



Electronic Properties of selected Metallophthalocyanines of iron using computational methods for ORR catalysis

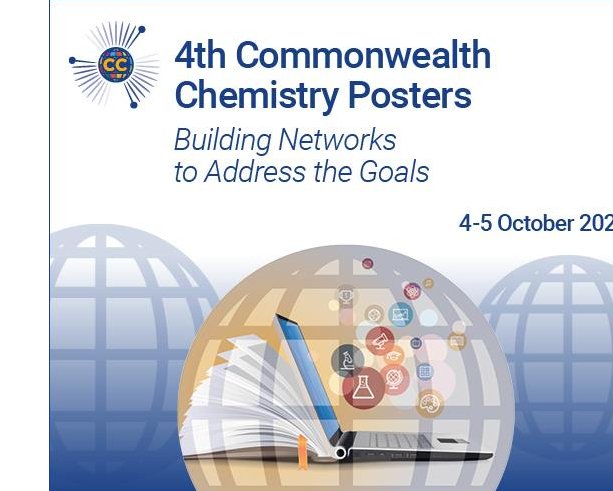
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Abstract

The ORR at the cathode is particularly challenging as it involves a complex four (4) electron transfer mechanism. As a result, the ORR kinetics is very slow and highly irreversible. Thus, highly efficient ORR electrocatalysts are needed to drive the fuel cells. The density functional theory at the B3LYP level using LANL2DZ basis set was used for the investigation of electronic properties of the selected iron phthalocyanines as the potential electrocatalysts for oxygen reduction reaction (ORR). The electronic properties and chemical activity of the titled compounds were investigated by means of several theoretical approaches including geometry optimization, excited states and UV-Vis, molecular electrostatic potential surface, natural bond orbital, and frontier molecular orbital analyses. It was established that the use of electron donor substituents like the ethoxy group and DMSO for push up effect might boost the catalytic behavior of iron phthalocyanines. This was based on the stability, shorter Fe-N bond lengths, the HOMO-LUMO gaps and the band gap analysis. It was established that the use of nitro substituent and pyridine for push up effect might boost the catalytic behavior of iron phthalocyanines and this could be due to their electron withdrawing behavior. Since the positive regions are localized on the Fe²⁺ site, which can be considered as possible sites for nucleophilic attack. Both NBO analysis and fukui function revealed that the Fe site is more electron deficient with the electron withdrawing substituents and electron donating axial ligands or bridging groups in a case of bimetallic systems.

Background

- The advancement of carbon-free energy sources is becoming both a political and a very important scientific issue, not only for transportation but also for stationary power sources.
- This is consistent with the United Nations Sustainable Development Goal 7 which aims to ensure access to affordable, reliable, sustainable, and modern energy for all.
- Polymer electrolyte membrane fuel cells (PEMFCs) appear to be very promising in playing an important role in the development of the “hydrogen economy (Fig.1)

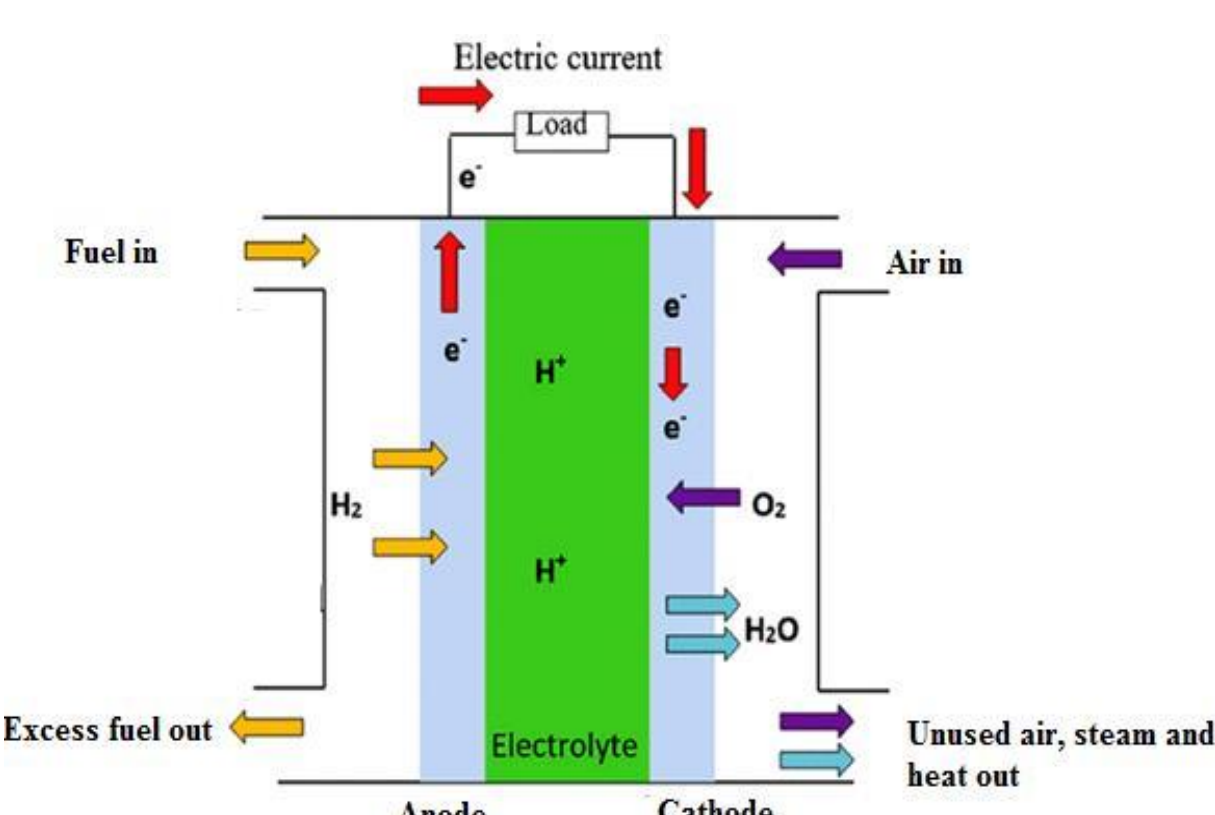


Fig.1: Schematic diagram of PEMFC [1].

- Several catalysts including PM have been used as ORR catalysts
- Theoretical calculations using density function theory (DFT) and time dependent density function theory (TD-DFT) could help in understanding the geometries and electronic properties of MPcs in the ground and excited states.

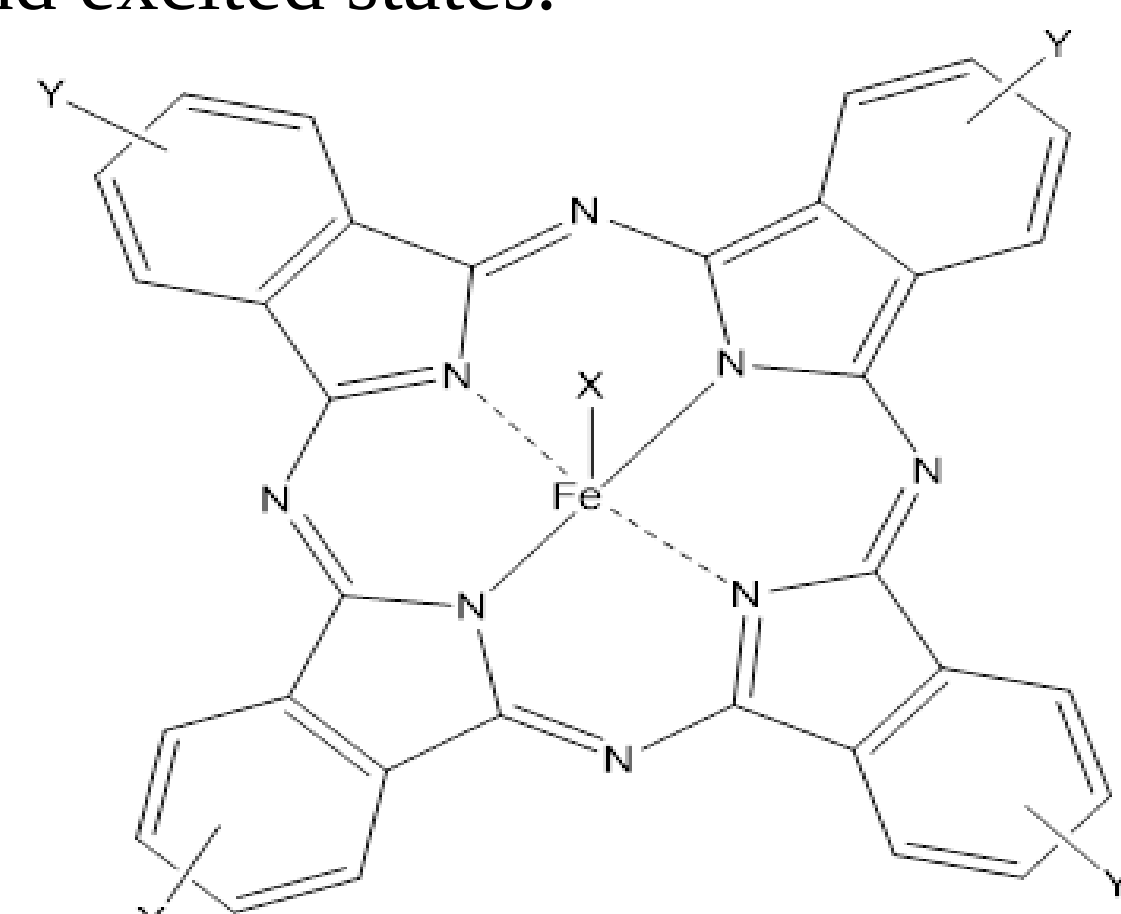


Fig.2: Chemical structures of studied mononuclear MPcs, Y= NO₂, CH₃CH₂O and CH₃CO; X= pyridine, DMF, DMSO, phloroglucinol and 2,7-dihydroxynaphthalene.

Methods

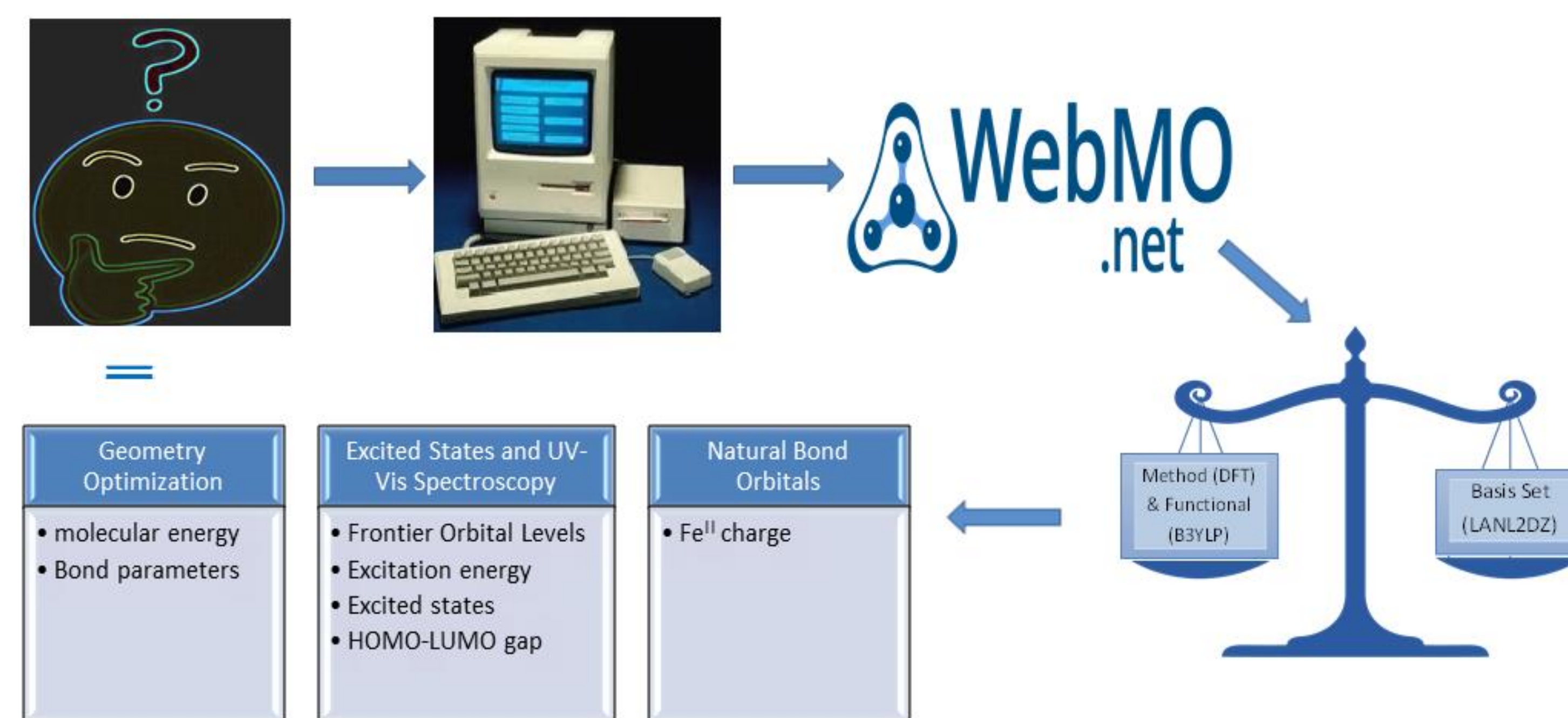


Fig.3: Summary of overall work flow

Results and Discussion

- Thermodynamically Stable (Molecular energy and chemical potential).
- Low excitation energies = low band gaps
- Frontier Orbital levels lying close to O₂ ∴ interact moderately with O₂.
- Redox activity (-0.5 V - +1.0 V), interact moderately with O₂ and consequently reduce O₂.
- Electronegativity and electrophilicity index values are in favour with BiMPcs.

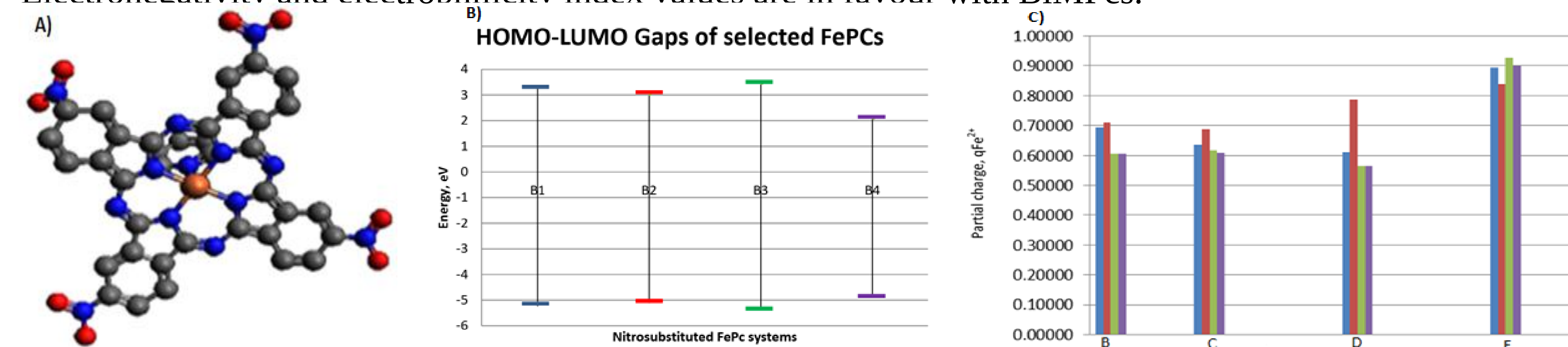


Fig.4 : **A)** Optimized geometry of (NO₂)₄FePcPy; **B)** HOMO-LUMO gap for selected FePcs; **C)** Partial charges on Fe^{II} in studied FePc molecules.

Acknowledgements

This work has been supported by African Union and European Union Intra Africa Mobility Scheme ESIMSAD (Grant Agreement Number 624175-PANAF-1-2020-1-ET-PANAF-MOBAF). We also acknowledge the support from Laboratory for Research on Structure of Matter (LRSM), University of Pennsylvania, USA

Conclusion and Future Work

- DMSO is the best axial ligand of the studied groups followed by pyridine.
- Axial coordination has more effect on the electronic properties than peripheral substitution.
- BiMPcs exhibit better electronic properties than mononuclear systems.
- It is crucial to ascertain iterative feedback by synthesising and characterizing these FePc systems by various spectroscopic and electrochemical techniques and ultimately characterize their catalytic activity in ORR.
- It is still unclear how the metal centers interact with each other in BiMPcs.

References

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