

Modelling the adsorption of natural organic matter on Ag (111) surface: Insights from dispersion corrected density functional theory calculations: Supplement

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Structural properties

The interatomic bonds of the HA, FA, and Cry molecules were calculated and compared before and after relaxation as summarized in Table S1. From the results, (Table S1) insignificantly small differences were noted for bond distances before and after relaxation. To the authors' knowledge, no previous theoretical and experimental studies on reported bond lengths of HA, FA and Cry to allow one to make a comparison results derived from this study. It should be noted the bond lengths were unchanged in the gas phase and water as a solvent without and with dispersion corrections. Generally, as the adsorption energy increases with increasing MW, we expected the geometrical parameters in this case the distance between C-H, C-C, O-H and C-O to be influenced by the MW and the solvent effects. However, a comparison of Cry bond lengths to compared to HA and FA, no such influence was apparent.

Table S1: Bond lengths of HA, FA and Cry before and after relaxation.

Adsorbate	d _{C-H} (Å)	d _{C-C} (Å)	d _{O-H} (Å)	d _{C-O} (Å)
Before relaxation				
HA	1.09	1.55	0.98	1.36
FA	1.08	1.39	0.97	1.36
Cry	1.08	1.45	0.97	1.43
After relaxation				
DFT-D gas phase				
HA	1.09	1.55	0.98	1.36
FA	1.08	1.39	0.97	1.36
Cry	1.08	1.45	0.97	1.42
DFT-D COSMO				
HA	1.09	1.55	0.98	1.36
FA	1.08	1.39	0.98	1.36
Cry	1.08	1.45	0.97	1.43

Abbreviation: d_{C-H}: is the distance between carbon and hydrogen, d_{C-C}: distance between carbon and carbon, d_{O-H}: is the distance between oxygen and hydrogen, and d_{C-O}: distance between carbon and oxygen.

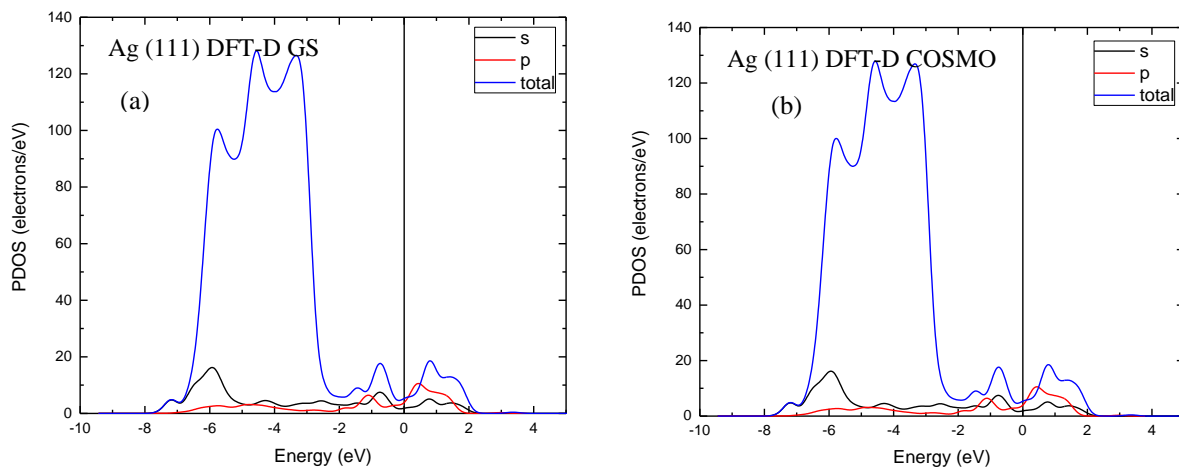


Figure S1: Projected density of states of pristine of Ag (111) surface (a-b) in gas phase and COSMO using DFT-D/GGA.

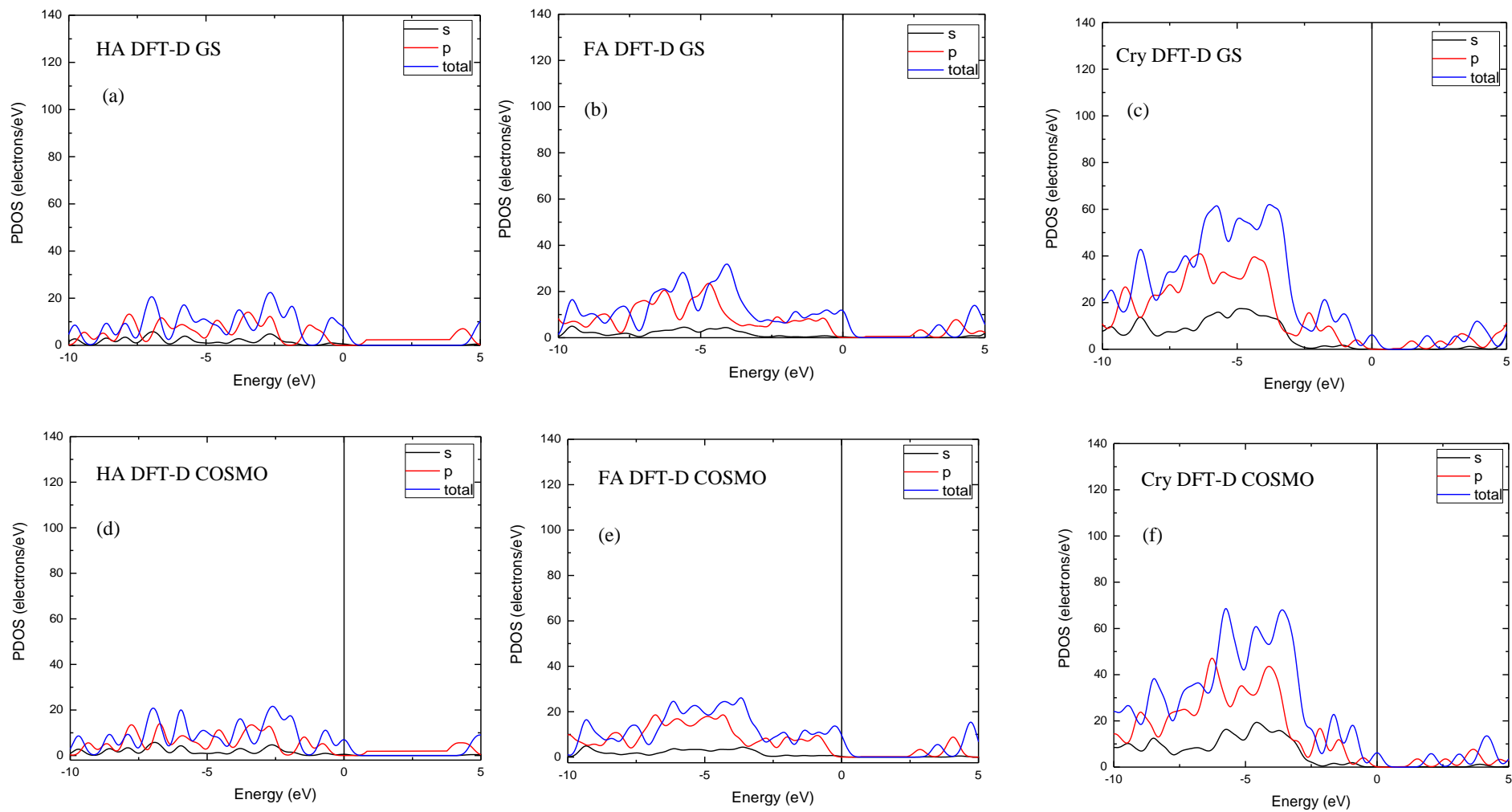


Figure S2: Projected density of states of HA, FA and Cry (a-f) in gas phase and COSMO using DFT-D/GGA level of theory.

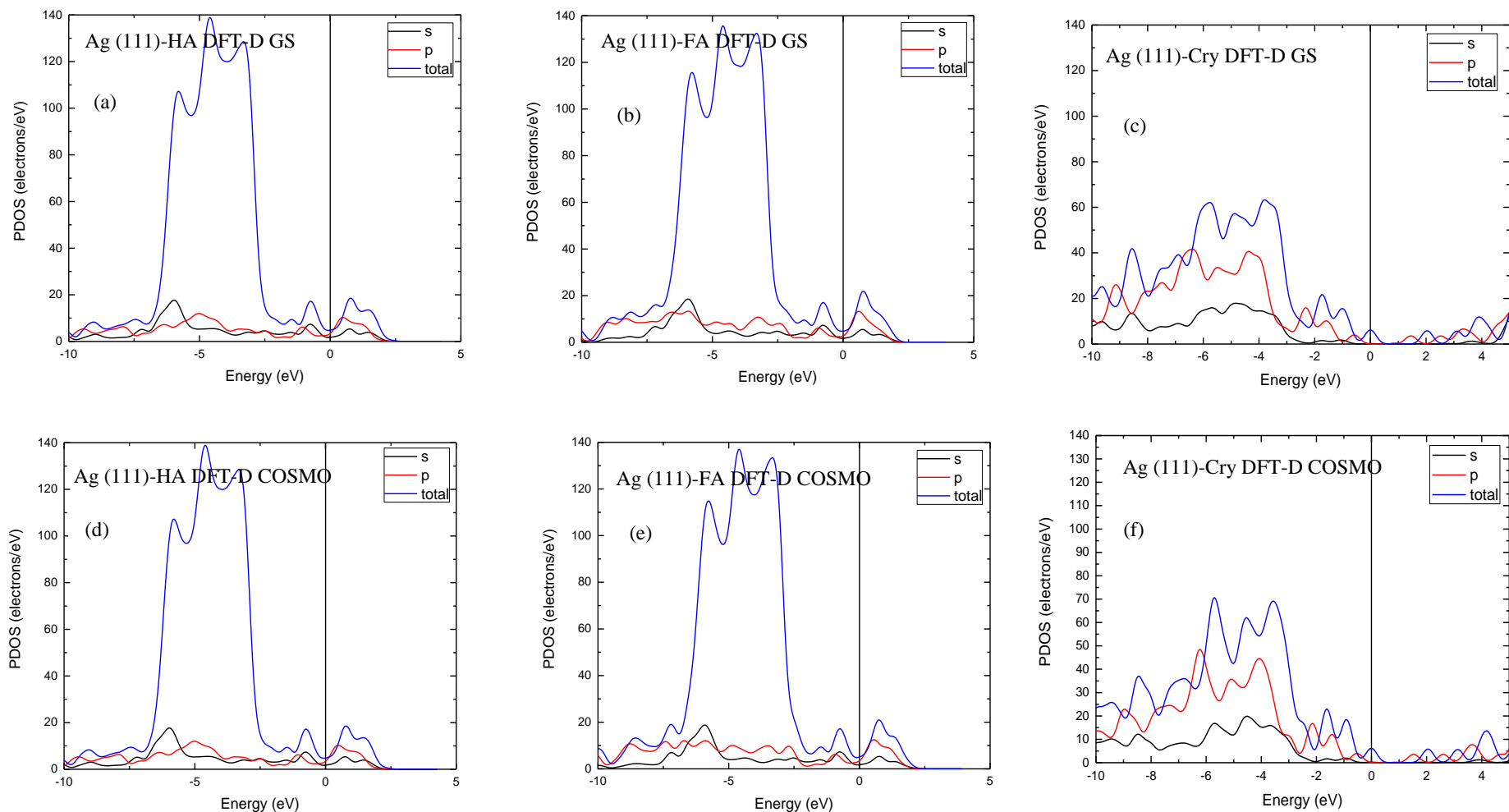


Figure S3: Projected density of states of HA, FA and Cry on Ag (111) surface (a-f) in gas phase and COSMO using DFT-D/GGA level of theory.

Charge deformation difference of adsorbates

The adsorption of the three NOMs on Ag (111) surface lead to charge redistribution due to electronic hybridization between the adsorbates and the adsorbent orbitals [2]. To better understand the distribution patterns of charges around the adsorbates, results on charge density were plotted in three dimensional (3D) images based on charge density difference at the interfaces of HA, FA, and Cry on Ag (111) surface as shown in Figure S4. For the FA and Cry shown in Figure S4 (b) and (c), respectively, a strong redistribution of charges between C=O, C-C, C-H and -OH group was observed, and plausibly could yield a change in electron structure. The 3D iso-surfaces Figure S4 (b-d) of charge redistribution at the interface indicate that the charge was localized mostly on the HA, FA, and Cry with smaller amounts on the pristine Ag (111) surface Figure S4 (a).

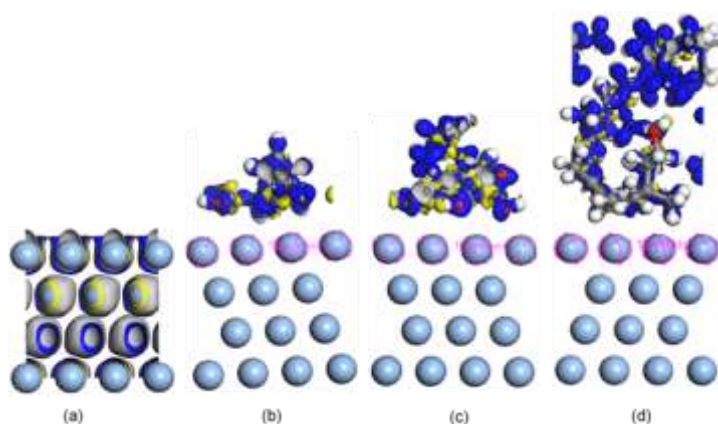


Figure S4: Isosurface charge density difference for (a) Ag (111) pristine, (b) Ag (111)-HA, (c) Ag (111)-FA, and (d) Ag (111)-Cry derived using DFT-D COSMO level of theory. The isovalue is taken as for Ag (111) pristine 0.009 au to -0.009 au and 0.09 to -0.09 au for the rest. Blue region(s) indicates charge accumulation, and yellow region(s) show areas with charge depletion.

Another significant finding from the charge redistribution analysis is that dispersion interactions play a significant role in altering the charge redistribution on Ag (111) surface than on HA, FA and Cry. For the adsorption of NOM's on Ag (111) surface in Figure S4 (b-d), the charge distribution on HA, FA and Cry is larger than that of the Ag (111) surface slab (see evidence shown by no color displacement on the slab after the adsorption). In addition, results in Figures S5-S7 (a) clearly show that regions with oxygen atom had higher charges, and hence the functional group likely to exert strong influence on the Ag (111) surface.

It should, however, be noted that this does not necessary suggest net charge transfer [2] between adsorbates and Ag (111) surface, but rather evidence of plausible charge transfer between surface and the adsorbates.

The isosurface charge density difference for (a) Ag (111) pristine, (b) Ag (111)-HA, (c) Ag (111)-FA and (d) Ag (111)-Cry were the same irrespective of formalism used to perform the calculations (Figures S8-S11).

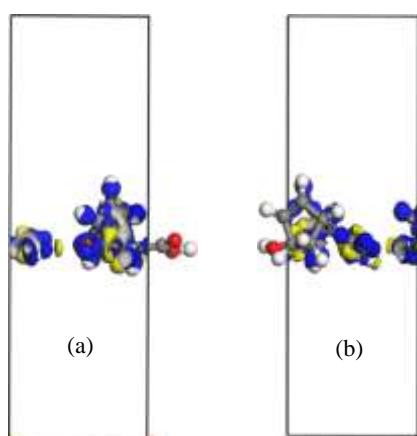


Figure S5: Charge density difference for (a) HA at DFT-D COSMO level of theory, (b) HA at DFT-D gas phase level of theory. The isovalue is taken as 0.009 au.

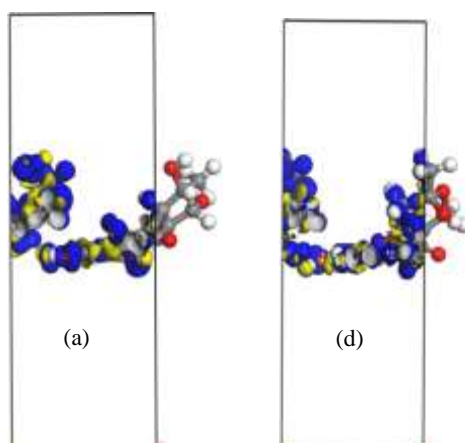


Figure S6: Charge density difference for (a) FA at DFT-D COSMO level of theory, (b) FA at DFT-D gas phase level of theory. The isovalue is taken as 0.009 au.

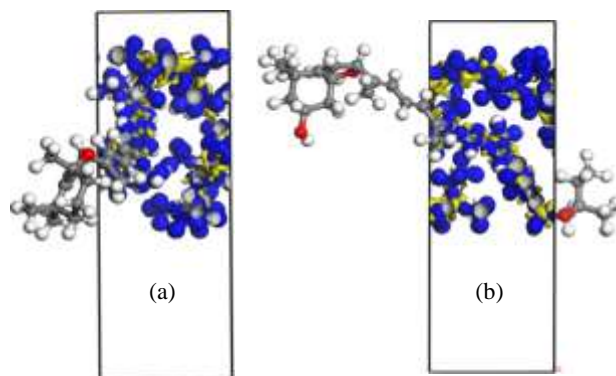


Figure S7: Charge density difference for (a) Cry at DFT-D COSMO level of theory, (b) Cry at DFT-D gas phase level of theory. The isovalue is taken as 0.009 au.

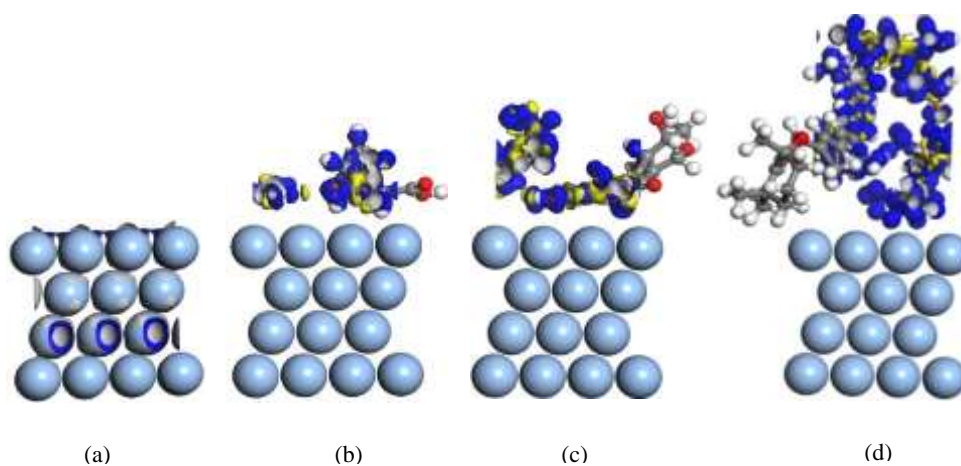


Figure S8: Charge density difference for (a) Ag (111) pristine, (b) Ag (111)-HA, (c) Ag (111)-FA and (d) Ag (111)-Cry at DFT-D COSMO level of theory. The isovalue is taken as 0.009 au.

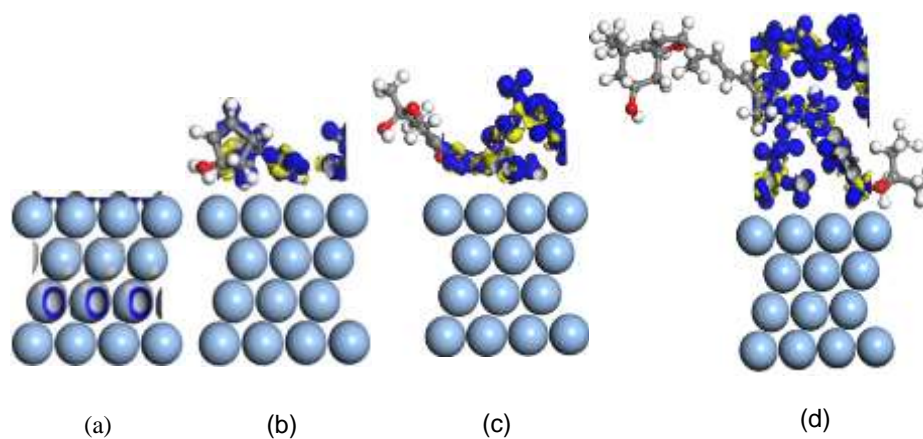


Figure 9: Charge density difference for (a) Ag (111) pristine, (b) Ag (111)-HA, (c) Ag (111)-FA and (d) Ag (111)-Cry at DFT-D gas phase level of theory. The isovalue is taken as 0.009 au.

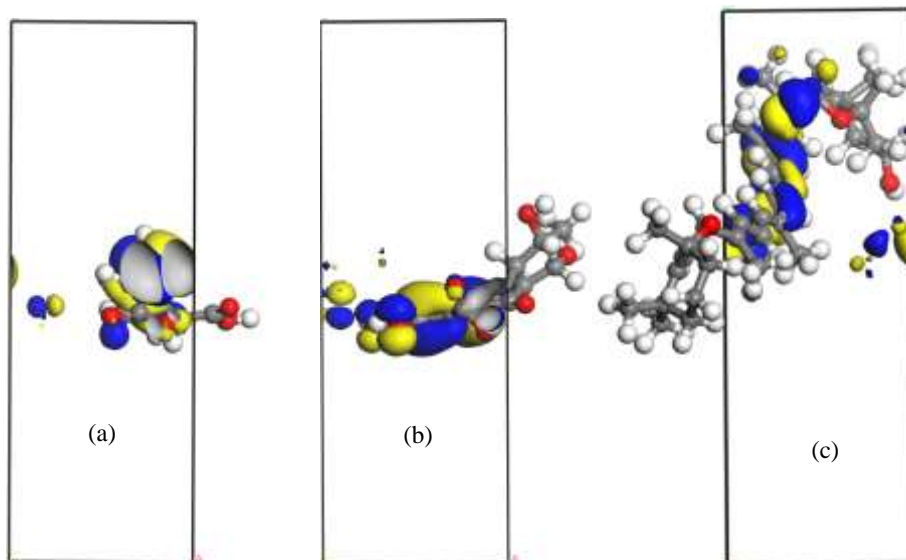


Figure S10: Highest Occupied Molecular Orbital for (a) HA, (b) FA (c) Cry at DFT-D COSMO level of theory. The isovalue is taken as 0.03 au.

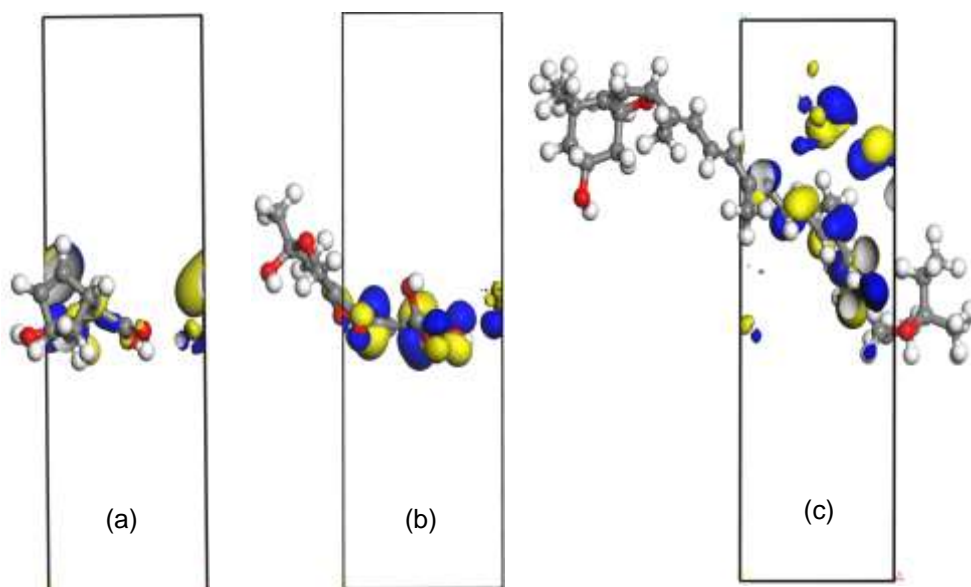


Figure S11: Highest Occupied Molecular Orbital for (a) HA, (b) FA (c) Cry at DFT-D gas phase level of theory. The isovalue is taken as 0.03 au.

References

- [1] M. Scheffler, C. Stampfl, Theory of adsorption on metal substrates, *Handb. Surf. Sci.* 2 (2000) 285.
- [2] B. Chilukuri, U. Mazur, K.W. Hipps, Effect of dispersion on surface interactions of cobalt (II) octaethylporphyrin monolayer on Au (111) and HOPG (0001) substrates: a comparative first principles study, *Phys. Chem. Chem. Phys.* 16 (2014) 14096–14107.