Computational study of CO_2 electrochemical reduction catalyzed by a manganese corrole complex

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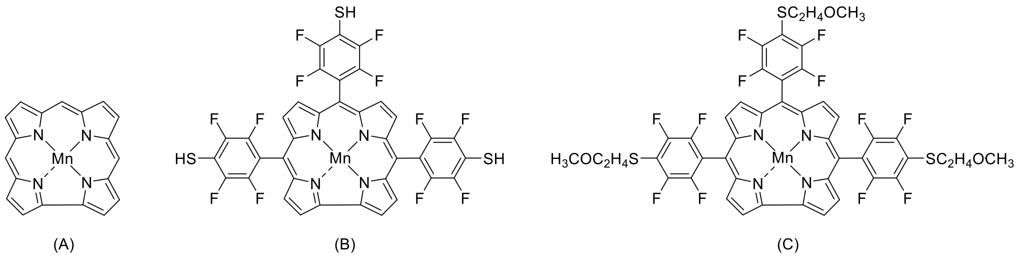
ABSTRACT

In this work, the electroreduction mechanism of CO_2 with a manganese corrole complex has been studied using DFT methods. This reaction yields acetic acid as the main product, in addition to CO, methanol and H_2. [1] Geometry optimizations and frequency calculations were carried out using the B3LYP functional and Def2-SVP basis set and energies were refined using PBE and Def2-TZVP. This method was chosen after a benchmark using different functionals and the models shown in Figure 1.

The redox potentials were calculated using the Fc/Fc^+ pair as a reference. Since this is an open shell system, all structures were optimized with different multiplicities to verify which is the most stable. No spin contamination was found in the structures involved in the reaction pathway. For the carbon-carbon bond step, it is interesting to highlight that the geometry and energy barrier of its transition state, as well as the resulting product, are highly dependent on the spin multiplicity.



(A) (B) (C)

Figure 1: Catalyst *models. A) Small. B) Medium. C) Large.*

References

[1] De, R.; *et al*. Electrocatalytic Reduction of CO_2 to Acetic Acid by a Molecular Manganese Corrole Complex. *Angew. Chem. Int. Ed*. **2020***, 59,* 10527–10534.