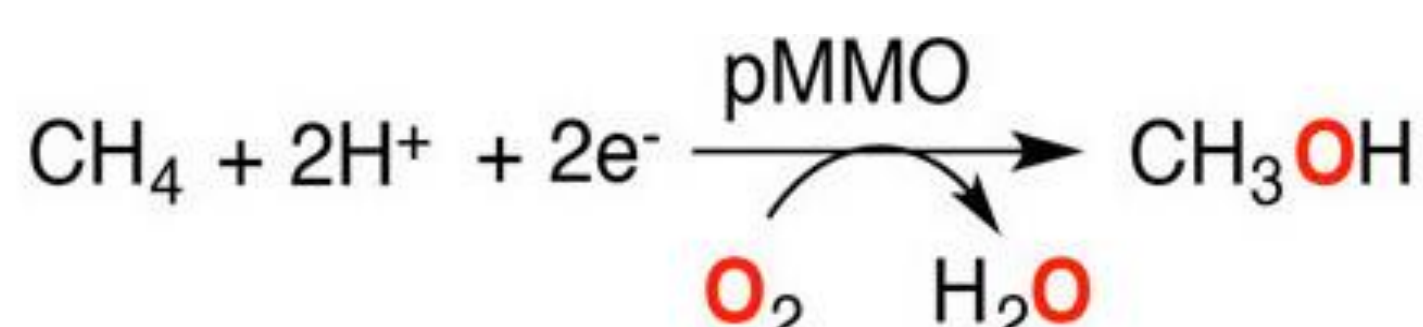


# Understanding the Oxidative Chemistry of Particulate Methane Monooxygenase Models

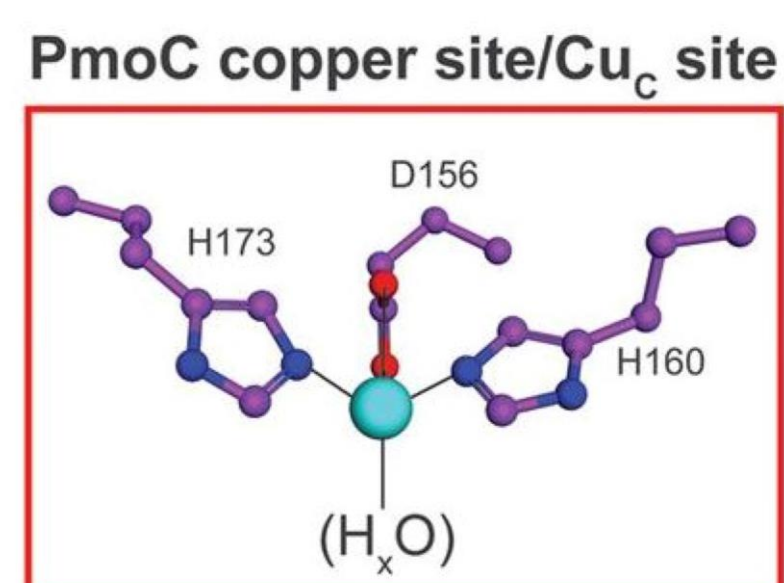
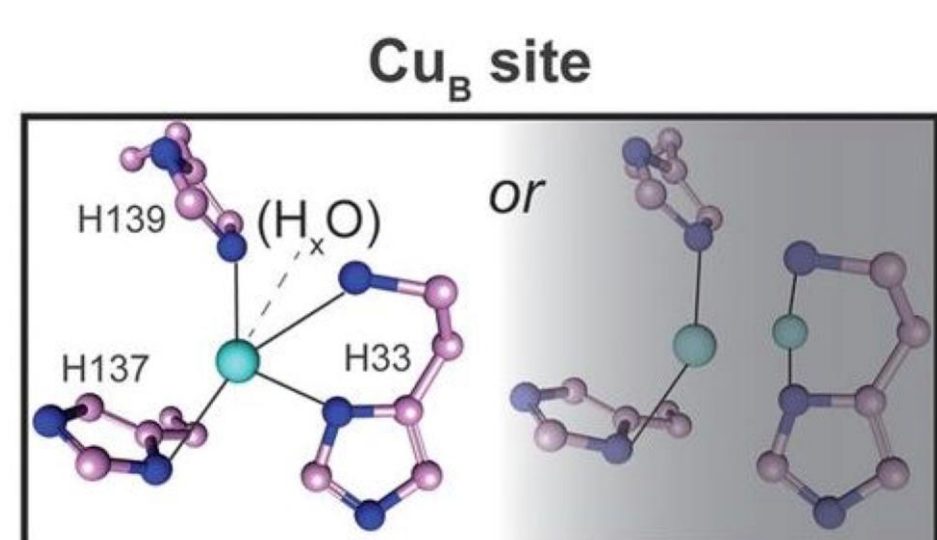
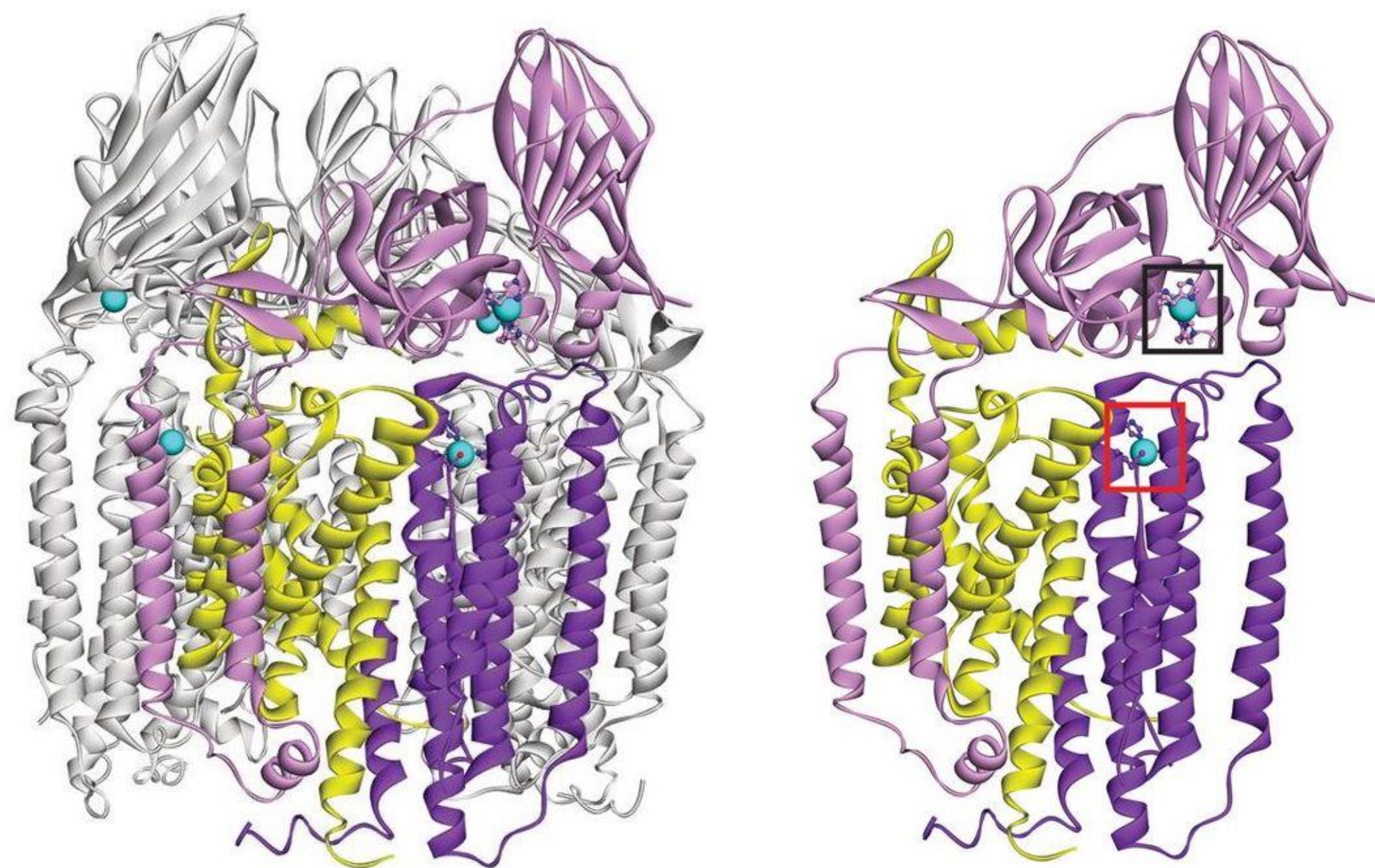
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## Background

Particulate methane monooxygenase (pMMO) is a membrane protein found in methanotrophic bacteria that catalyzes the two-electron reduction of dioxygen to form an unknown reactive intermediate that performs the partial oxidation of methane to methanol.



This reaction has generated significant interest for its potential for both carbon sequestration and for use of methane as an alternative energy source. Methane is one of the main forms of atmospheric carbon and greenhouse gas, as well as the major component of natural gas. Industrial processes for the oxidation of methane to methanol require high temperatures and pressures and suffer from low yields, making them dangerous and expensive. This difficult oxidative chemistry is performed by pMMO under ambient conditions at one of two unique copper sites.

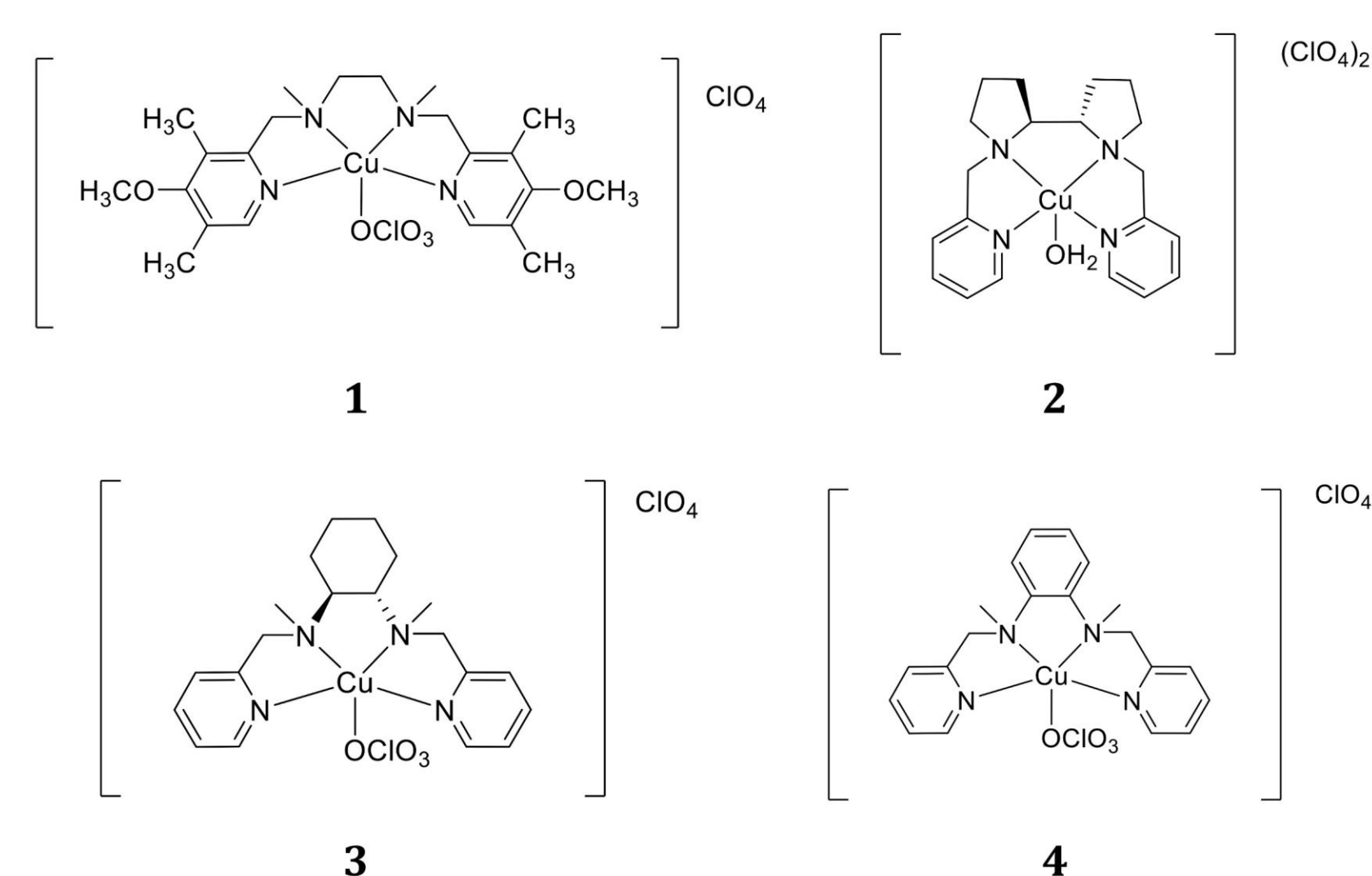


Upper left: crystal structure of pMMO; upper right: crystal structure of one protomer of pMMO indicating both of its copper binding sites; lower left: structure of the Cu<sub>B</sub> site of pMMO; lower right: structure of the Cu<sub>C</sub> site of pMMO.

The structure of the Cu<sub>B</sub> site was originally modelled as a dinuclear site and remained ambiguous until 2019, when it was demonstrated to be mononuclear. This has left the site of substrate oxidation an open question, with some reports proposing the Cu<sub>B</sub> site and others the Cu<sub>C</sub> site as the site of substrate binding and oxidation. Synthetic model studies may provide some insight.

*Science*. 2019. 364 (6440), 566-570

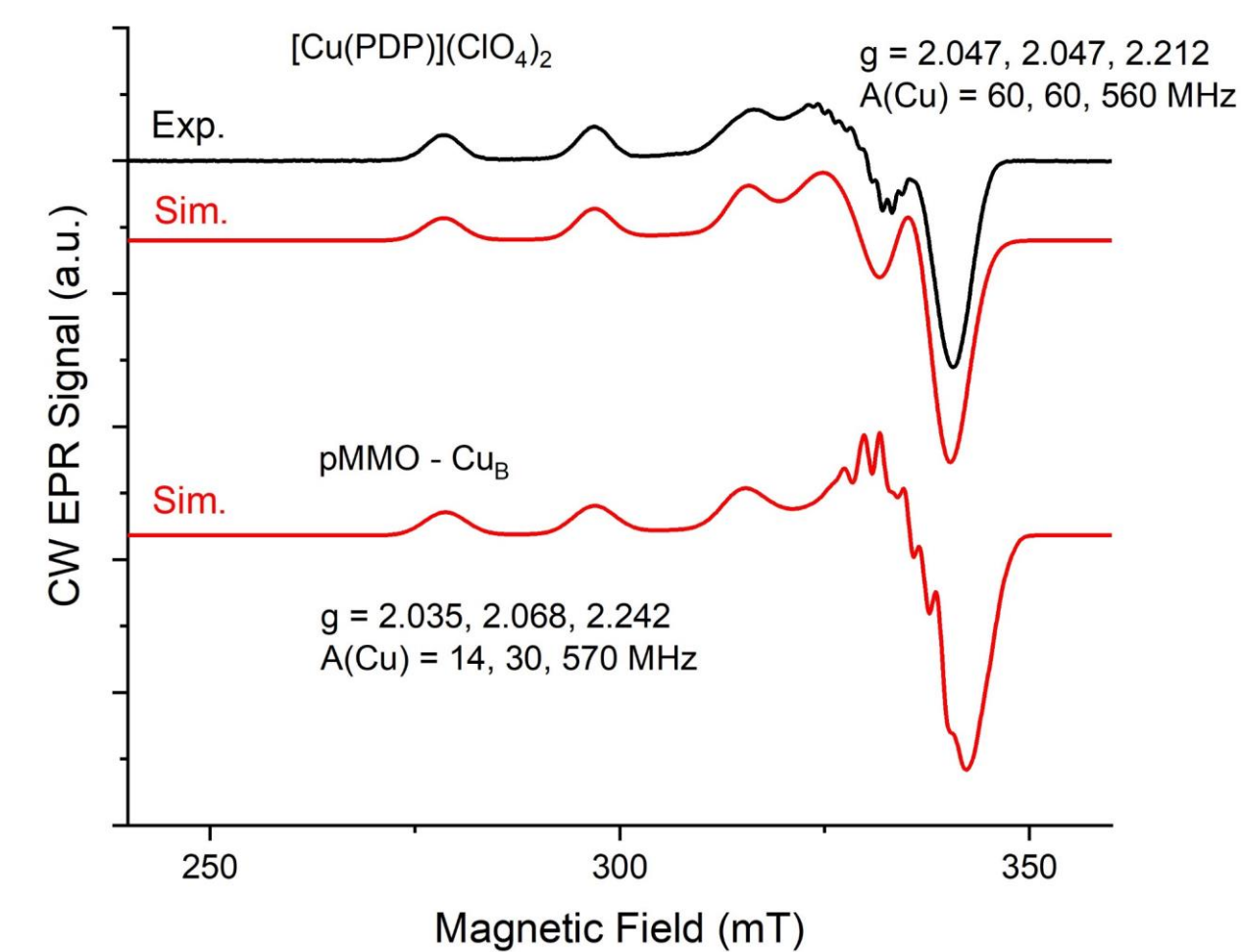
## Reactivity of pMMO Models



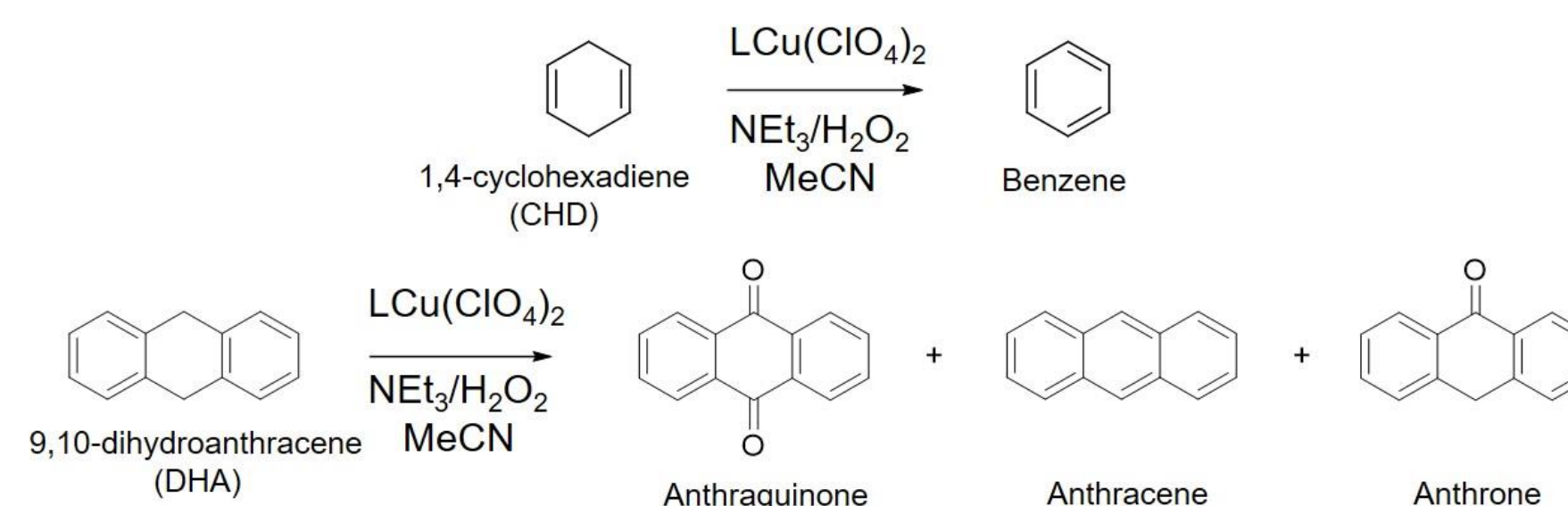
All of the four complexes above feature both aliphatic and aromatic nitrogen donor atoms, reminiscent of the coordination environment of the Cu<sub>B</sub> site of pMMO. The variations to the ligand framework across complexes **1-4** are meant to vary the steric and electronic properties of the complex to study which factors affect the complex's reactivity. Reactivity studies were halted for **4** due to solubility issues.

Complex **2** exhibited EPR spectroscopic parameters very similar to those observed for the Cu<sub>B</sub> site of pMMO, generating curiosity regarding its reactivity.

*Inorganica Chim. Acta*. 2018. 483, 71-78



Oxidation of CHD and DHA as external substrates was explored for complexes **1-3**.



Complex	Benzene	Anthraquinone	Anthracene	Anthrone
<b>1</b>	47%	20%	19%	3%
<b>2</b>	52%	21%	19%	3%
<b>3</b>	52%	21%	20%	4%
Control	3%	2%	2%	0%

Complexes **1-3** were capable of C-H bond activation and substrate oxidation in the case of CHD and DHA, but not for substrates with higher bond dissociation energies. The variations to the ligand framework did not seem to affect reactivity. Further investigation will be required to determine what factors dictate the observed reactivity.

## Acknowledgements

Department of Chemistry - College of Science  
Funding – UAH IIDR Award