Electronic Supplementary Information

Effects of functional groups in iron porphyrin on the mechanism and activity of oxygen reduction reaction

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Table S1 The bond distance (Å) between the oxygen atoms ($d_{O\text{-}O}$), and from the nearest oxygen atom of the intermediates to the iron atom of the substrate ($d_{O\text{-}Fe}$), in the most stable adsorption configuration of the intermediates on FePor, FeTMP, FeTAP, and FeTCP.

Intermediates	d_{O-Fe} / Å				d_{O-O} / Å			
	FePor	FeTMP	FeTAP	FeTCP	FePor	FeTMP	FeTAP	FeTCP
O_2^*	1.807	1.807	1.815	1.819	1.303	1.306	1.313	1.299
HOO^*	1.768	1.764	1.772	1.767	1.523	1.536	1.556	1.519
$HOOH^*$	1.844	1.874	1.862	1.878	2.160	2.231	2.281	2.169
$O^* + H_2O^*$	1.661	1.666	1.679	1.661	2.811	2.827	2.848	2.856
$HO^* + H_2O^*$	1.823	1.829	1.864	1.818	2.820	2.798	2.785	2.896
$2\ H_2O^*$	2.458	2.526	2.597	2.321	2.912	2.949	3.046	3.097
$O^* + O^*$	1.656	1.660	1.669	1.639	4.634	4.672	4.639	4.621
$O^* + HO^*$	1.817	1.822	1.842	1.811	4.742	4.825	4.694	4.678
$HO^* + HO^*$	1.817	1.824	1.870	1.813	5.116	5.087	5.143	5.221

Table S2 Bader point charge (e^-) of each oxygen atom of the intermediates on the substrates. The oxygen atoms: (O1) nearest to the Fe site and (O2) on another site.

Order number	Intermediates	FePor		FeTMP		FeTAP		FeTCP	
		O1	O2	O1	O2	O1	O2	O1	O2
1	O_2^*	0.282	0.157	0.325	0.141	0.331	0.173	0.250	0.143
2	HOO^*	0.440	1.029	0.448	1.049	0.488	1.070	0.455	1.018
3	$HOOH^*$	1.303	1.214	1.394	1.272	1.307	1.383	1.374	1.239
4	$O^* + H_2O^*$	0.717	2.018	0.714	2.020	0.714	2.026	0.707	2.015
5	$HO^*+H_2O^*$	1.482	2.023	1.507	2.025	1.530	2.035	1.482	2.019
6	$2\ H_2O^*$	1.965	2.021	1.974	2.017	1.986	2.012	1.952	2.012
7	$O^* + O^*$	0.716	0.882	0.645	0.861	0.729	0.831	0.687	0.859
8	$O^* + HO^*$	1.441	0.871	1.441	0.863	1.465	0.853	1.428	0.847
9	$HO^* + HO^*$	1.450	1.694	1.451	1.669	1.496	1.642	1.438	1.678

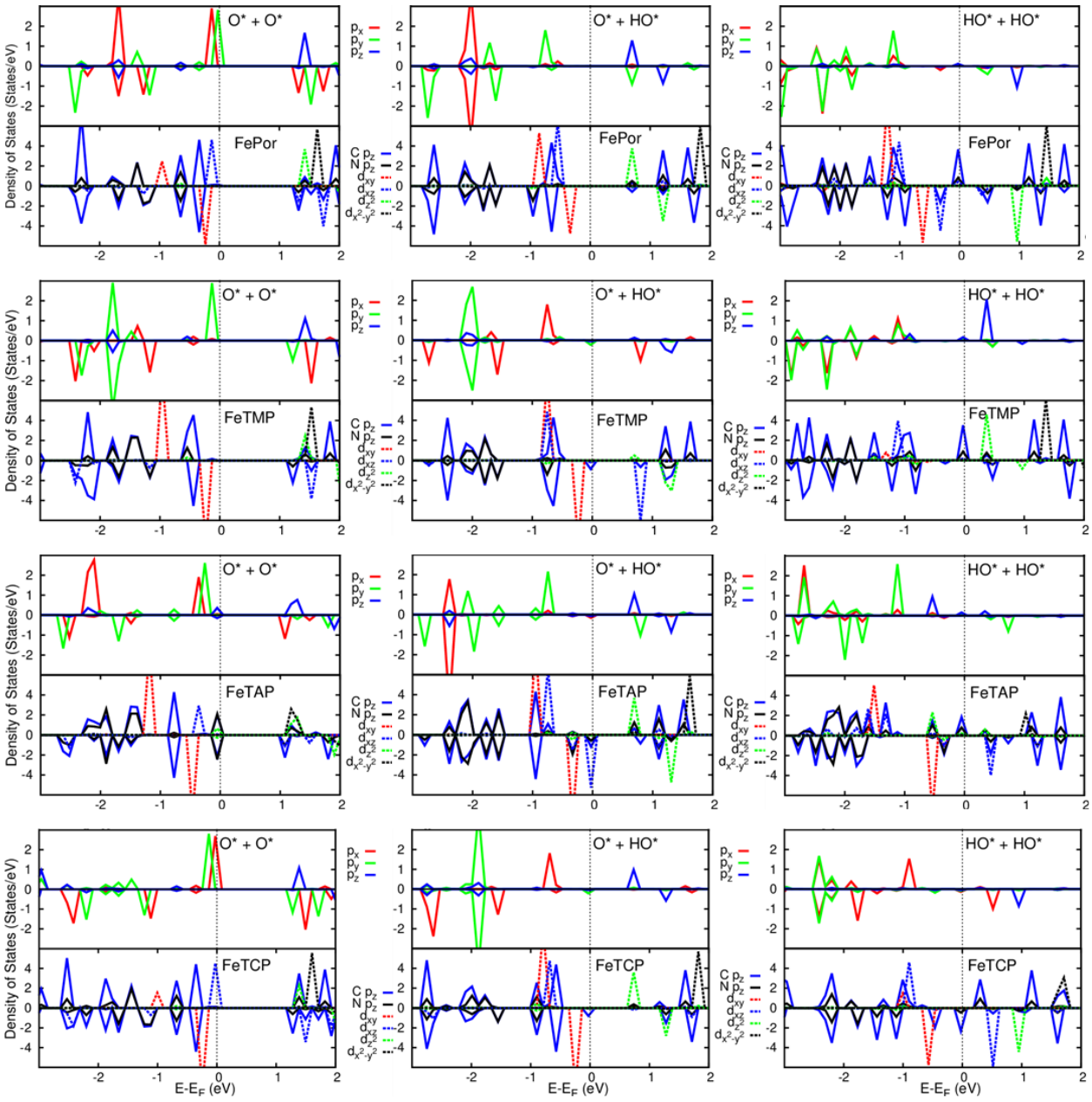

Fig. S1 Electronic density of states for the systems of the substrates with O^* + O^*, O^* + HO^*, and HO^* + HO^*. The d_{xz} and d_{yz} orbitals are identical.

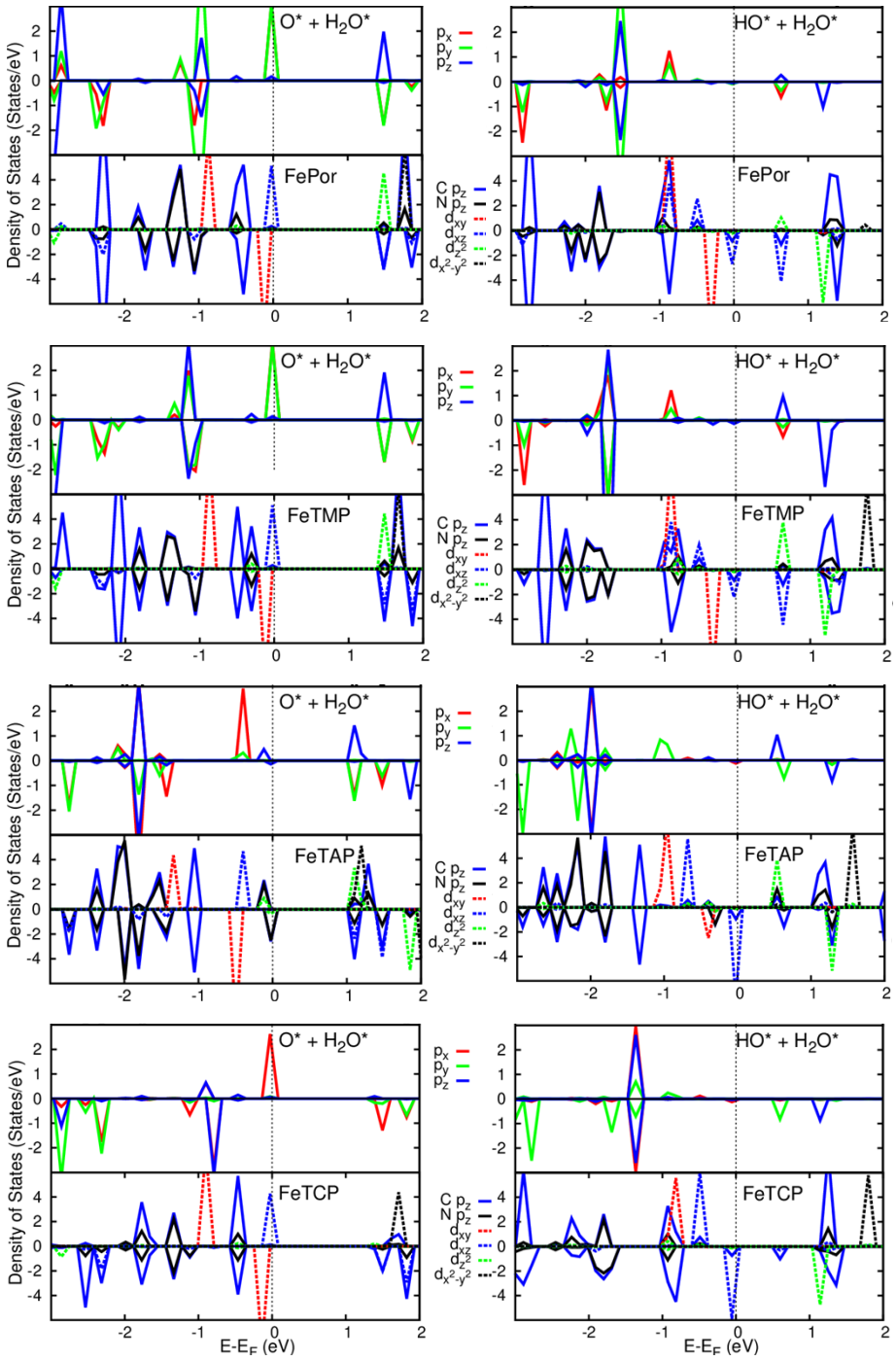

Fig. S2 Electronic density of states for the systems of the substrates with $O^* + H_2O^*$ and $HO^* + H_2O^*$. The d_{xz} and d_{yz} orbitals are identical.