

Metalated Porphyrins and Phthalocyanines on Surfaces: potential for environmental and energy applications

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[01] ABSTRACT: Porphyrins are planar aromatic molecules comprising a core tetrapyrrolic macrocycle. Molecular functionalization of the porphyrins has become significant in synthetic chemistry, molecular electronics, and surface science. High symmetrical D_4h nature of metalated porphyrins is of great interest in the perspective of two-dimensional assemblies on surfaces and three-dimensional frameworks. Most of the transition metal elements can be incorporated into the core macrocycle. Such complex systems are widely investigated in the context of higher order or dimensional arrangement of functionalized adsorbates on surfaces. Recent investigations on thermodynamic self-assembly of porphyrins are significant in illustrating the behavior of substrates on metallic surfaces. Functionalized porphyrin species are advantageous for photocatalysis, degradation, energy conversion and storage, and metal pollutant detection. The applications of surface-deposited porphyrin species are not widely investigated. This would serve as a potential mechanism for efficient surface processes for environmental and energy applications. In this study, porphyrins with metal centers Ni, V, Cu and Co and phthalocyanines (Pc) adsorbed to gold (Au111) and highly ordered pyrolytic graphite (HOPG0001) surfaces are investigated. Favorable binding sites of metal-centered octa ethyl porphyrins (MOEP) and Pc on the surfaces are investigated. Further, adsorption energy trends with different metal centers, surfaces and binding sites and orbital-hybridization driven charge redistribution are investigated based on quantum mechanical density functional theory-level calculations. Density of states of isolated MOEP, Pc and MOEP/ Pc - Surface systems provide insights on energy level alignment. This study aims to demonstrate a systematic and comparative analysis of the adsorbate - surface interactions in terms of substrate conformations, energy level alignment, local electronic structure and charge redistribution employing periodic DFT calculations.

[02] INTRODUCTION

Porphyrins: These are macrocyclic organic molecules possessing a large π electron-conjugated system. Porphyrins play crucial role as structural elements and functional components. Blood proteins and photosynthetic pigments like chlorophyll have porphyrin rings. Further, porphyrin molecules have become significant in biosensors, oncotherapy, synthetic organic chemistry, molecular electronics, and solar cells [1].

Structural uniqueness of porphyrins:

- ❖ Porphine backbone
- ❖ Tetrapyrrolic groups
- ❖ Basic chelating system
- ❖ Large pi-conjugation
- ❖ Porphyrin core

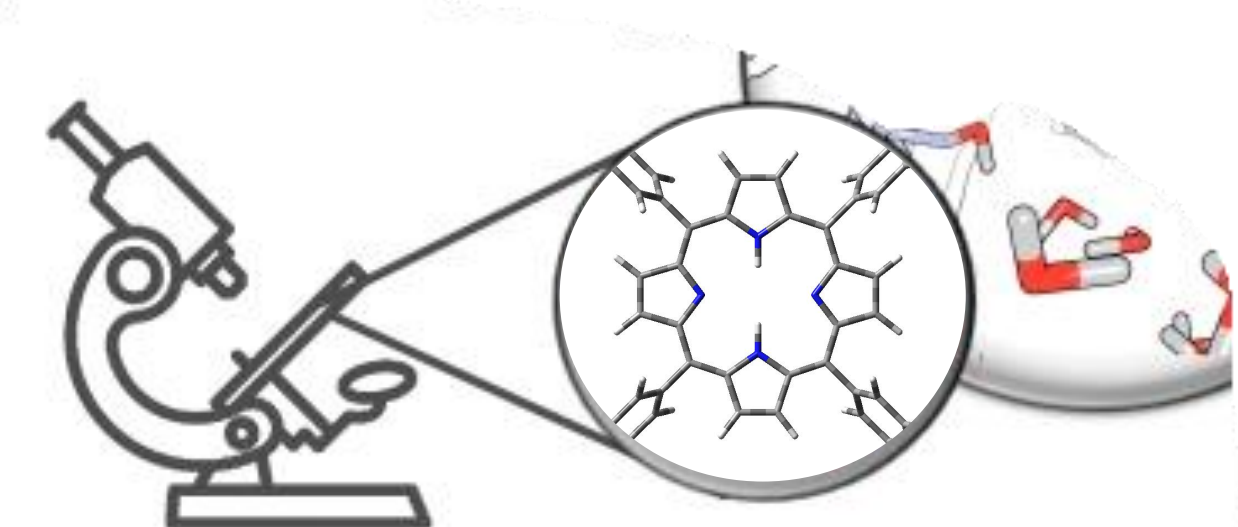
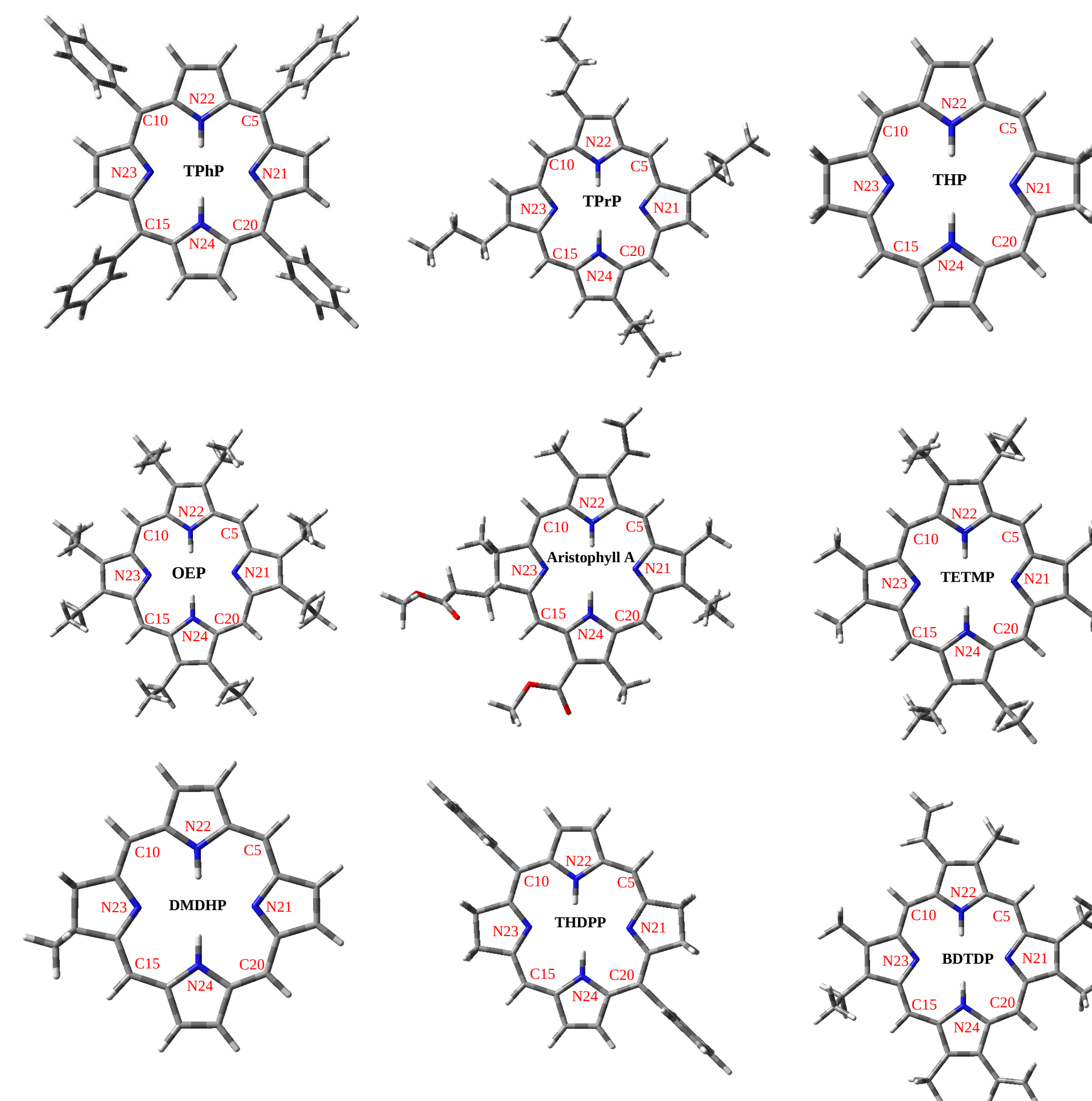


Figure 1. DFT study as “computational microscope” (Adapted from [2])

[03] COMPUTATIONAL METHODS

Up on utilizing density functional theory method (DFT), the electronic molecular structures for ground state of the above compounds were computed. The electronic molecular geometry optimizations were computed at the B3LYP/ 6-31 + G(d) level of theory in gaseous state. B3LYP is a hybrid function which has become a standard method used to study organic chemistry in the gas phase [4].

04.A Ground State Structure Calculations:



[04] RESULTS AND DISCUSSION

Parameters	Optimized Structures									Reference [9]
	TPhP	TPrP	THP	OEP	Aristophyll A	TETMP	DMDHP	THDPP	BDTDP	
Angle X	89.99994°	89.98027°	89.99978°	89.99808°	90.33263°	90.00006°	90.27087°	86.81235°	89.92474°	90.00 ± 0.42°
Angle Y	88.20866°	87.80820°	91.19811°	87.93771°	87.76309°	87.62219°	89.69853°	91.41314°	87.47898°	90.00 ± 1.01°
L1 / Å	2.93961	2.94133	3.00177	2.94470	2.93226	2.94224	2.93146	3.11266	2.94679	2.87 ± 0.12
L2 / Å	4.09173	4.08046	4.28928	4.08880	4.13016	4.07371	4.18546	4.29794	4.07103	4.06 ± 0.16
L3 / Å	6.93938	6.88093	6.89637	6.87170	6.86096	6.87144	6.88197	7.10823	6.87693	6.83 ± 0.35
L4 / Å	4.93036	4.88257	4.91712	4.87907	4.87699	4.87743	4.90024	4.93454	4.87655	4.83 ± 0.34

Table 1. Comparison of structural parameters of computed structures with reported values.

04.C Chemical Quantum Parameters: dipole moment (μ), chemical potential (ρ), electronegativity (χ), and chemical hardness (η).

Chemical quantum parameters	Porphyrin systems								
	TPhP	TPrP	THP	OEP	Aristophyll A	TETMP	DMDHP	THDPP	BDTDP
E_{HOMO}	-0.1918	-0.1928	-0.1733	-0.1886	-0.1888	-0.1876	-0.1903	-0.1727	-0.1916
E_{LUMO}	-0.0925	-0.0854	-0.0926	-0.0815	-0.0986	-0.0817	-0.0923	-0.0926	-0.0903
$\Delta E = E_{HOMO} - E_{LUMO}$ / eV	2.7021	2.9225	2.1960	2.9143	2.4545	2.8817	2.6667	2.1796	2.7565
ρ / eV	-3.8681	-3.7851	-3.6178	-3.6749	-3.9103	-3.6640	-3.8450	-3.6096	-3.8354
χ / eV	3.8681	3.7851	3.6178	3.6749	3.9103	3.6640	3.8450	3.6096	3.8354
η / eV	1.3510	1.4613	1.0980	1.4572	1.2272	1.4408	1.3334	1.0898	1.3783
μ / Debye	0.0426	0.2814	0.0002	0.0003	4.4342	0.0007	2.2409	0.0004	0.29978

Table 2. Chemical quantum parameters of porphyrin systems.

04.B Study of Molecular Orbitals:

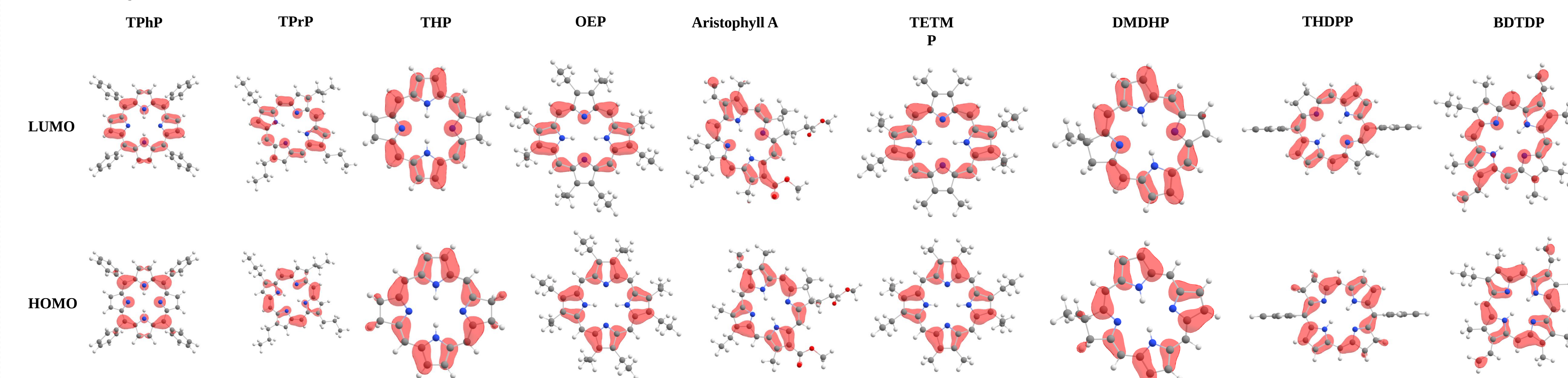
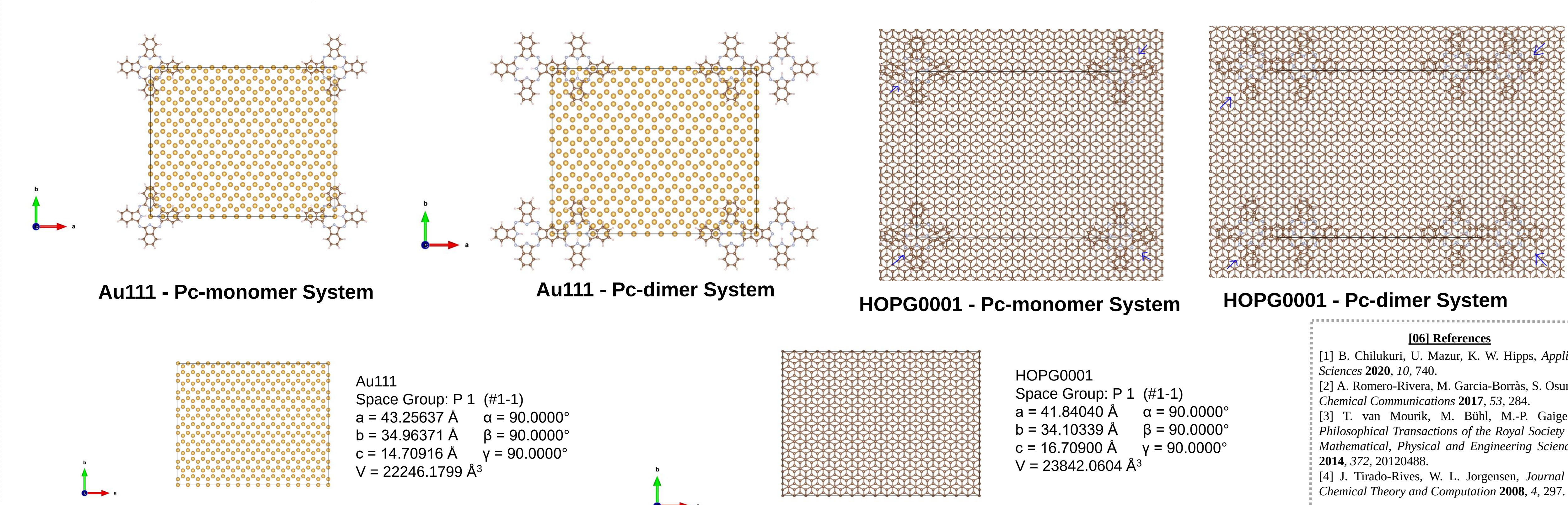


Figure 2. Graphical presentation of frontier molecular orbitals (FMO) for the porphyrin systems

04.D Adsorbate-Surface Systems (isolated molecules):



[06] References

- [1] B. Chilukuri, U. Mazur, K. W. Hipps, *Applied Sciences* **2020**, *10*, 740.
- [2] A. Romero-Rivera, M. Garcia-Borrás, S. Osuna, *Chemical Communications* **2017**, *53*, 284.
- [3] T. van Mourik, M. Bühl, M.-P. Gaigeot, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2014**, *372*, 20120488.
- [4] J. Tirado-Rives, W. L. Jorgensen, *Journal of Chemical Theory and Computation* **2008**, *4*, 297.

[05] Summary

Electronic molecular geometry optimizations were computed at B3LYP/ 6-31+ G(d) level in gaseous state.

Optimized structural parameters are consistent with the reported values.

FMO analysis shows ΔE is higher in TPrP and OEP. This indicates TPrP and OEP are less polarized and less reactive.

Energy gap of smaller band space gap accounts for a higher reactive nature and polarization (e.g.: as observed in Aristophyll A). Such porphyrins can easily donate their electrons to an acceptor. Lowering of energy gap values indicate the effect of intramolecular charge transfer (ICT).

MEP surface investigation depicts molecular regions either attracted to or repulsive to protons. Negative potential surfaces are associated with N and O atoms of the systems.

The β_{tot} values of TPrP, THP, Aristophyll A, THDPP, and BDTDP are greater than the β_{tot} of urea. Comparatively these porphyrin molecules are likely to behave as good NLO materials.

Future Works: involve metalated systems of the corresponding porphyrins.