

Introduction

Development of catalysts for efficient, ecologically benign, and economical catalytic oxidation faces several challenges:

- Ensure oxidative stability
- Prevent catalyst oligomerization
- Provide high selectivity
- Reduce waste

Electrocatalytic System

An electrocatalyst uses electrical potential to carry out oxidation.

- Requires an electrode to conduct oxidative current
- Electrode surface often functions as the catalyst
- Bulk surface has lower selectivity than discrete molecular catalyst

Our system combines molecular catalysts with a conductive electrode:

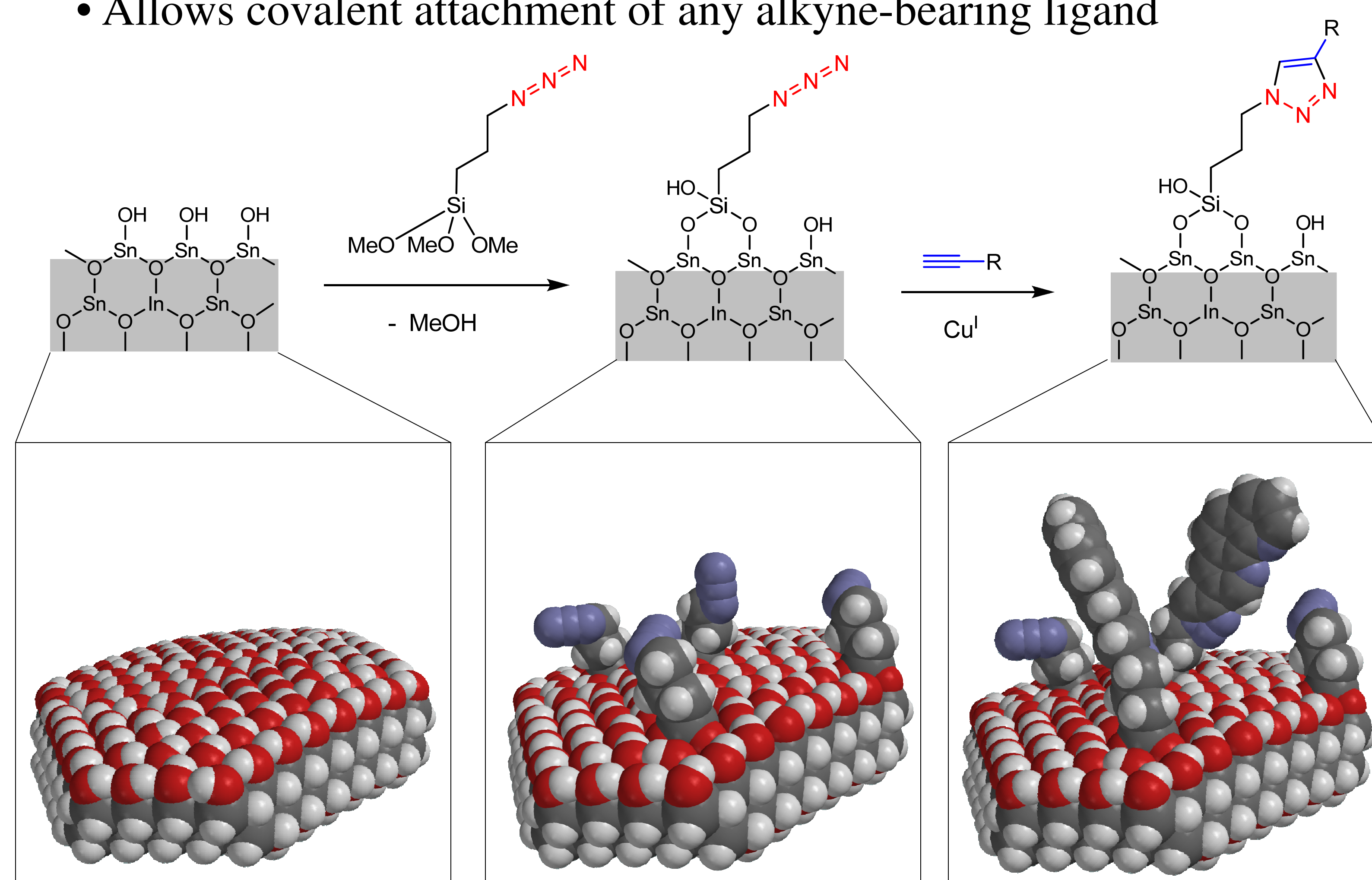
- Indium tin oxide (ITO) electrode is a conductive oxide surface that is stable under oxidative conditions
- Catalyst is covalently linked to electrode to prevent desorption
- Synthetic modularity to tune selectivity
- Potential site-isolation to prevent oxidative ligand damage and catalyst oligomerization
- Use in any medium (aqueous or organic)

Covalent Attachment Method

- Modular, two-step covalent attachment strategy:

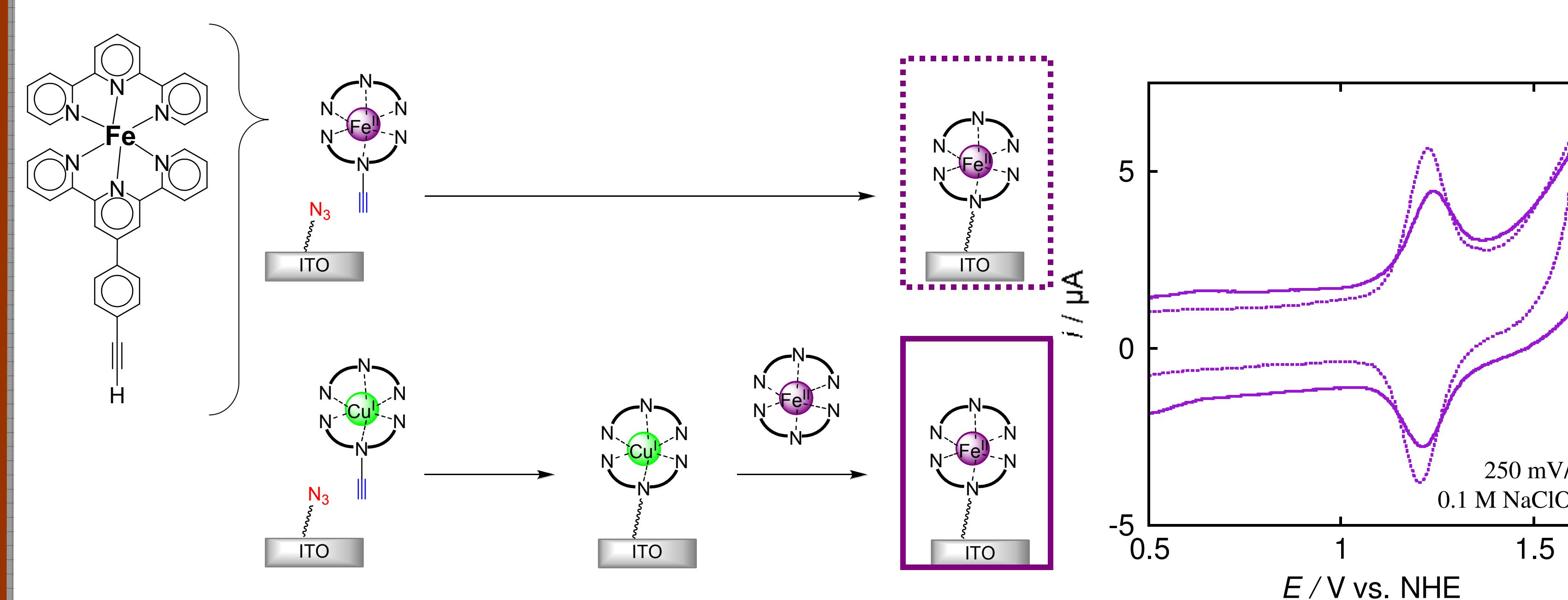
- (1) Attach organo-azide linker through condensation
- (2) Attach alkyne through Cu-catalyzed alkyne-azide 'click' coupling

- Allows covalent attachment of any alkyne-bearing ligand

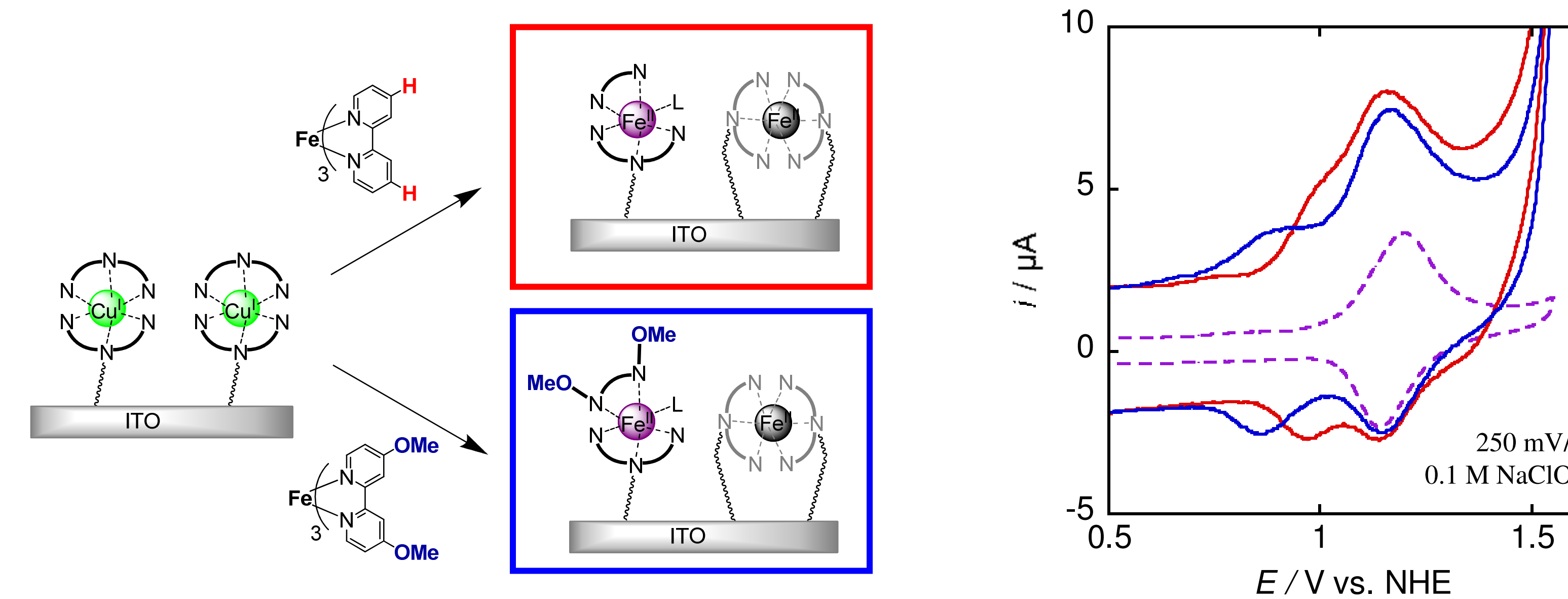


Synthetic Modularity on the ITO Surface

The azide-modified surface is loaded with electroactive complexes by either (A) forming the complex and then clicking it directly, or (B) covalently attaching the ligand, then building up the desired complex.

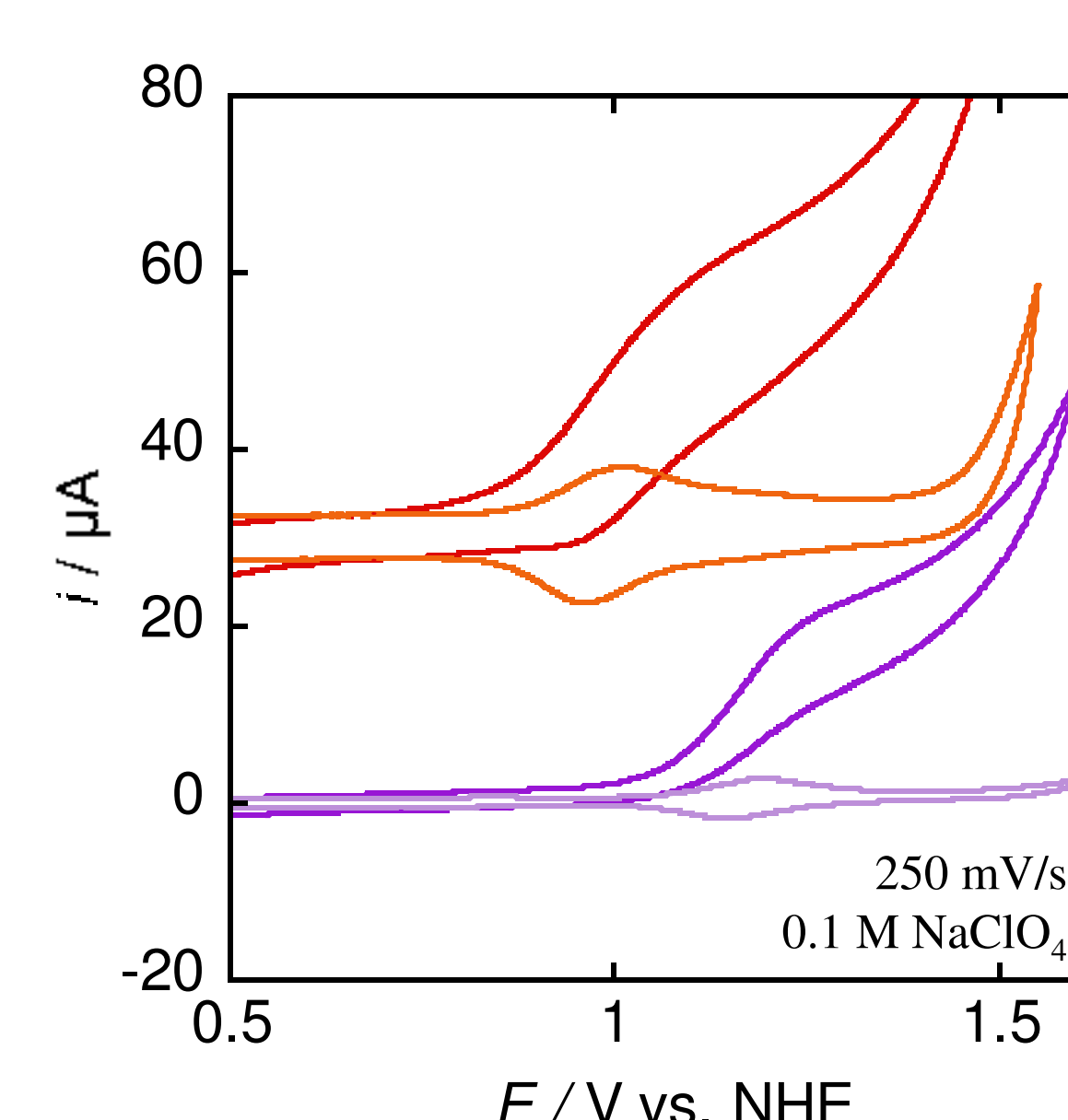


Changes in the redox potential reflect changes in the composition of the complex. The complex can be modified (A) with a different type of ligand, or (B) with variations on the same type of ligand.



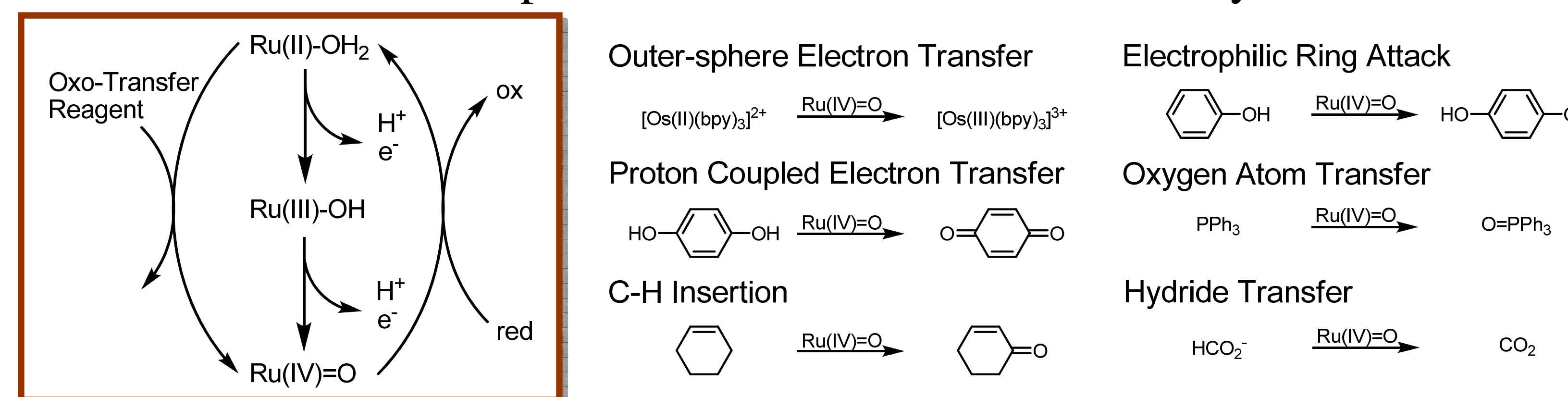
Better Efficiency Through Synthesis: Catalytic Oxidation of H₂O₂

- Oxidation by outer-sphere electron transfer¹
- Proof of concept: Synthetic modification → Modified redox potential → Lower catalytic overpotential
- Catalytic performance: observed overpotential (0.61 V) similar to recent electrocatalytic materials²
- Ongoing work toward inner-sphere catalysis

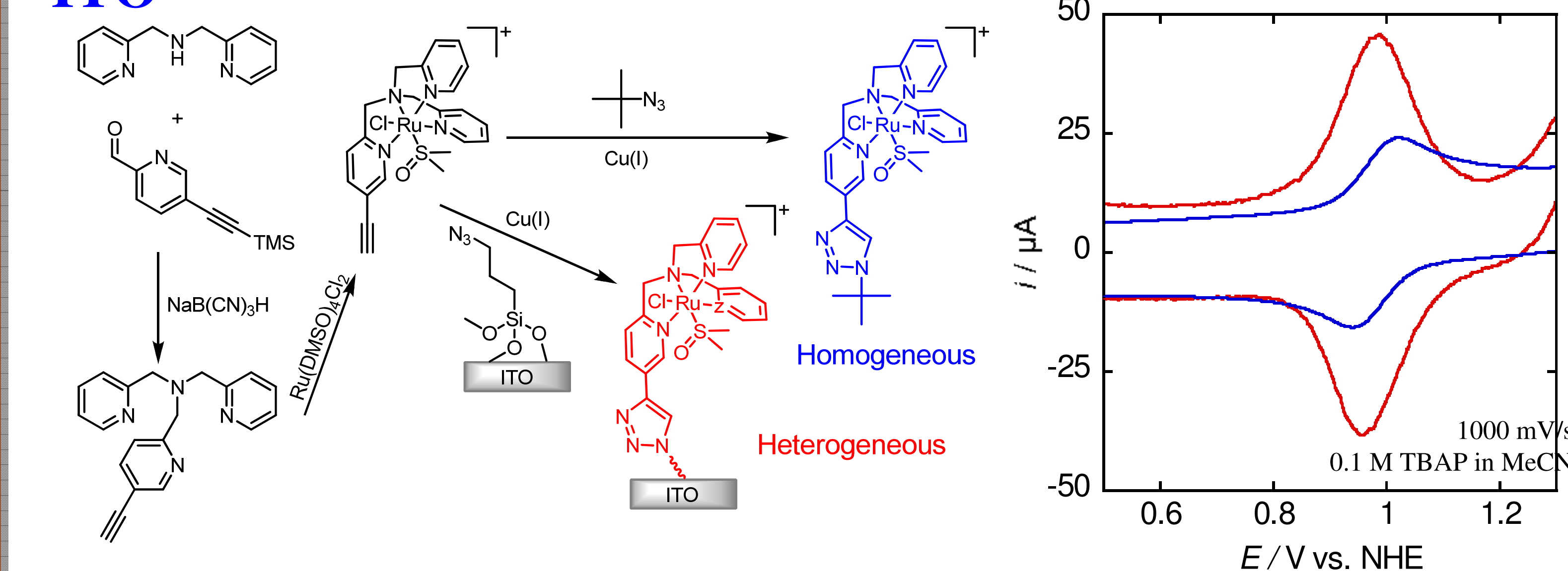


Ruthenium Oxidation Catalysis

- Ruthenium-oxo complexes are versatile oxidation catalysts³

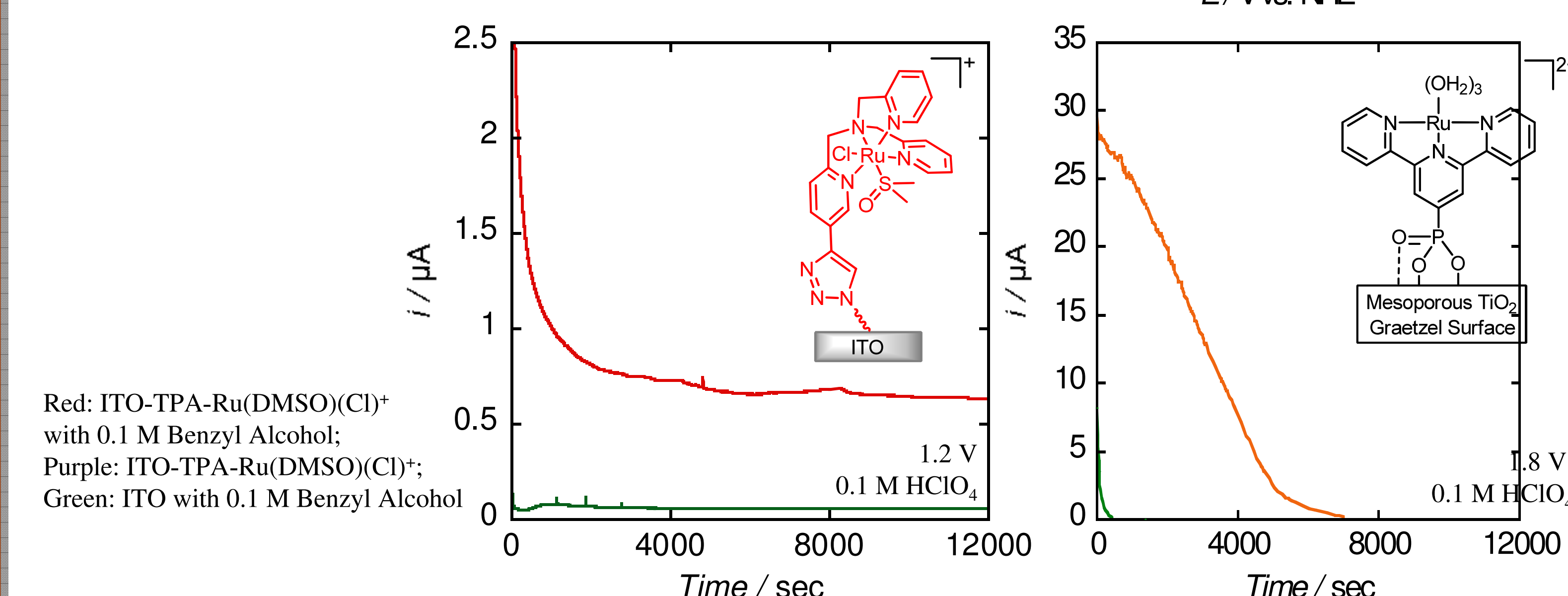


Synthesis and Immobilization of a Ruthenium Complex on ITO



Electrocatalytic Oxidation of Alcohol

- The immobilized Ru-TPA complex shows higher TONs & TOF at lower potentials for alcohol oxidation compared to literature⁴
- The immobilized Ru-TPA complex is a more durable catalyst compared to literature⁴



Red: ITO-TPA-Ru(DMSO)(Cl)⁺ with 0.1 M Benzyl Alcohol; Purple: ITO-TPA-Ru(DMSO)(Cl)⁺; Green: ITO with 0.1 M Benzyl Alcohol

Catalytic Voltage	1.2 V	1.8 V
TON	350	115
TOF _{avg}	105 hr ⁻¹	60 hr ⁻¹
Coverage	7•10 ¹³ molecules cm ⁻²	2•10 ¹⁷ molecules cm ⁻²

Conclusions

- Developed a stable system for catalyst immobilization
- Characterized immobilized complexes electrochemically
- Demonstrated redox tuning through synthetic manipulation
- Achieved electrocatalysis of multiple substrates

References

1. McCartney, D. *Can. J. Chem.* **1986**, *64*, 1936.
2. Niwa *et al.* *Anal. Chem.* **2003**, *75*, 2080; Zhang *et al.* *Int. J. Electrochem. Sci.* **2009**, *4*, 407
3. Meyer, T.J. *et al.* *Inorg. Chem.* **2003**, *42*, 8140.
4. Hornstein, B. J. *et al.*; *Inorg. Chem.* **2007**, *46*, 8139-8145.

* All reported voltages vs. NHE