Electronic Supplementary Information

Two-Dimensional Iron-Phthalocyanine (Fe-Pc) Monolayer As a Promising Single-Atom-Catalyst for Oxygen Reduction Reaction: A Computational Study

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Table S1. Adsorption energies of O_2 molecule on TM-Pc monolayers (TM = Fe, Mn, Ni, Cu).

	Fe-Pc	Mn-Pc	Ni-Pc	Cu-Pc
E_{ad} (eV)	–0.83	–0.71	0.54	0.67

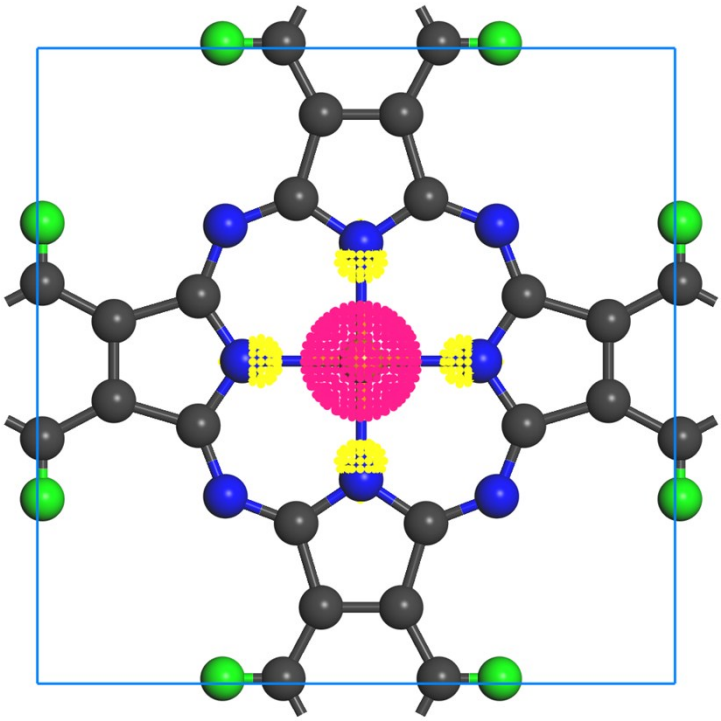

Fig. S1 Spin-polarized density for Fe-Pc monolayer in the 3D isosurface version with a value of 0.01 electrons $Å^{-3}$. The spin up and spin down are represented in red and yellow, respectively.

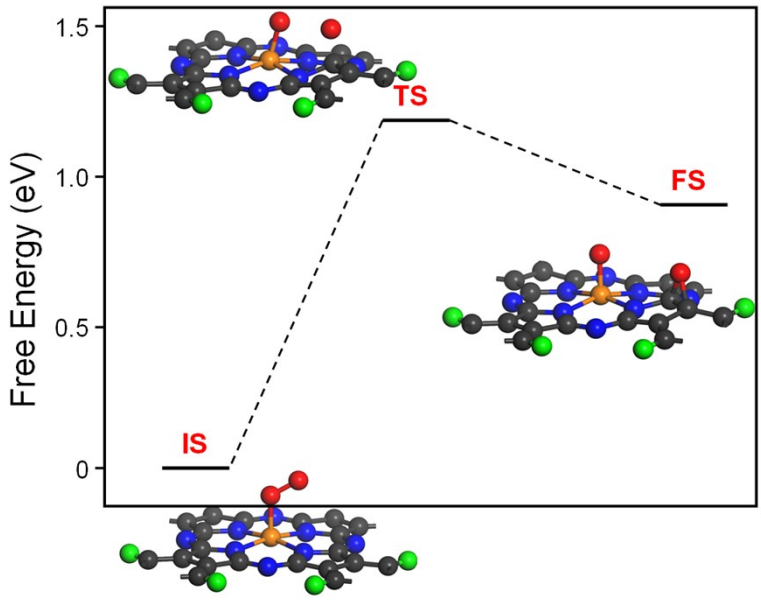

Fig. S2 Free energy profile for the O_2 dissociation reaction on the surface of Fe-Pc monolayer. The IS, TS, and FS represents initial state, transition state, and final state, respectively.

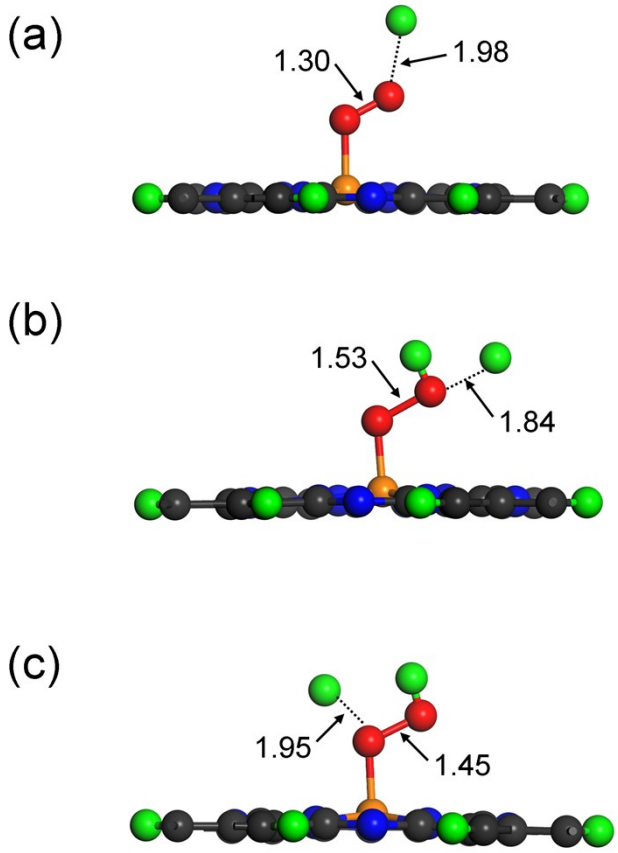

Fig. S3 The transition state structures of ORR step of (a) O_2* + H^+ + e^-→ OOH*, (b) OOH* + H^+ + e^- → O* + H_2O, and (c) OOH* + H^+ + e^- → * + H_2O_2. The labeled distances are in angstroms.

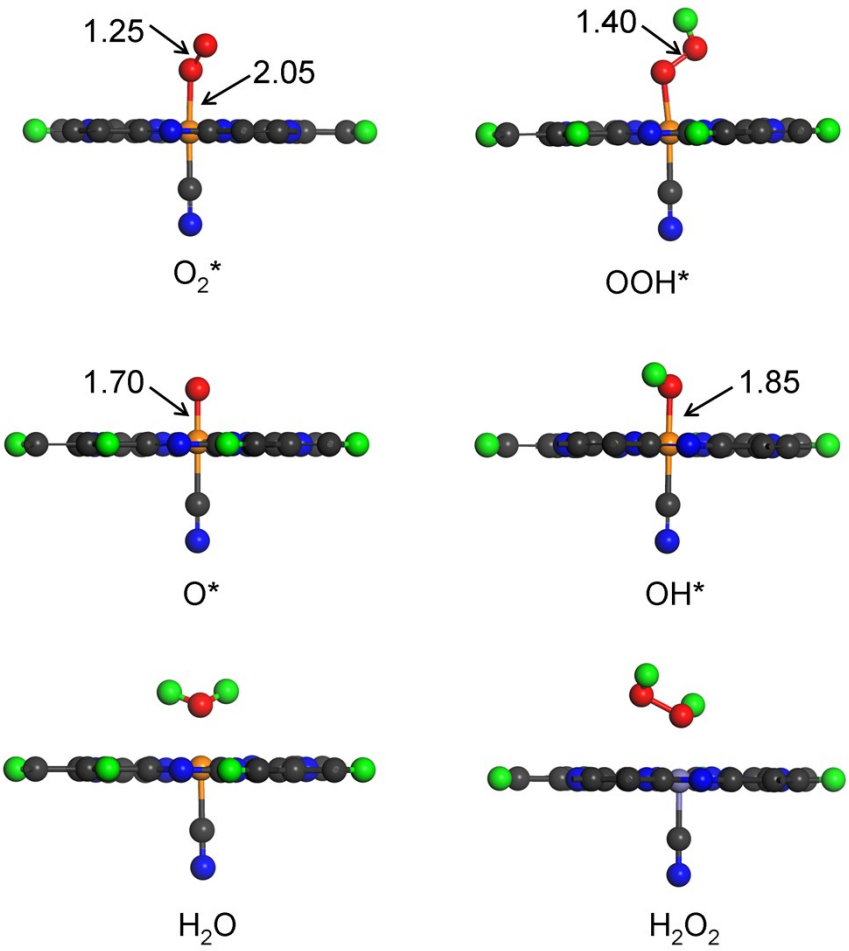

Fig. S4 The optimized geometric structures of various states (O_2*, OOH*, O*, OH*, H_2O, and H_2O_2) along the reaction path of ORR proceeded on Fe-Pc-CN monolayer. The labeled distances are in angstroms.

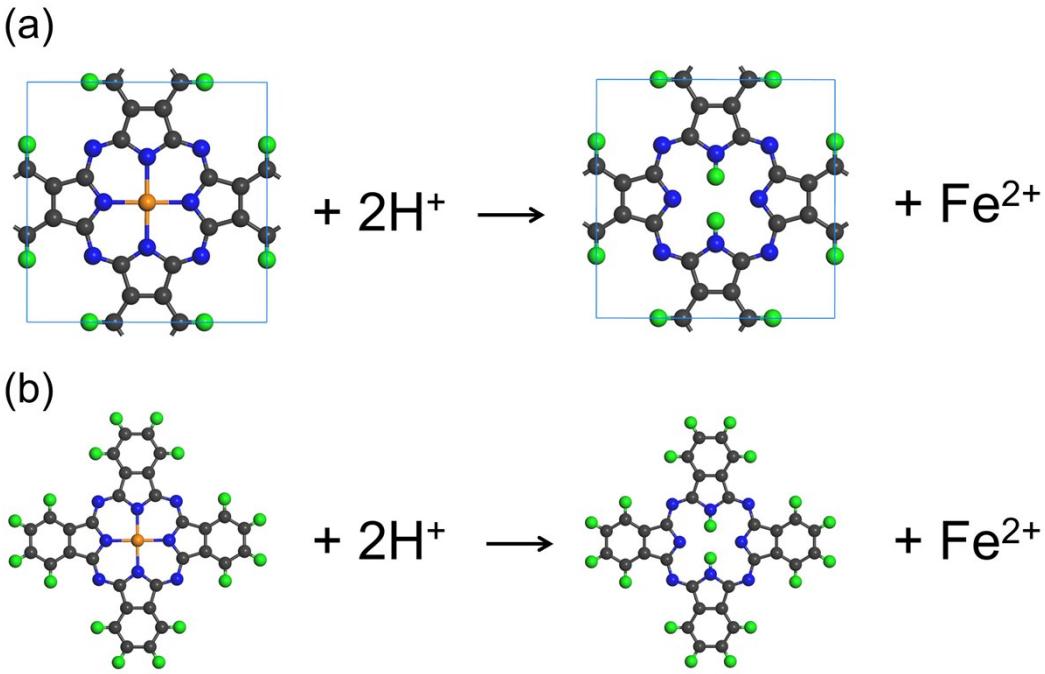

Fig. S5 Schematic diagrams of Fe/H substitution reaction for (a) Fe-Pc monolayer and (b) Fe-Pc molecule, respectively.

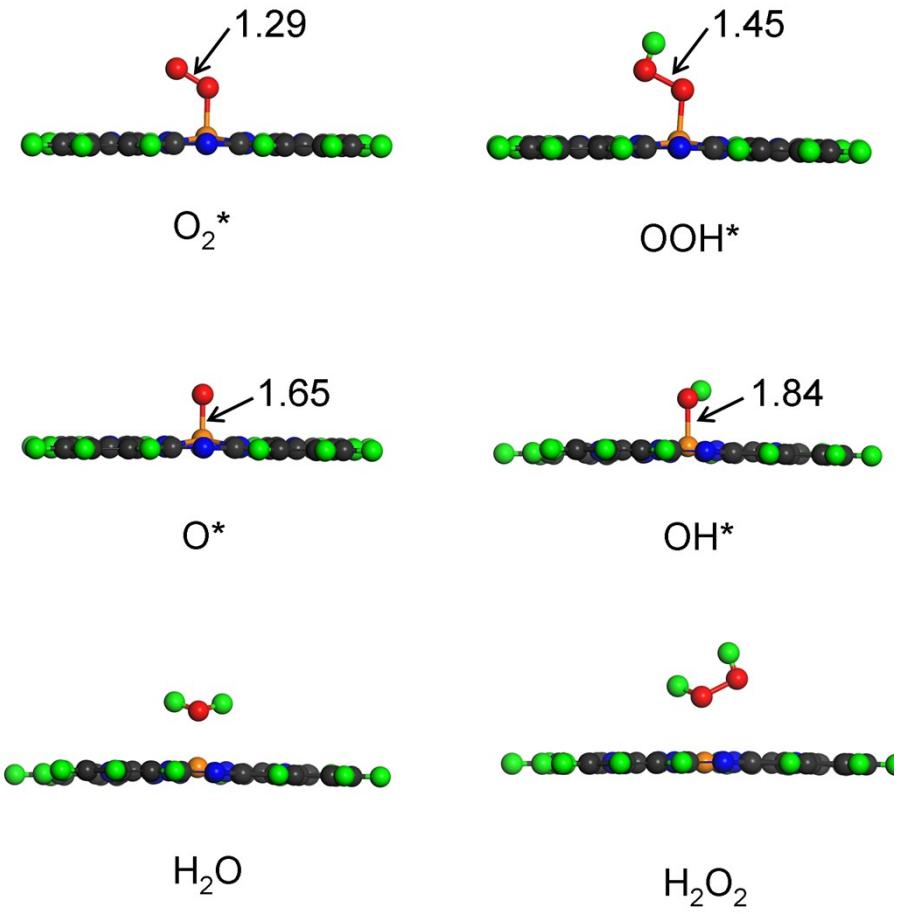

Fig. S6 The optimized geometric structures of various states (O_2*, OOH*, O*, OH*, H_2O, and H_2O_2) along the reaction path of ORR proceeded on Fe-Pc molecule. The labeled distances are in angstroms.

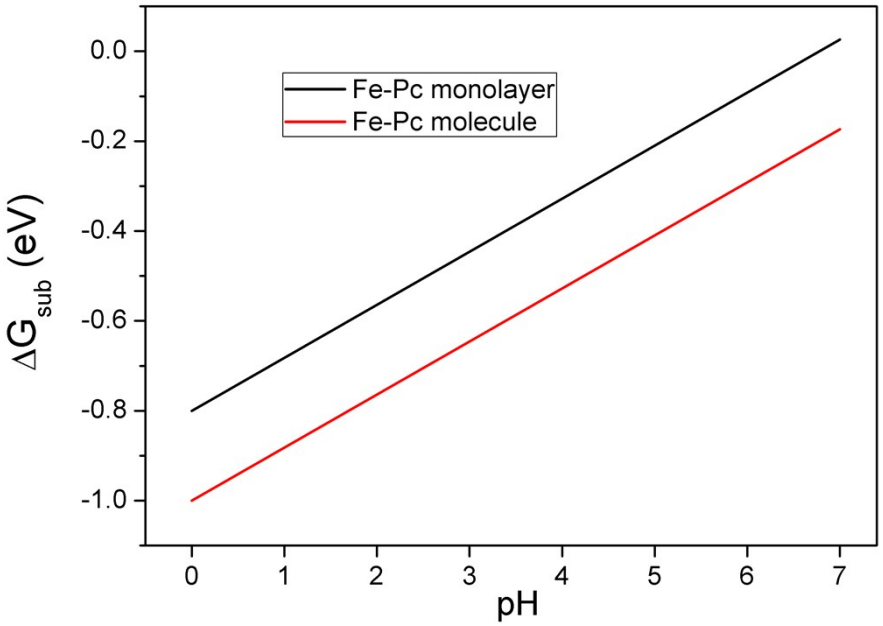

Fig. S7 The free energy change caused by substituting one Fe atom with two protons (ΔG_{sub}) in both Fe-Pc monolayer and molecule as a functional of pH.