Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Effect of Dispersion on Surface Interactions of Cobalt(II) Octaethylporphyrin Monolayer on Au(111) and HOPG(0001) Substrates: A Comparative First Principles Study

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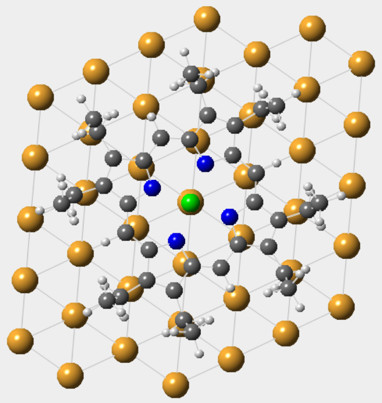
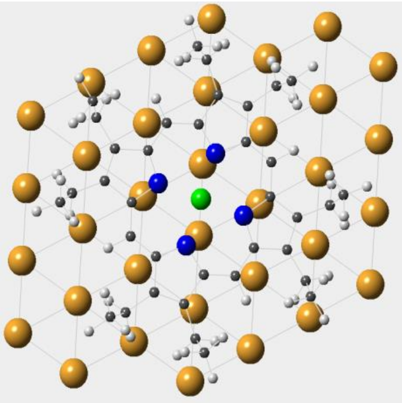
A. Determination of binding sites for CoOEP molecule on Au(111) surface

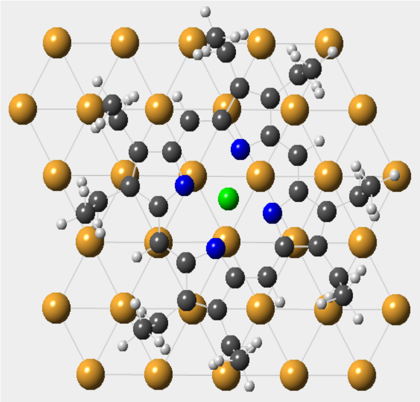
Cobalt(II) octaethylporphyrin (CoOEP) molecule in “*crown*” configuration has a *C4v* symmetry. CoOEP molecule, with respect to central metal atom has 3 possible binding sites, 3-fold center site, bridge site and atop site on Au(111) surface. Single point calculations (with and without dispersion) of a CoOEP molecule at the 3 different binding sites were performed. The total electronic energies at the 3 binding sites are listed in Table S1. Energy difference between with respect to the bridge site indicates that 3-fold center site has the lowest energy. Further calculations were performed on the lowest energy center site by rotating the porphyrin molecule around the central metal atom. Considering the symmetrical constraints with *C4v* point group for CoOEP, the molecule repeats its orientation upon rotating every 30°. So a total of two calculations namely center-A and center-B with 15° rotation with respect to each other were performed on the center site. It was found that orientation at the center-A site with shortest Au~N bonds prefers to have the lowest energy.



Top Site



Bridge Site



Center Site

Table S1: Electronic energies at different binding sites for Au(111) surface (with dispersion DFT).

System	Relative Energy Difference
Bridge	0.0000
Top	0.1206
Center-A	-0.1477
Center-B (15° rotation)	0.0907

B. Determination of binding sites for CoOEP molecule on HOPG(0001) surface

Similar to the Au(111) surface, CoOEP molecule with respect to central metal atom has 3 possible binding sites, 6-fold center site, bridge site and atop site on HOPG(0001) surface. Molecular symmetry of CoOEP molecule allows the rotations of molecule around the Co atom and electronic energies at each binding site and their respective rotations were plotted in Figure S1. The electronic energies from Figure S1 indicates that CoOEP molecule binds strongly to the 6-fold center site with lowest energy orientation when 2 nitrogens of the porphyrin aligns along the carbon atoms and the other 2 nitrogens in between the carbons atoms. Calculations with and without dispersion DFT yielded similar binding trends.

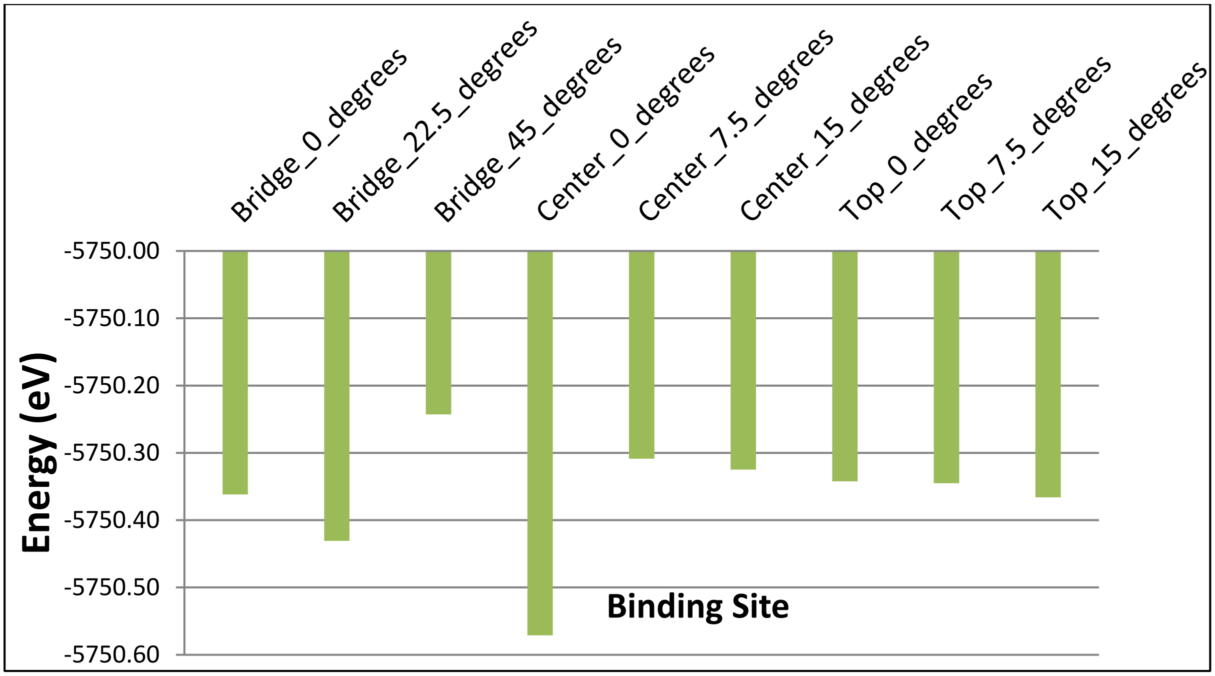


Fig. S1: Electronic energies of different binding sites for CoOEP molecule on HOPG(0001) surface.

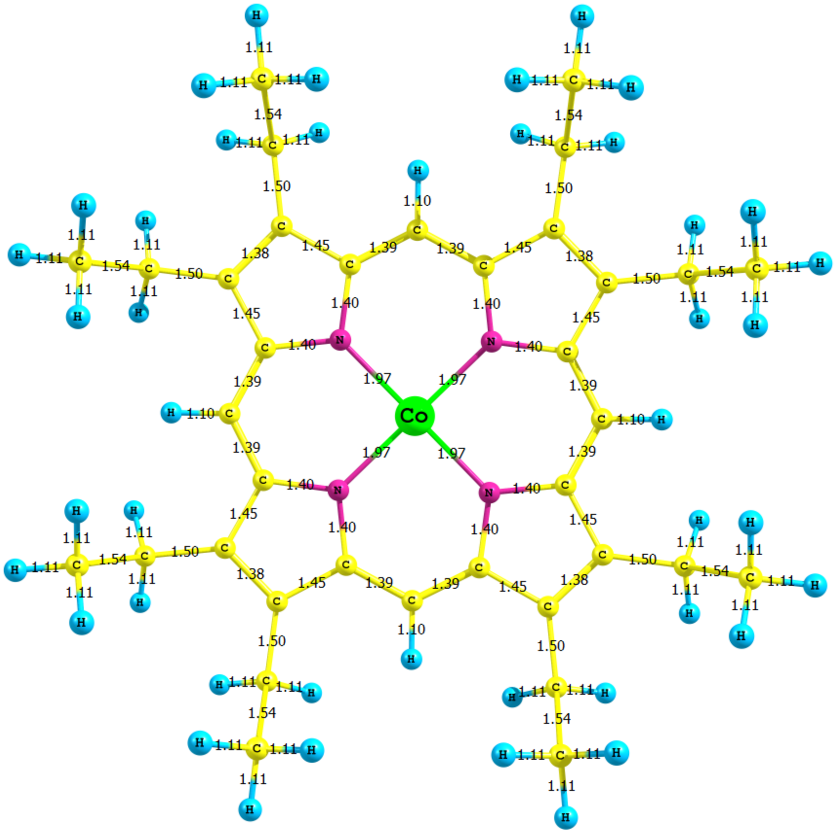


Fig. S2: Bond lengths for CoOEP molecule optimized from molecular DFT (see reference 9 in the manuscript for calculation details).

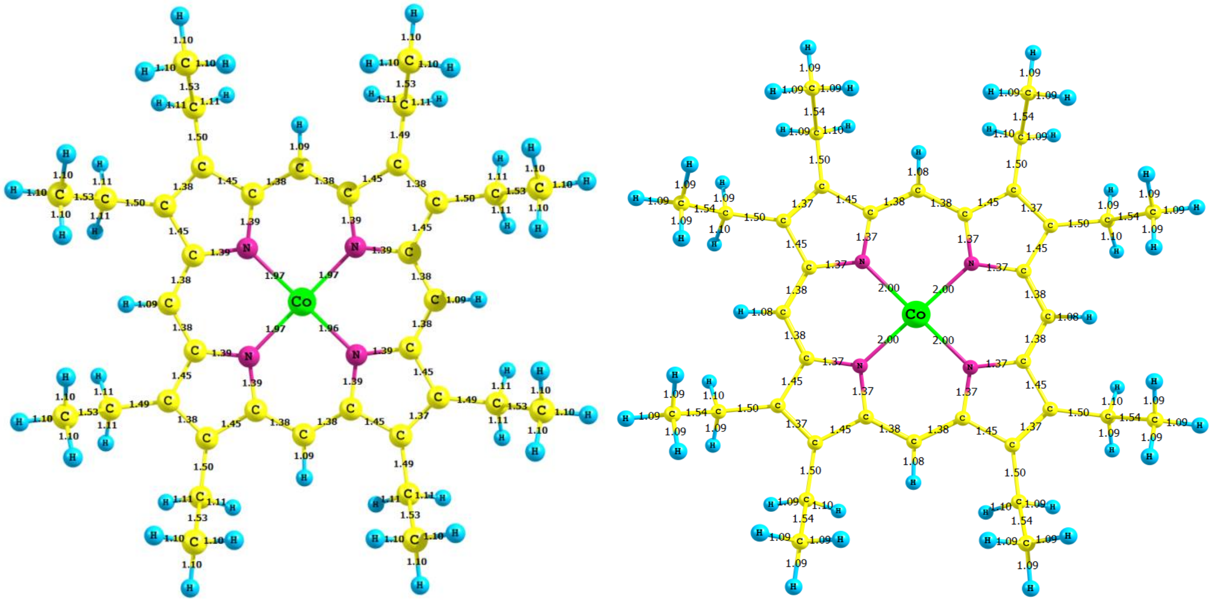


Fig. S3: Bond lengths for CoOEP molecule as optimized in 30x30x30 box with GGA functional with (left) and without (right) dispersion corrections.

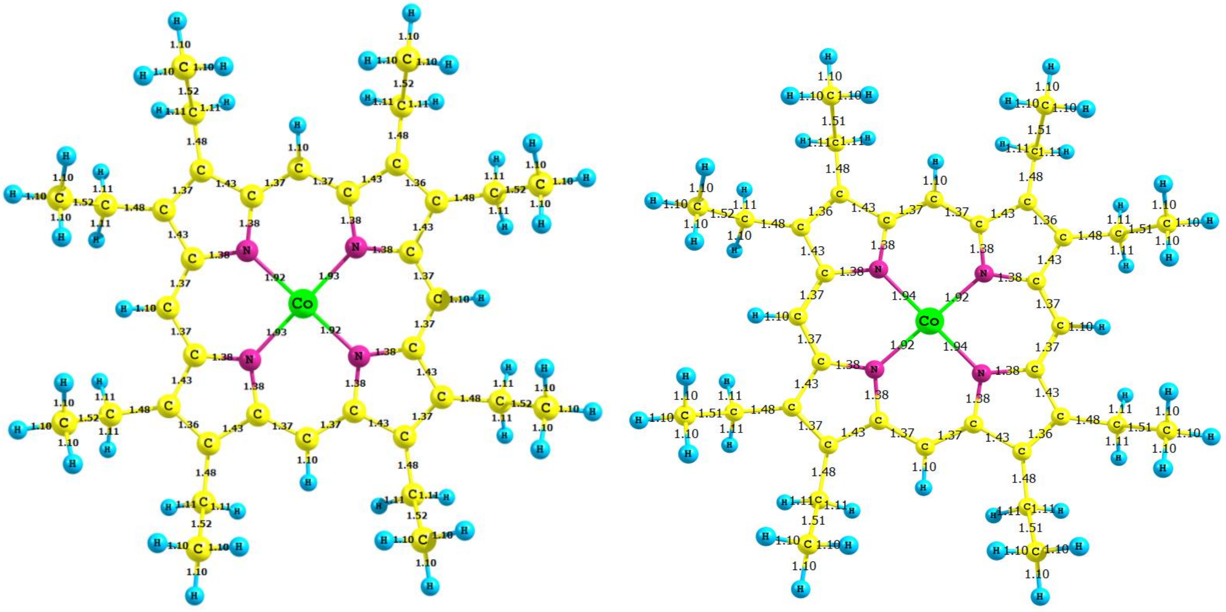


Fig. S4: Bond lengths for CoOEP molecule as optimized in 30x30x30 box with LDA functional with (left) and without (right) dispersion corrections.

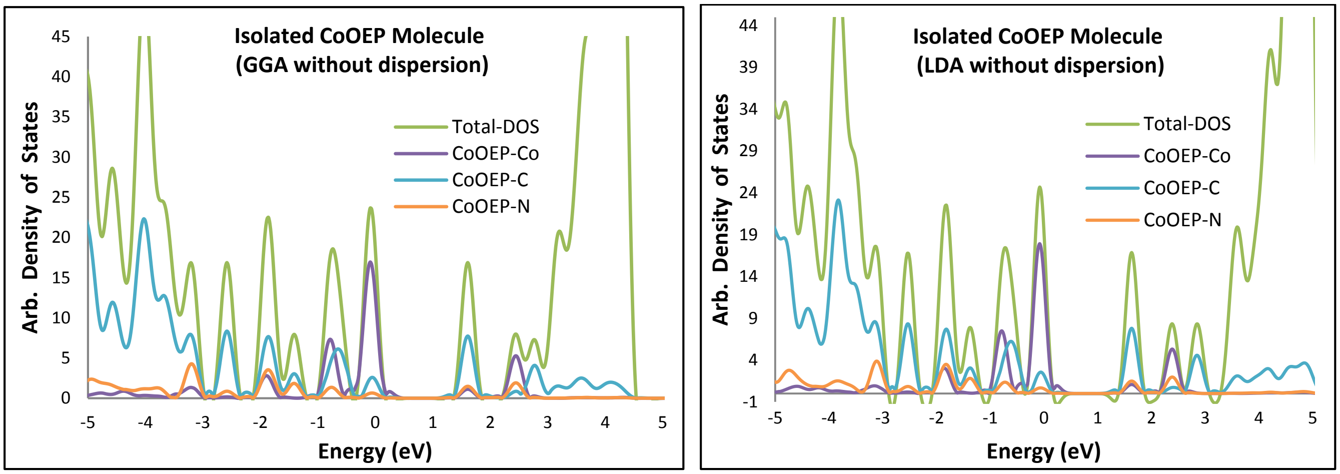


Fig. S5: Density of states of isolated CoOEP molecule without dispersion DFT. Fermi energy is located at 0 eV.

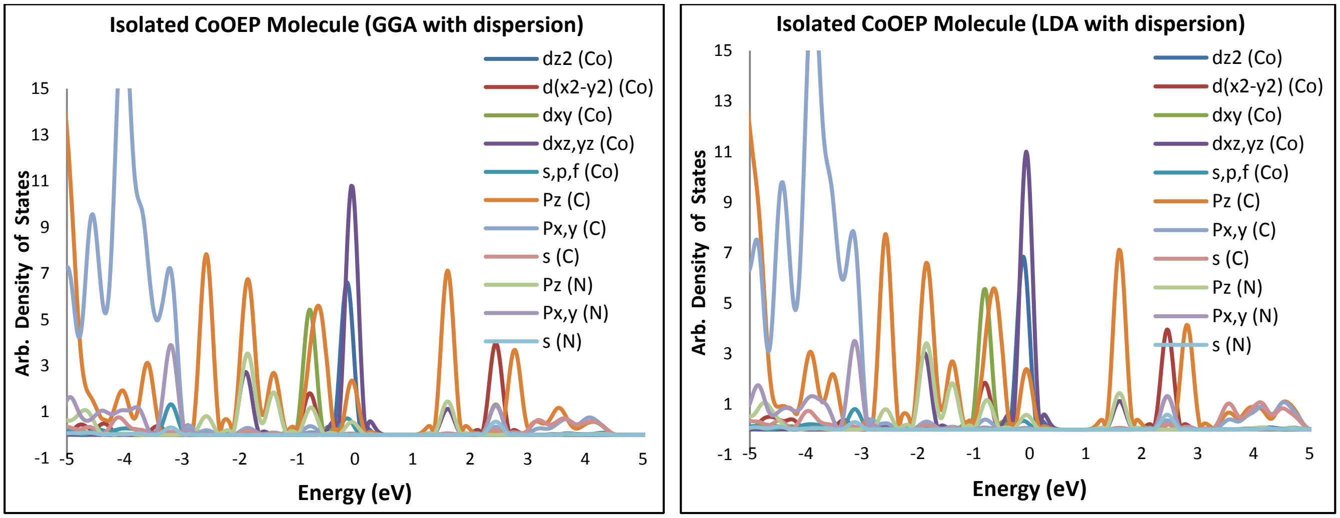


Fig. S6: Density of states (top) and pojected density of states (orbital contributions) (bottom) of isolated CoOEP molecule. Fermi energy is located at 0 eV.

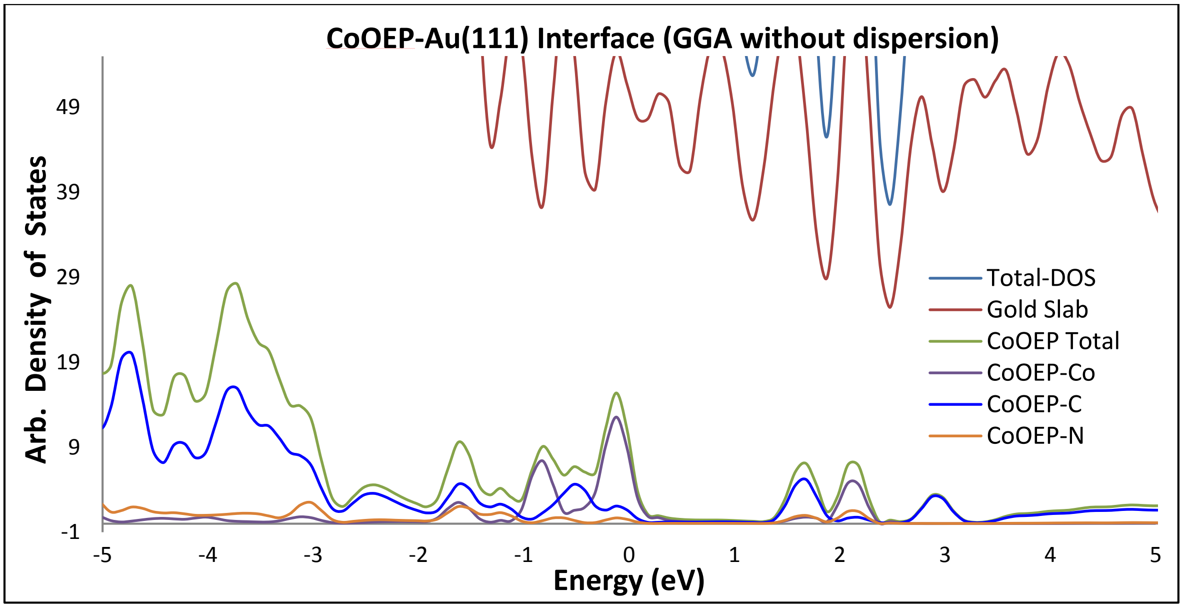


Fig. S7: Density of States (DOS) for CoOEP/Au(111) system without dispersion. Fermi energy is aligned to 0 eV.

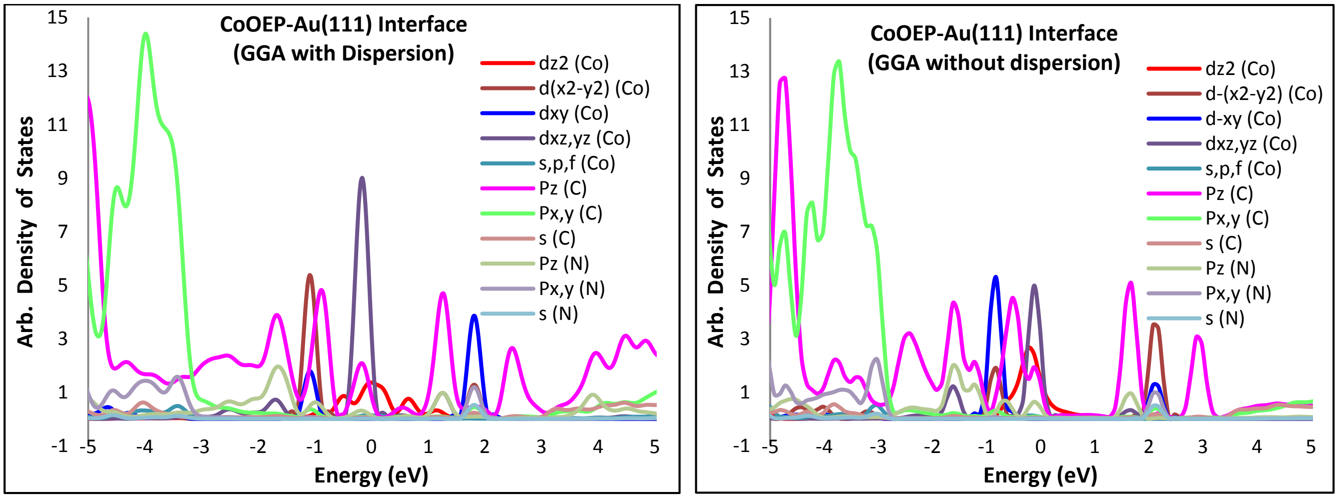


Fig. S8: Projected DOS of orbital contributions of CoOEP molecule on Au(111) surface. DOS for Au(111) are hidden for clarity. Fermi energy is located at 0 eV.

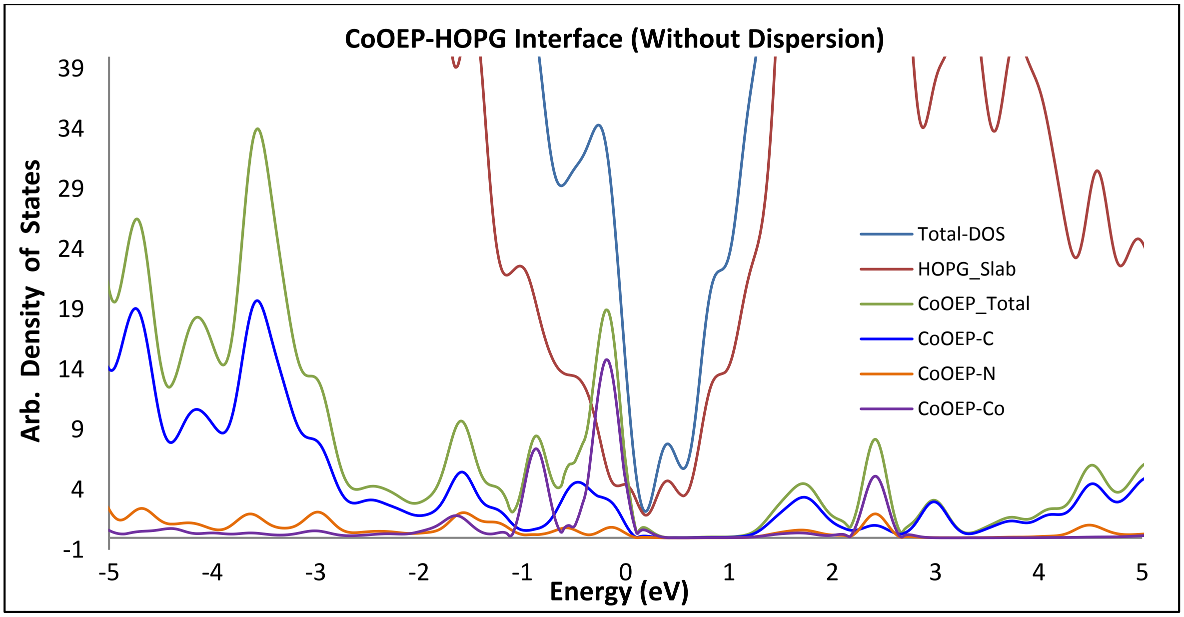


Fig. S9: Density of States (DOS) for CoOEP/HOPG system without dispersion. Fermi energy is aligned to 0 eV.

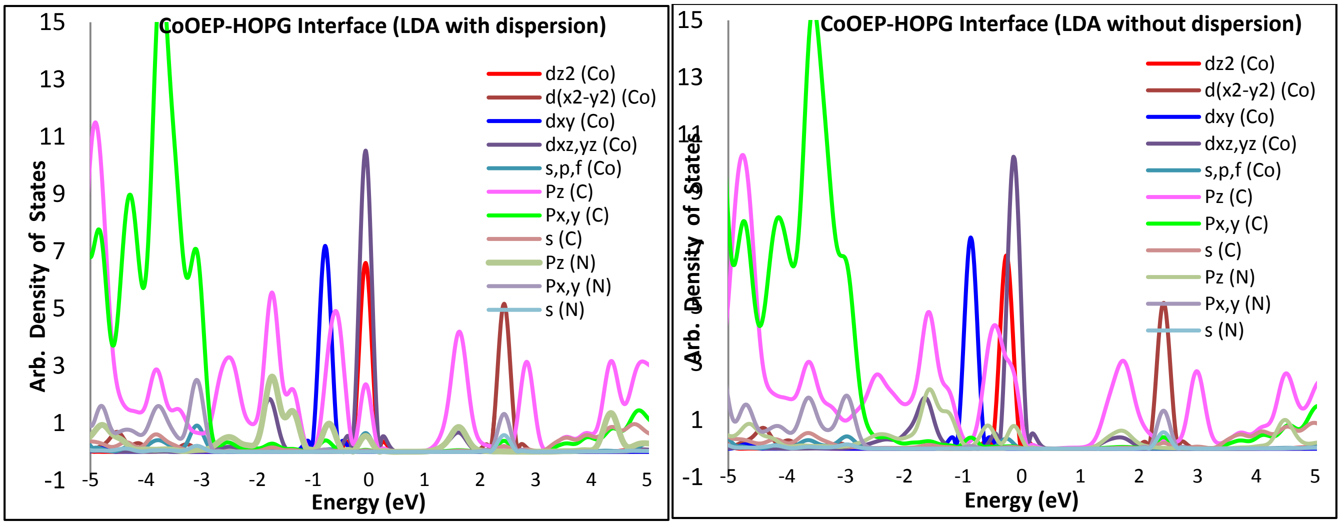


Fig. S10: Projected density of states of orbital contributions of CoOEP molecule on HOPG(0001) surface. Fermi level is located at 0 eV.