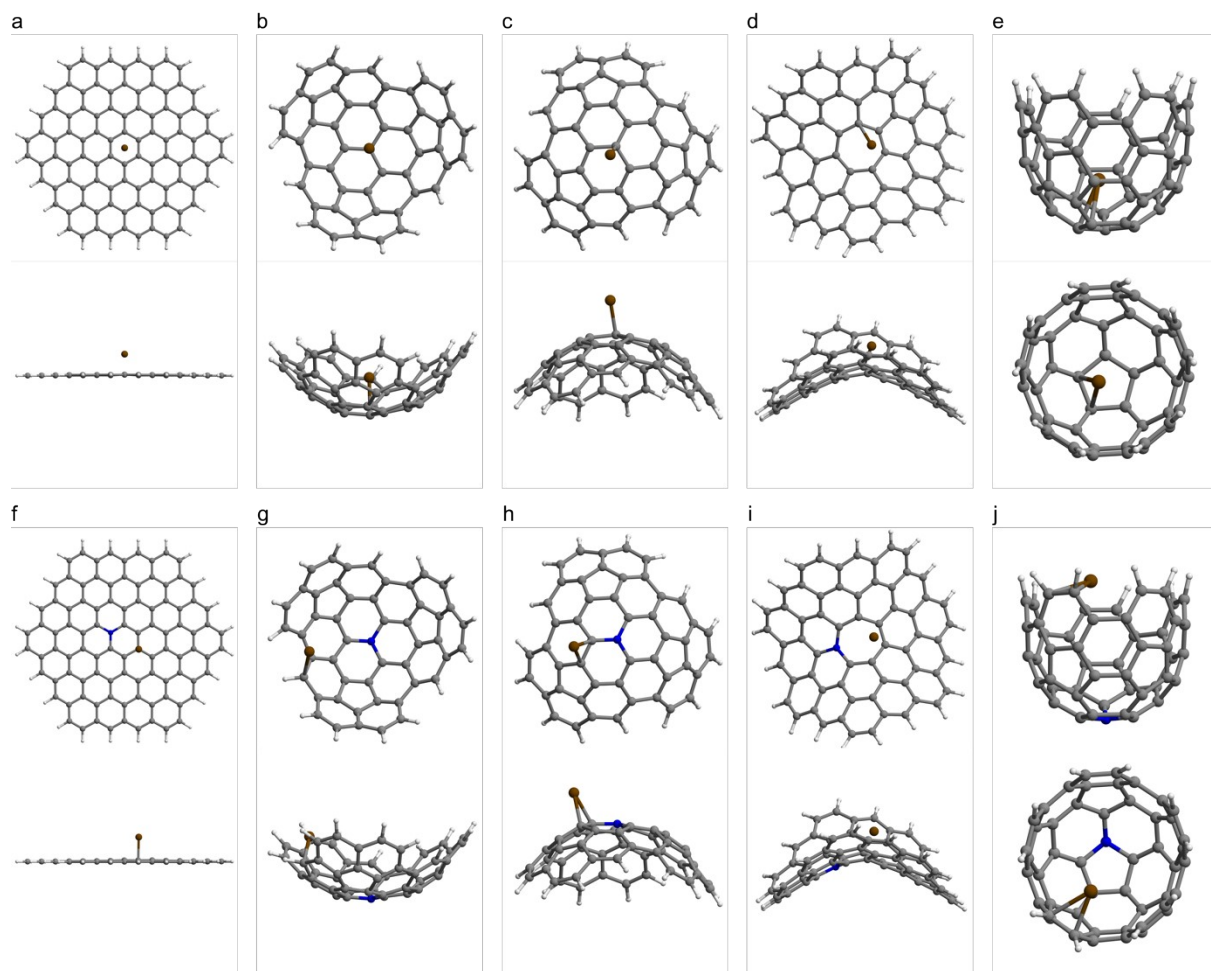## Supporting information

Optimised geometries

Figure S1. Optimised geometries of the Fe(II) complexes in their most stable spin multiplicity configuration: a) Fe(II)@Planar (M=5); b) Fe(II)@Endo (M=4); c) Fe(II)@Exo (M=4); d) Fe(II)@Negative (M=4); e) Fe(II)@Well (M=5); f) Fe(II)@N-Planar (M=4); g) Fe(II)@N-Endo (M=5); h) Fe(II)@N-Exo (M=5); i) Fe(II)@N-Negative (M=5); j) Fe(II)@N-Well (M=4)
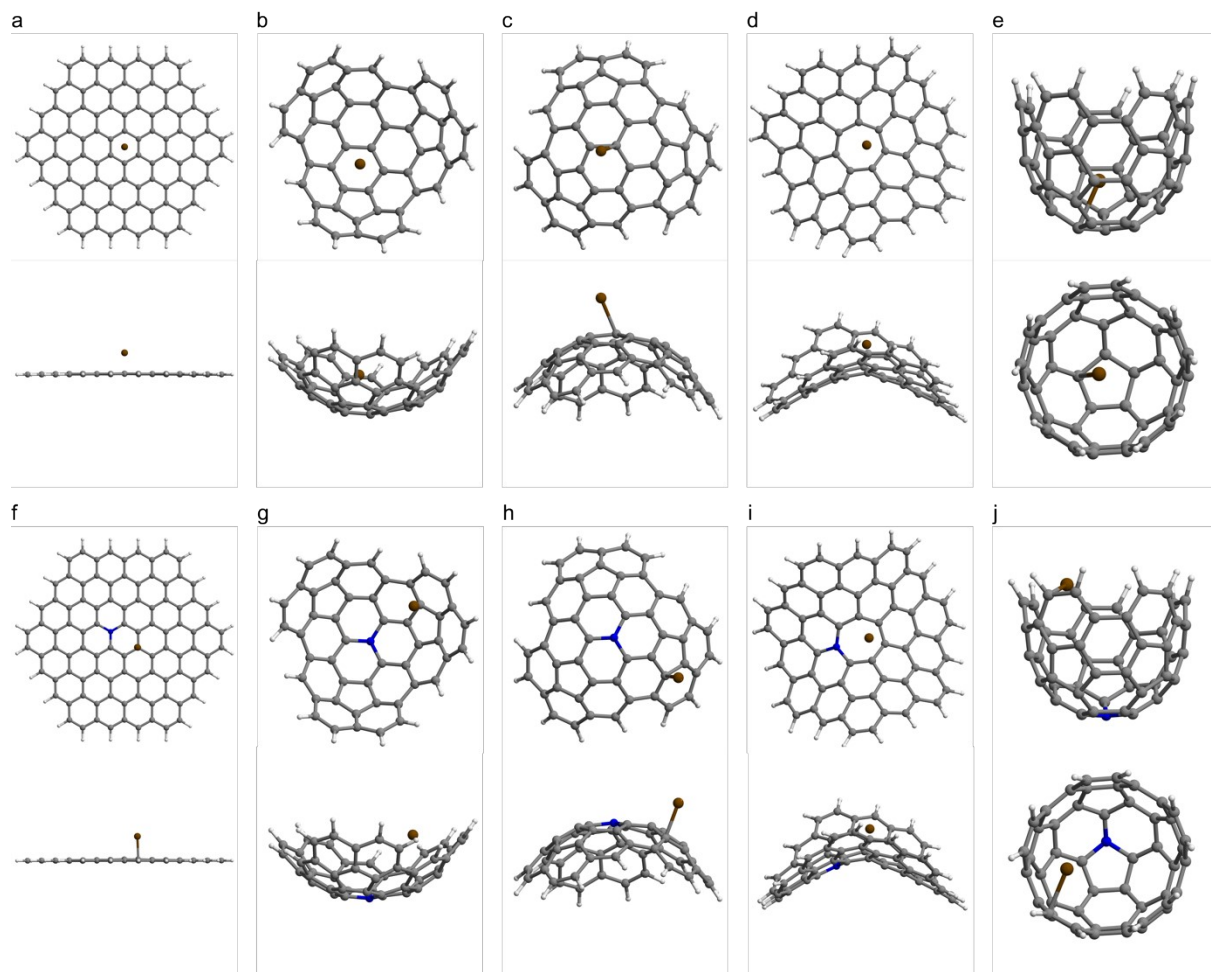
Figure S2. Optimised geometries of the Fe(III) complexes in their most stable spin multiplicity configuration: a) Fe(III)@Planar (M=6); b) Fe(III)@Endo (M=5); c) Fe(III)@Exo (M=5); d) Fe(III)@Negative (M=5); e) Fe(III)@Well (M=6); f) Fe(III)@N-Planar (M=5); g) Fe(III)@N-Endo (M=6); h) Fe(III)@N-Exo (M=6); i) Fe(III)@N-Negative (M=6); j) Fe(III)@N-Well (M=5)
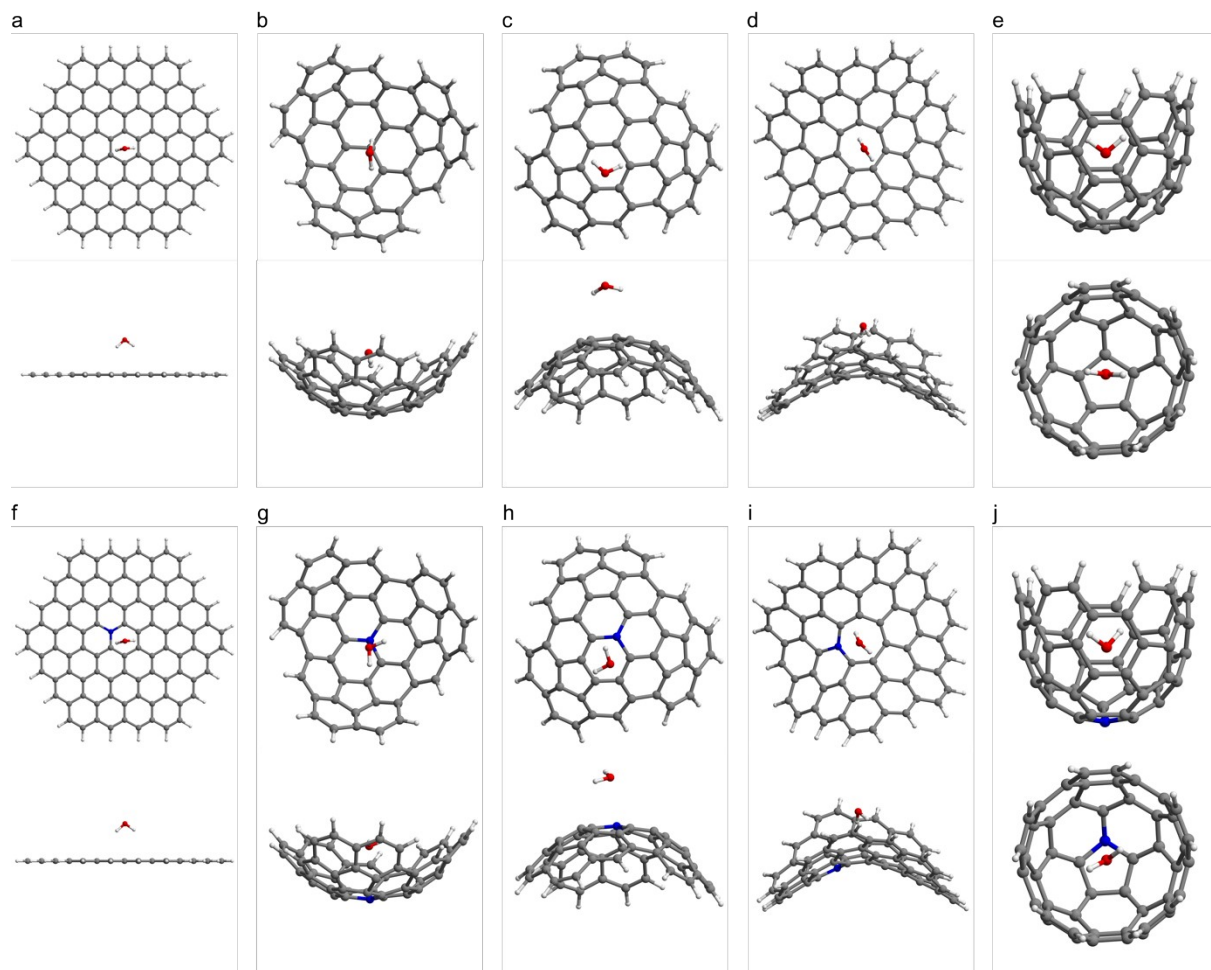
Figure S3. Optimised geometries of the H$_2$O complexes: a) Fe H$_2$O@Planar; b) H$_2$O@Endo; c) H$_2$O@; d) H$_2$O@Negative; e) H$_2$O@Well; f) H$_2$O@N-Planar; g) H$_2$O@N-Endo; h) H$_2$O@N-Exo; i) H$_2$O@N-Negative; j) H$_2$O@N-Well

The role of spin multiplicity in the adsorption of ions on carbon surfaces

Since iron is a transition metal with a natural tendency to form coordination complexes in solution, it is important to consider the possible multiplicities that iron ions could adopt upon adsorption at the electrocatalyst surface. This is key to properly quantify binding energies in carbon electrocatalysts, but it also requires calculating the spin contamination, as mentioned in the methods section. As shown in **Figure S4**, the most stable spin multiplicities are $M = 5$ for Fe(II), and $M = 6$ for Fe(III), indicating that iron in both oxidation states prefers to maximise the number of unpaired electrons and stay in open-shell configuration.
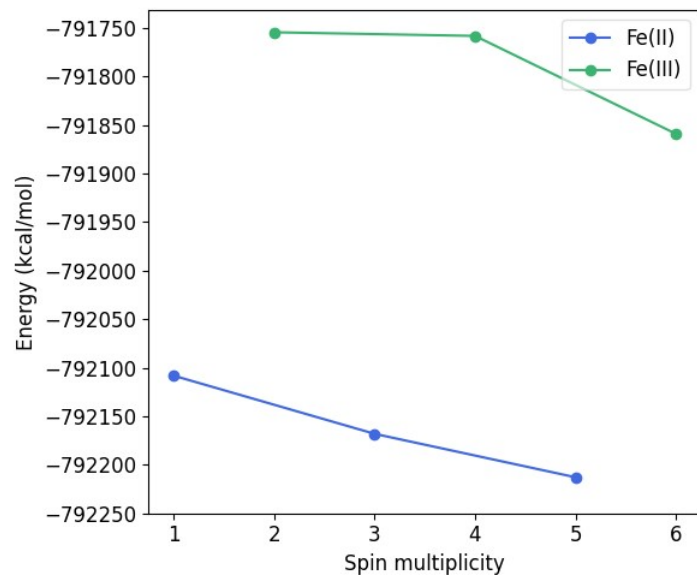
Figure S4. Total energy values of Fe(II) at $M = 1,3,5$ and Fe(III) at $M = 2,4,6$.

In the case of water, as expected, the spin multiplicity was always $M = 1$ for all the complexes studied. The exact energy values of all the adsorbates and the spin contamination associated to the calculation can be found in **Table S1**.

Table S1. Multiplicity, total energy, and spin contamination values of the adsorbates

Adsorbate	Multiplicity	Energy (kcal·mol^{-1})	Spin contamination
Fe(II)	1	-792108.282	0.000000
	3	-792168.135	0.947420
	5	-792212.844	0.001309
Fe(III)	2	-791754.649	2.001283
	4	-791758.409	0.000697
	6	-791859.164	0.000189
H_2O	1	-47860.032	0.000000

For the complexes formed upon adsorption of both ions and water, the inclusion of nitrogen in the surface structures includes an additional unpaired electron, changing the multiplicity by one with respect to the pristine carbon structures. For example, the pristine Planar and pristine Well surfaces have no unpaired electrons, therefore, $S = 0$, whereas their N-doped forms have one unpaired electron, with $S = 1/2$. The other curved surfaces experience the opposite effect. Due to their structure, the pristine forms have got $S = 1/2$ whilst their N-doped forms present $S = 0$. The spin multiplicity of each surface along their energy values and spin contamination are shown in **Table S2**.

Table S2. Multiplicity, total energy, and spin contamination values of the pristine and N-doped surfaces.

Surface	Multiplicity	Energy (kcal·mol⁻¹)	Spin contamination
Planar pristine	1	-2300090.307	0.000000
Planar N-doped	2	-2310481.269	0.343969
Positive pristine	2	-1174816.528	0.143257
Positive N-doped	1	-1185233.421	0.000000
Negative pristine	2	-1511265.406	0.199996
Negative N-doped	1	-1521677.169	0.000000
Well pristine	1	-1196703.934	0.000000
Well N-doped	2	-1207109.353	0.055630

The binding energies of the complexes that Fe(II), Fe(III), and H_2O formed with the surfaces are presented in **Figure S5**. The Endo complexes are discussed first, whereas Exo and Well complexes are discussed later in this paper.

Fe(II) complexes showed a stronger binding energy with higher spin multiplicities (**Figure S5 (a-b)**), when adsorbed onto both pristine and N-doped surfaces, regardless of the curvature. All the biding energies are in the range of $35.5\ kcal \cdot mol^{-1}$ to $-63.4\ kcal \cdot mol^{-1}$, and the values decrease as the multiplicity increases (bear in mind that more negative E_B imply a stronger interaction). The cases in which the total electronic spin of the complex is reduced by ½, it is caused by the unpaired electron from the surface model. The more negative E_B, depending on the increase of multiplicity, indicate that Fe(II) ion prefers maximising the number of unpaired electrons to coordinate with the π electrons of the carbon surface and/or the nitrogen atom when binding to the surface.
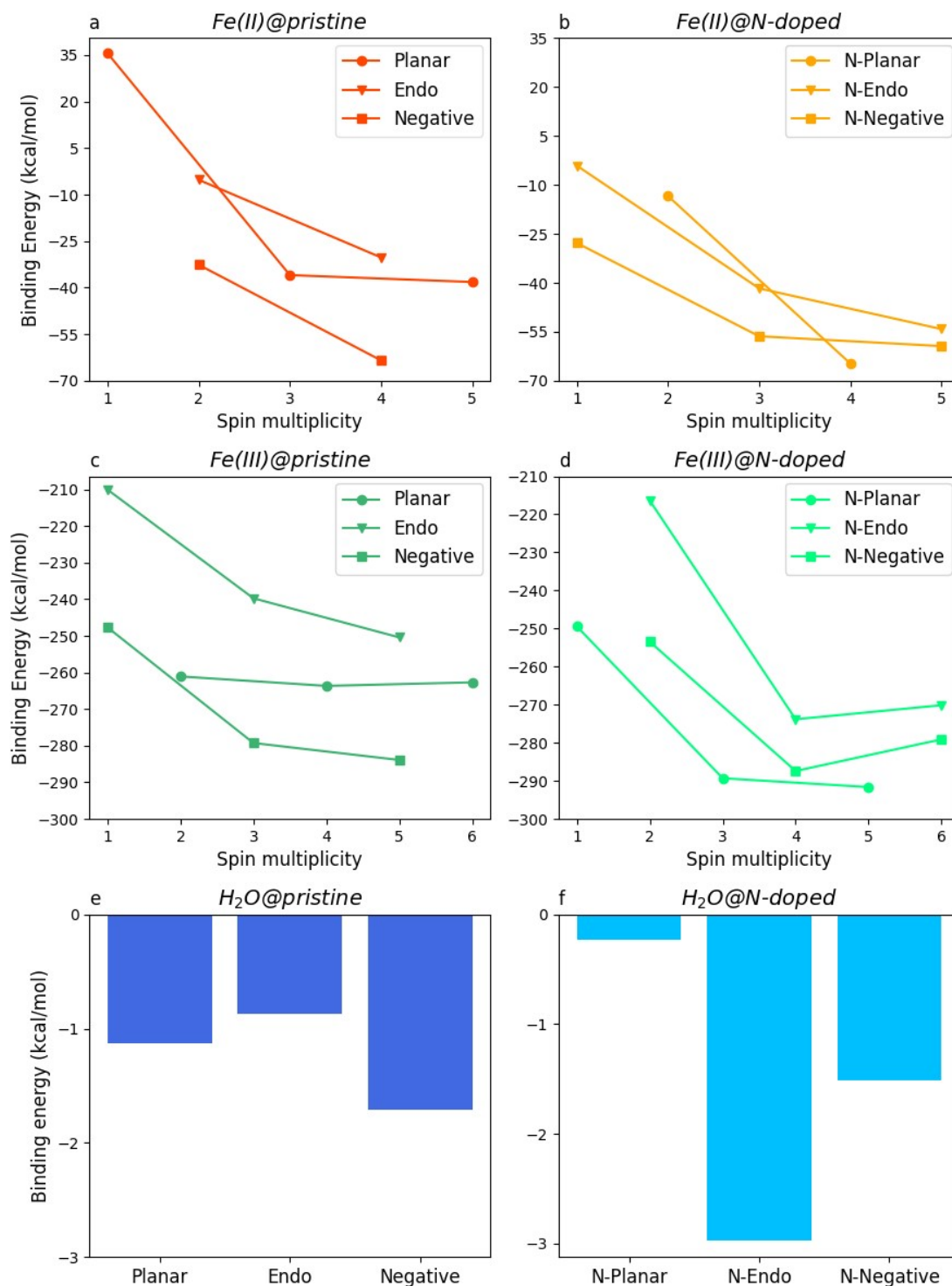
Figure S5. Binding energy values of Fe(II), Fe(III), and H$_2$O adsorbed onto pristine (a, c, e) and N-doped (b, d, f) surfaces, respectively.

The results of the adsorption of Fe(III) are considerably different to those for Fe(II). To begin with, all the binding energies are below $-200\ kcal \cdot mol^{-1}$, which is around 30 times stronger than the

E_B for Fe(II) in some cases. Furthermore, the binding energies, as observed in **Figure S5 (c-d)**, do not always decrease with increasing spin multiplicity.

For the complexes with spin multiplicities $M = 1, 3, 5$, the binding energy is more favourable at $M = 5$, which follows the same trend as Fe(II) complexes, but the same behaviour is not observed with complexes with the possible spin multiplicities being $M = 2, 4, 6$, in which the lowest E_B is at $M = 4$. This apparent discrepancy is due to the existence of spin contamination. In the case of complexes with $M = 4$, the spin contamination was too high to be neglected, whereas the same complexes at $M = 6$ offer little to no spin contamination. Therefore, the complex with $M = 6$ is considered as the most stable and these energy values will be used in the discussion.

Energies and spin contamination

Table S3. Multiplicity, total energy, and spin contamination values of the Planar complexes

Complex	Multiplicity	Energy (kcal·mol^{-1})	Binding energy (kcal·mol^{-1})	Spin contamination
Fe(II)@Planar	1	-3092267.618	35.533	0.000141
	3	-3092339.082	-35.931	1.222092
	5	-3092341.311	-38.161	0.251855
Fe(III)@Planar	2	-3092210.551	-261.081	2.160763
	4	-3092213.127	-263.657	1.425138
	6	-3092212.159	-262.689	0.200200
H$_2$O@Planar	1	-2347951.467	-1.129	0.000000

Table S4. Multiplicity, total energy, and spin contamination values of the N-Planar complexes

Complex	Multiplicity	Energy (kcal·mol^{-1})	Binding energy (kcal·mol^{-1})	Spin contamination
Fe(II)@N-Planar	2	-3102707.516	-13.403	1.004518
	4	-3102758.820	-64.707	0.184464
Fe(III)@N-Planar	1	-3102589.903	-249.470	2.136784
	3	-3102629.744	-289.311	1.259786
	5	-3102632.060	-291.627	0.247289
H$_2$O@N-Planar	2	-2358341.534	-0.233	0.398753

Table S5. Multiplicity, total energy, and spin contamination values of the Exo complexes

Complex	Multiplicity	Energy (kcal·mol^{-1})	Binding energy (kcal·mol^{-1})	Spin contamination
Fe(II)@Exo	2	-1967044.651	-15.279	0.985276
	4	-1967076.637	-47.265	0.291456
Fe(III)@Exo	1	-1966895.284	-219.593	1.800387
	3	-1966920.820	-245.129	1.546378
	5	-1966937.431	-261.739	0.032621
H$_2$O@Exo	2	-1222678.207	-1.647	0.142934

Table S6. Multiplicity, total energy, and spin contamination values of the N-Exo complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@N-Exo	1	-1977462.761	-16.496	2.055909
	3	-1977494.061	-47.796	1.226647
	5	-1977492.834	-46.569	0.180271
Fe(III)@N-Exo	2	-1977325.912	-233.328	0.978551
	4	-1977346.385	-253.801	0.571825
	6	-1977363.501	-270.917	0.109782
H₂O@N-Exo	1	-1233095.935	-2.482	0.000000

Table S7. Multiplicity, total energy, and spin contamination values of the Endo complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@Endo	2	-1967034.605	-5.233	1.810695
	4	-1967059.608	-30.236	0.467706
Fe(III)@Endo	1	-1966885.777	-210.086	1.808712
	3	-1966915.424	-239.733	1.916191
	5	-1966926.103	-250.411	0.02093
H₂O@Endo	2	-1222677.434	-0.875	0.142686

Table S8. Multiplicity, total energy, and spin contamination values of the N-Endo complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@N-Endo	1	-1977450.378	-4.113	2.046278
	3	-1977487.961	-41.696	1.13029
	5	-1977500.422	-54.157	0.045688
Fe(III)@N-Endo	2	-1977309.015	-216.431	1.010387
	4	-1977366.405	-273.821	0.947873
	6	-1977362.715	-270.131	0.090225
H₂O@N-Endo	1	-1233096.426	-2.973	0.000000

Table S9. Multiplicity, total energy, and spin contamination values of the Negative complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@Negative	2	-2303510.870	-32.619	1.012424
	4	-2303541.669	-63.418	0.505693
Fe(III)@Negative	1	-2303372.273	-247.704	2.102796
	3	-2303403.829	-279.259	1.582532
	5	-2303408.464	-283.894	0.017842
H₂O@Negative	2	-1559127.147	-1.709	0.196656

Table S10. Multiplicity, total energy, and spin contamination values of the N-Negative complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@N-Negative	1	-2313917.810	-27.797	1.962175
	3	-2313946.370	-56.357	1.175701
	5	-2313949.393	-59.379	0.046291
Fe(III)@N-Negative	2	-2313789.800	-253.468	1.029873
	4	-2313823.740	-287.407	0.653655
	6	-2313815.437	-279.104	0.048079
H₂O@N-Negative	1	-1569538.709	-1.508	0.000000

Table S11. Multiplicity, total energy, and spin contamination values of the Well complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@Well	1	-1988882.519	34.259	1.749815
	3	-1988895.998	20.780	0.923656
	5	-1988926.629	-9.851	0.013516
Fe(III)@Well	2	-1988728.680	-165.582	1.779090
	4	-1988735.671	-172.573	0.894414
	6	-1988766.775	-203.677	0.027676
H₂O@Well	1	-1244569.917	-5.951	0.000000

Table S12. Multiplicity, total energy, and spin contamination values of the N-Well complexes

Complex	Multiplicity	Energy (kcal·mol⁻¹)	Binding energy (kcal·mol⁻¹)	Spin contamination
Fe(II)@N-Well	2	-1999348.146	-25.948	1.012607
	4	-1999380.538	-58.340	0.099468
Fe(III)@N-Well	1	-1999173.403	-204.886	1.733996
	3	-1999227.147	-258.630	1.136541
	5	-1999242.965	-274.448	0.019218
H₂O@N-Well	2	-1254976.347	-6.962	0.054908

Energy vs Multiplicity for positive surfaces (Endo and Exo)

Like in Fe(II) adsorbed at Endo, the most stable spin configuration and lowest binding energy is given by $M = 4$ (**Figure S6a**). The same occurs in Fe(III), where the most stable configuration is still that of highest multiplicity ($M = 5$) as observed in **Figure S6c**.
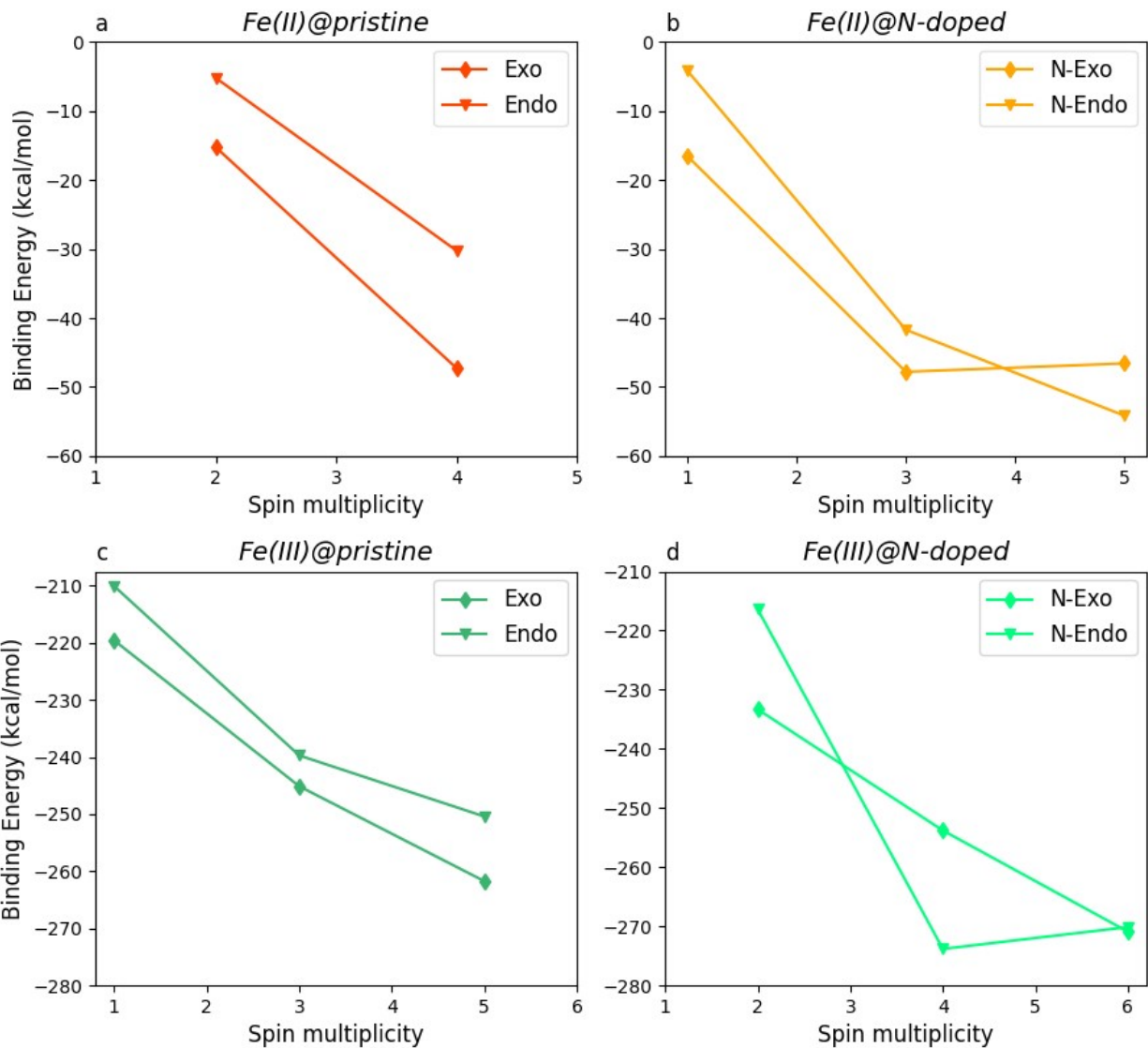
Figure S6. Comparison of Endo and Exo binding energies of Fe(II), and H_2O onto pristine (left) and N-doped (right) positive surfaces.

Energy vs Multiplicity for different pore radii surfaces (Endo and Well)

Like in the other complexes studied, the general trend for adsorption of iron at Well (**Figure S7(a, c)**) is for the E_B to decrease with the increase of spin multiplicity, being the systems with the highest M those with lowest E_B.
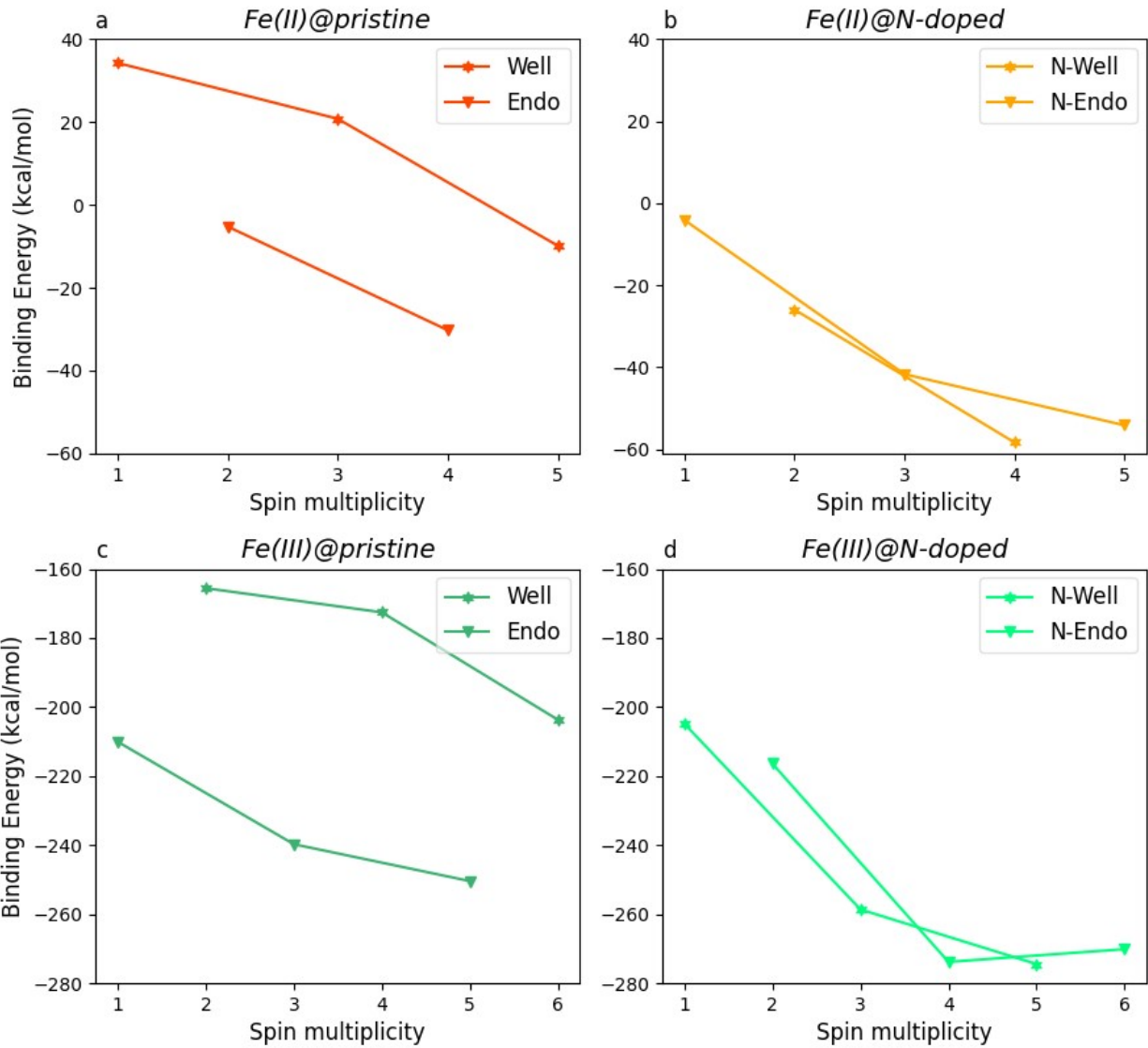
Figure S7. Comparison of Endo and Well binding energies of Fe(II), and H_2O onto pristine (left) and N-doped (right) positive surfaces.