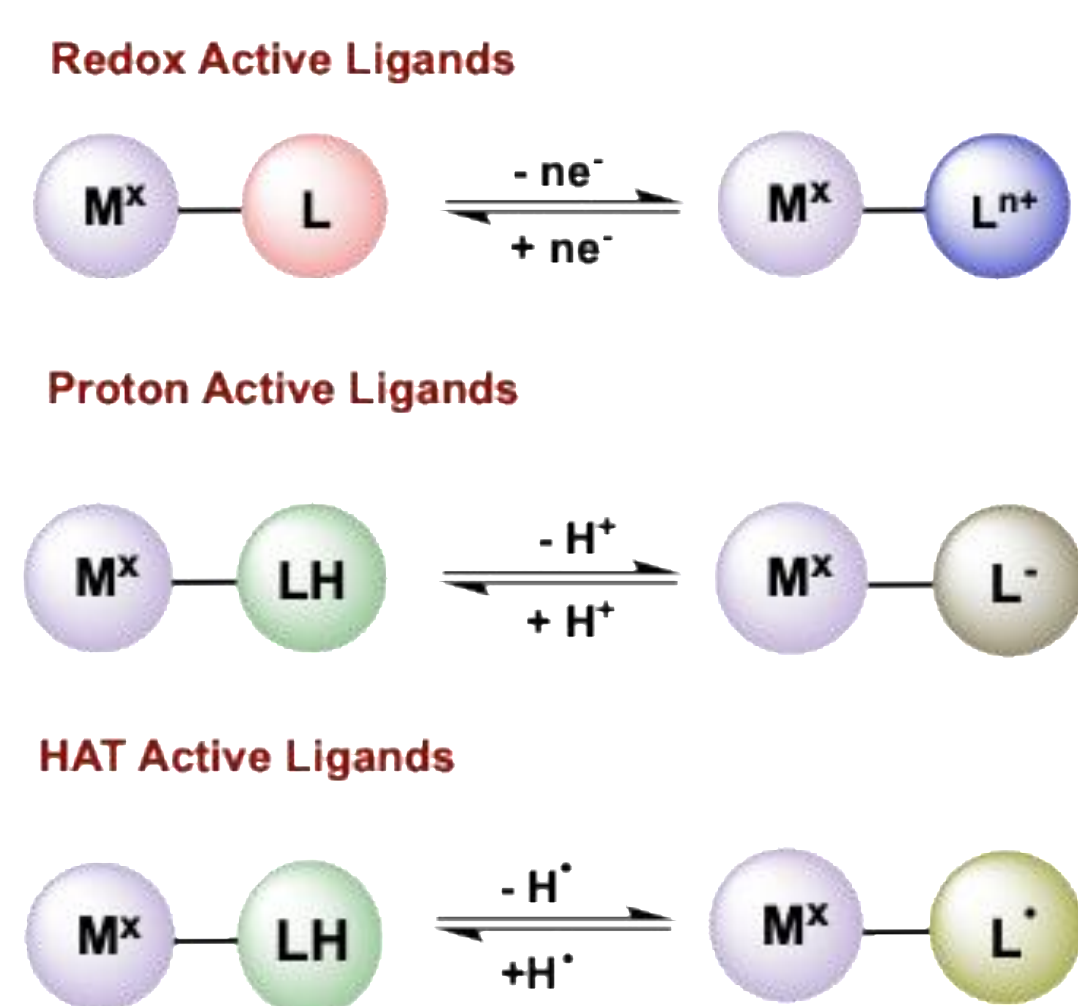
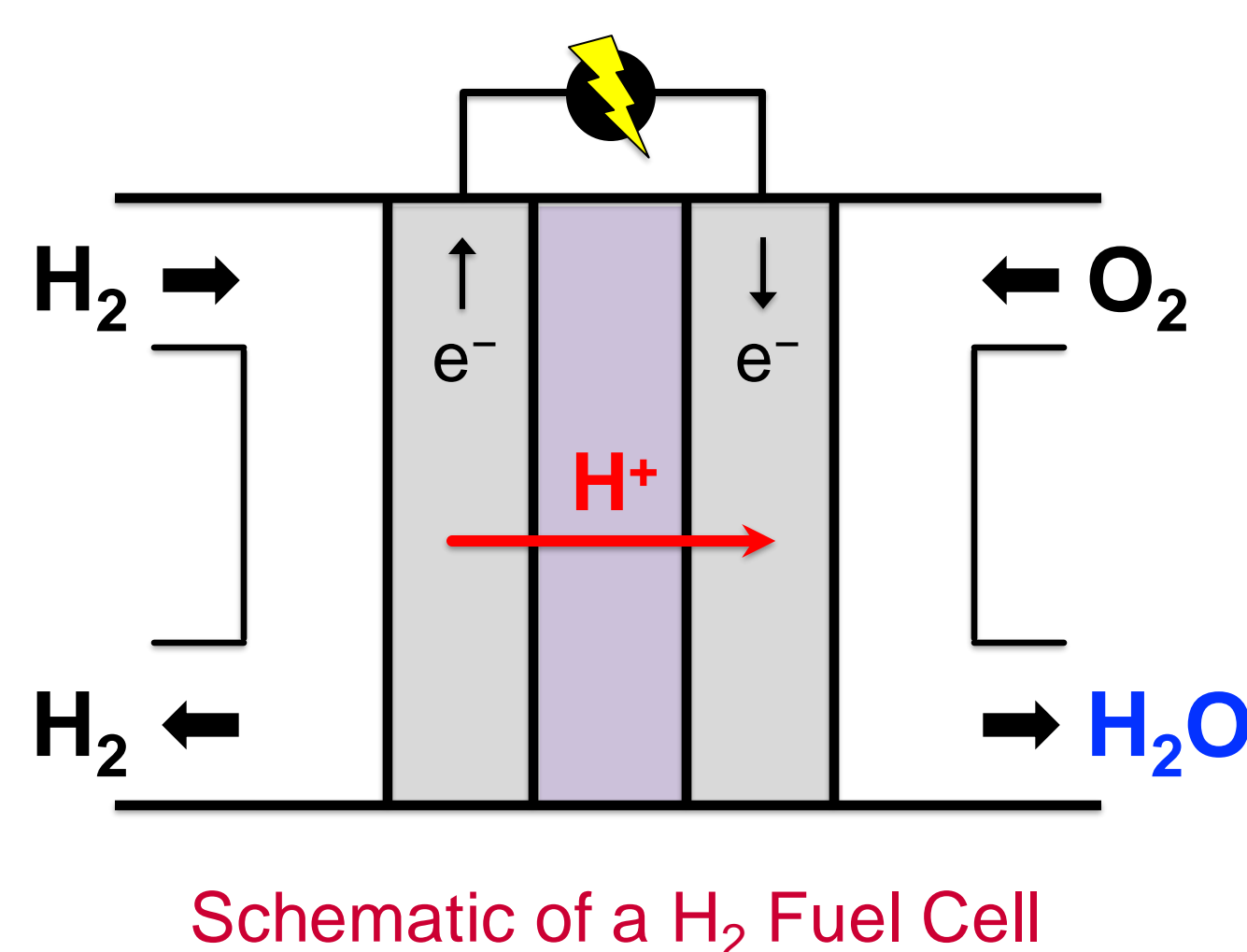




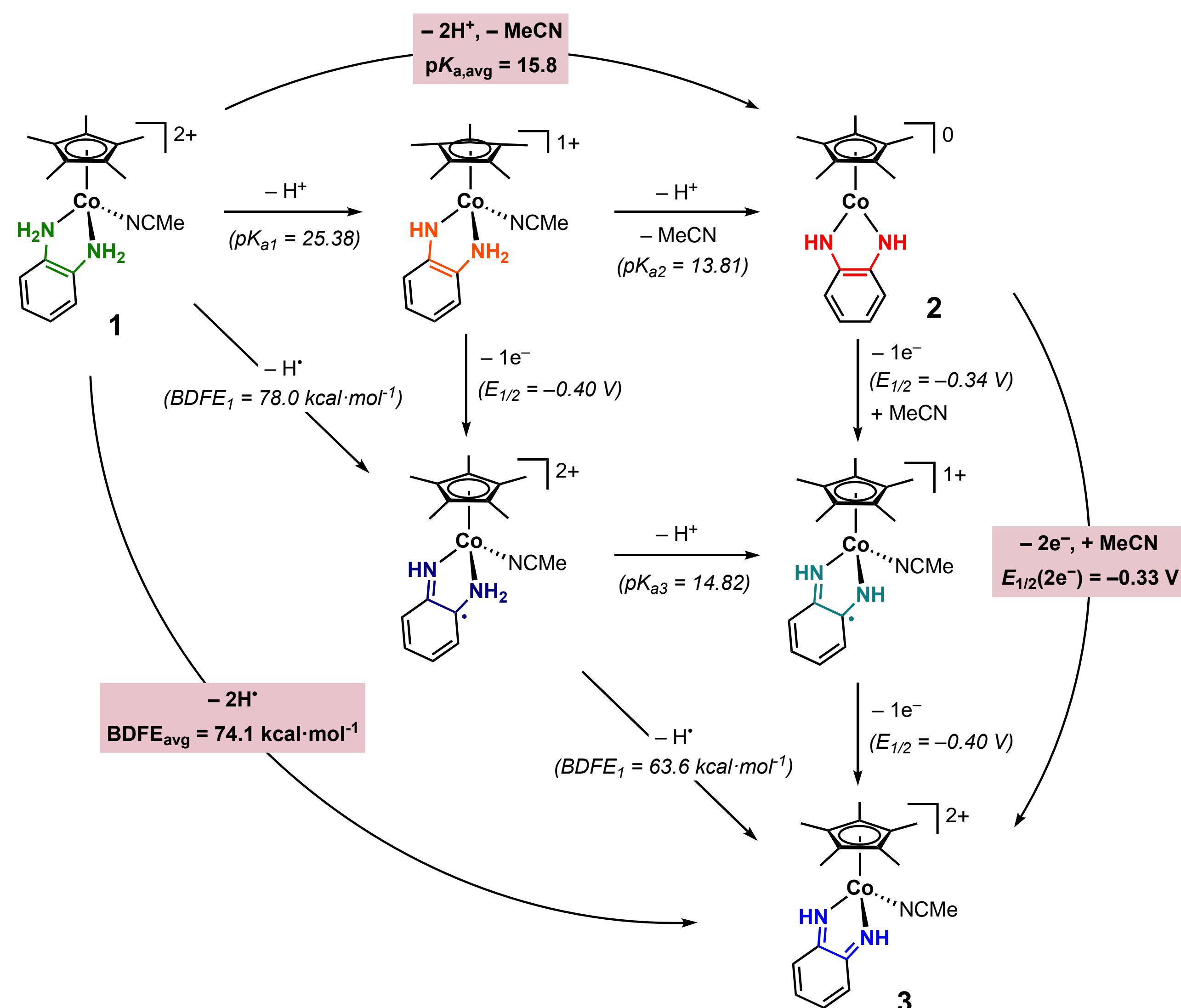
Introduction and Motivation

The oxygen reduction reaction (ORR) is integral to emerging renewable energy technologies, serving as the reduction half-reaction for fuel cells. Developing non-noble metal systems for this process and understanding how catalyst structure and ligand design govern ORR selectivity for water over hydrogen peroxide are important research areas. The majority of studies into molecular transition metal complexes based on earth-abundant metals have used macrocyclic ligands, while studies to explore the possible roles of redox-active ligands are scarce. Redox-active ligands with protic sites may engage in proton-coupled electron transfer or hydrogen-atom transfer (HAT) with oxygen to favor water formation, opening new avenues for electrocatalyst design.



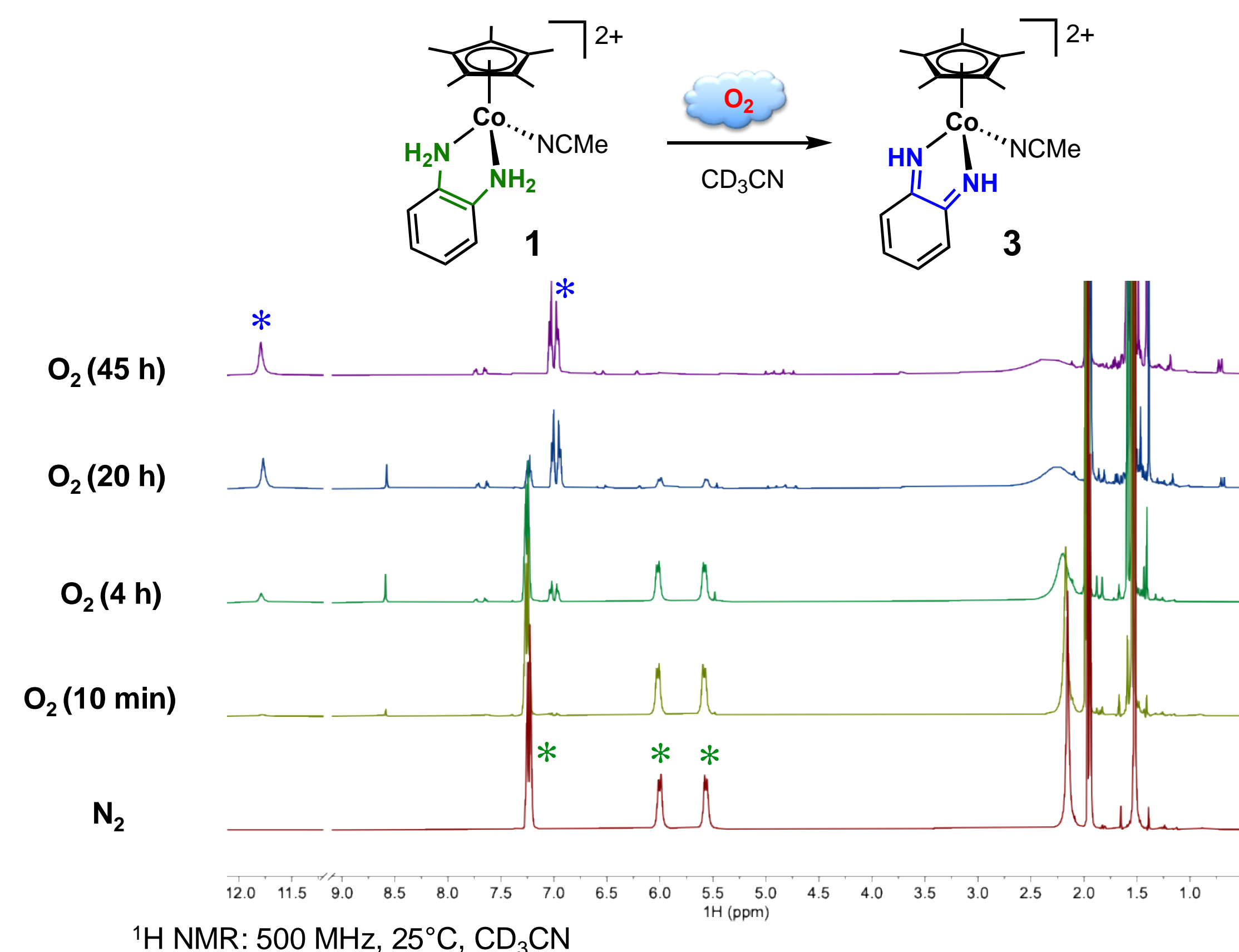
HAT Reactivity of a Cobalt Complex

Complex **1** features a phenylenediamine ligand, which has an average acidity of $pK_a = 15.8$ in MeCN. The resulting complex **2** can be oxidized in a $2e^-$ process at $E_{1/2} = -0.33$ V vs. $Fc^{+/0}$. Taken together, the $2e^-/2H^+$ square scheme can be constructed (*DFT energies in brackets*).



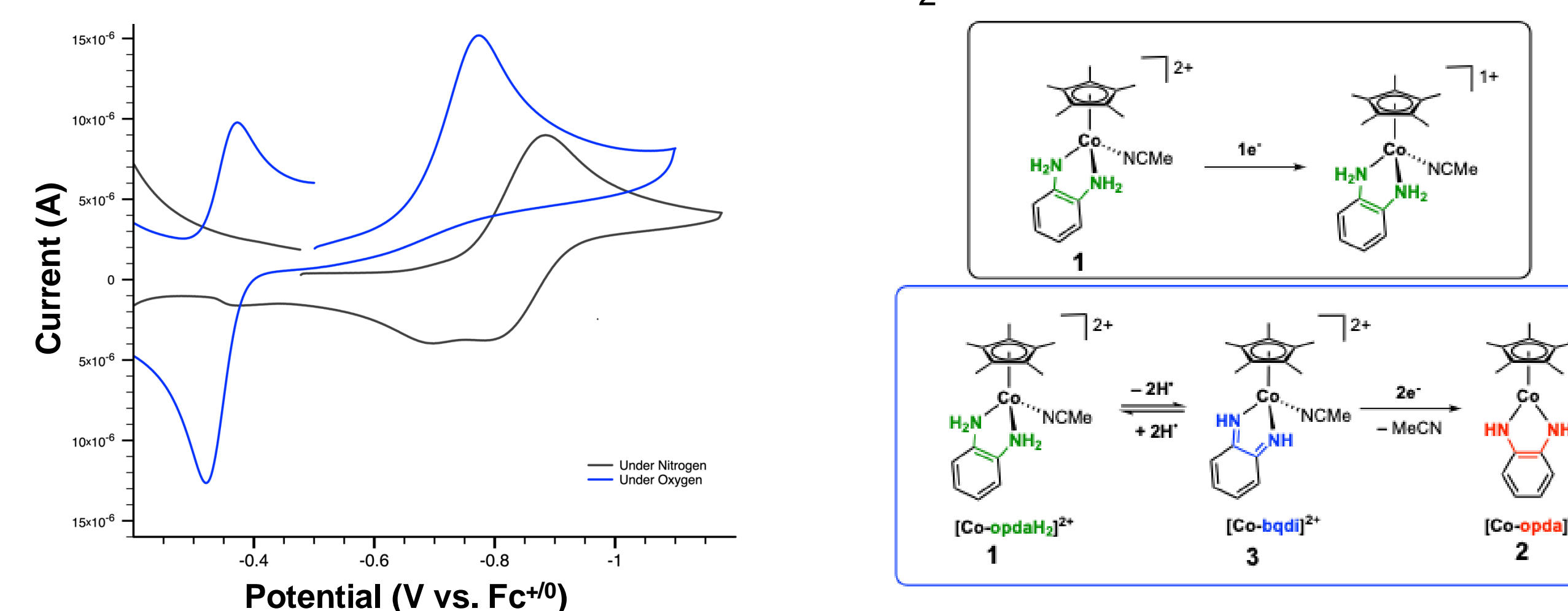
Stoichiometric Reactivity with Oxygen

Exposure of a solution of complex **1** in CD₃CN to an O₂ atmosphere leads to a gradual color change indicative of the formation of complex **3**, which was confirmed by ¹H NMR. This reactivity suggests that **1** can transfer two hydrogen atoms to oxygen.

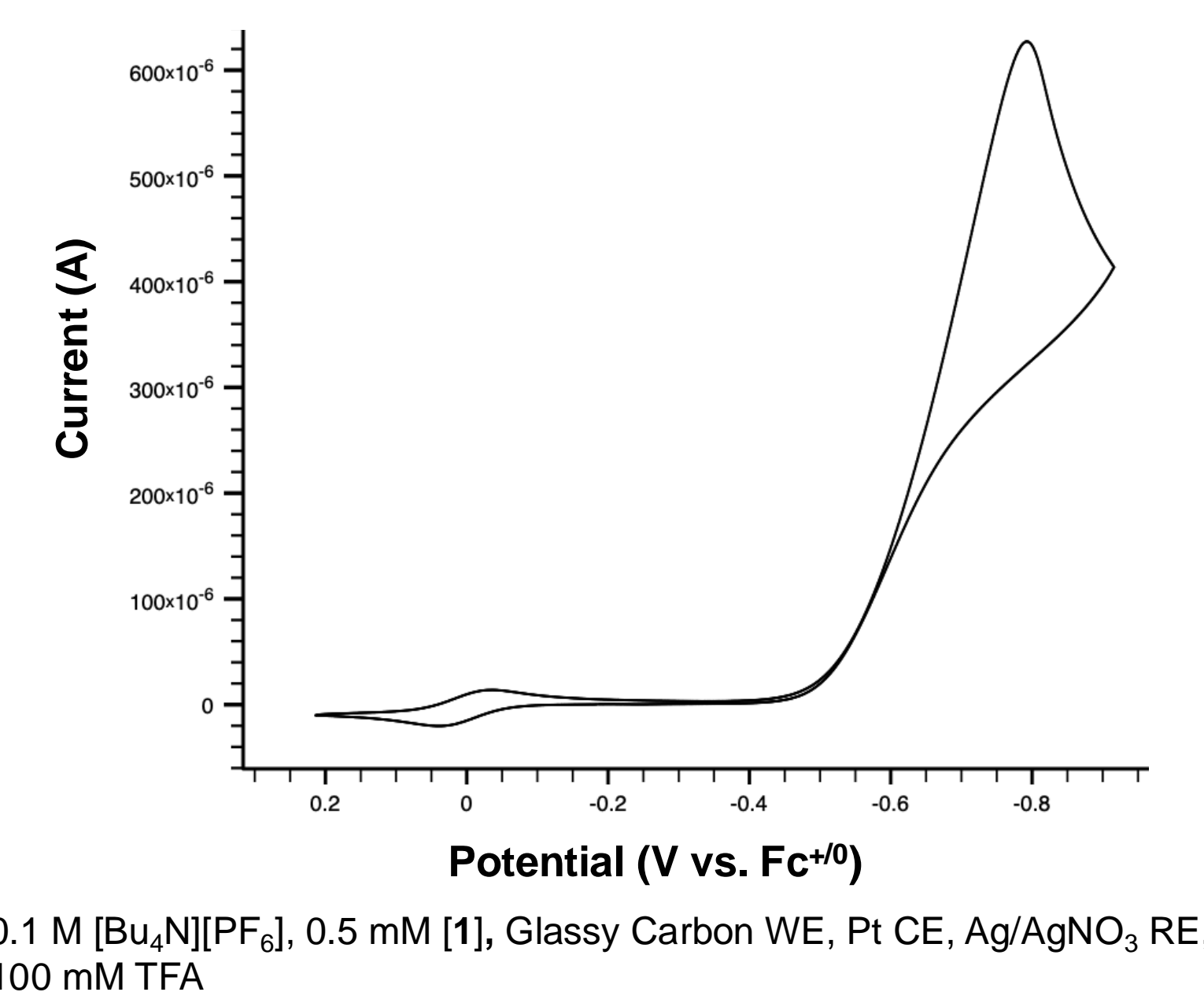


Electrochemical Studies

By cyclic voltammetry (CV), complex **1** is reduced at -0.82 V vs. $Fc^{+/0}$ under N₂ atmosphere. Upon O₂ saturation, a new reversible redox couple at -0.33 V vs. $Fc^{+/0}$ is observed, which is consistent with the $2e^-$ reduction of complex **3** formed *in situ* after the reaction of **1** with O₂.

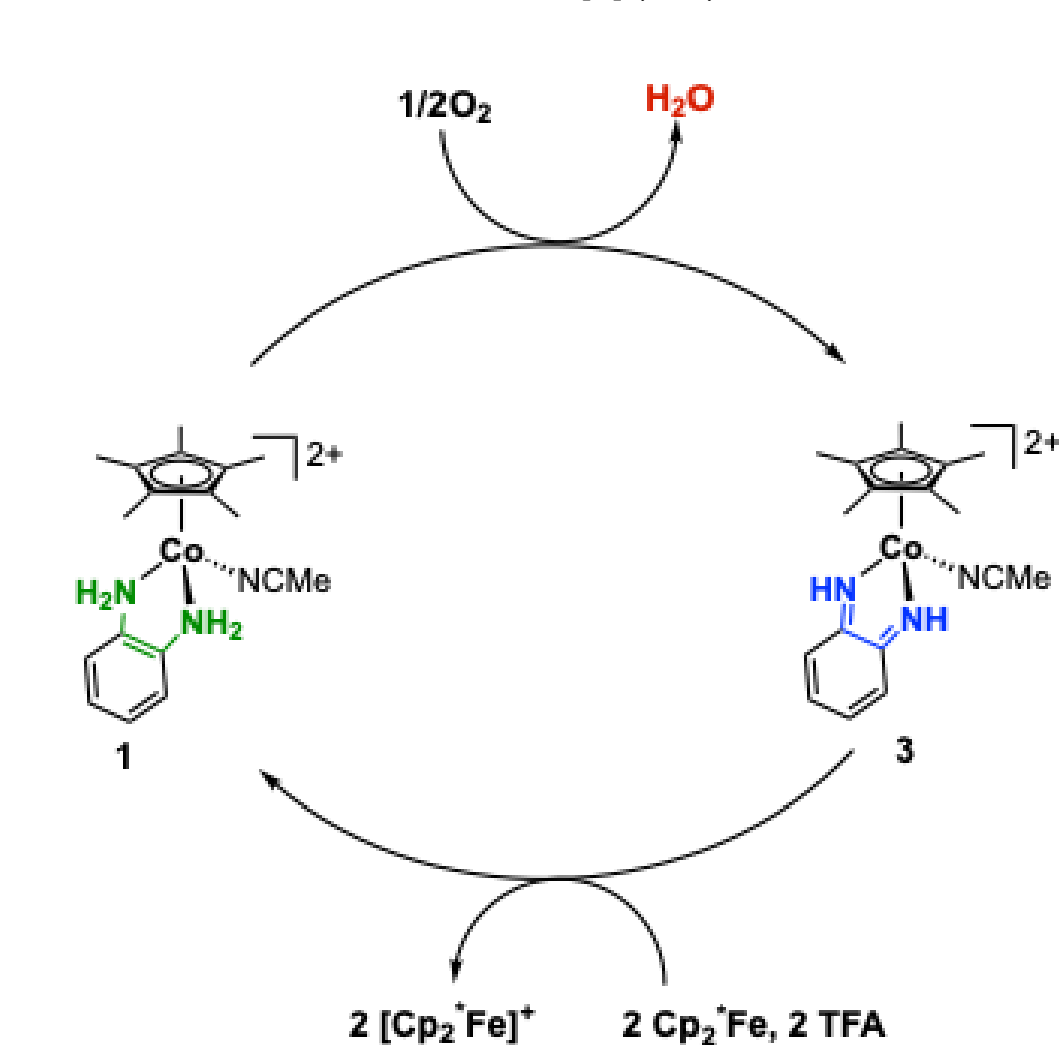
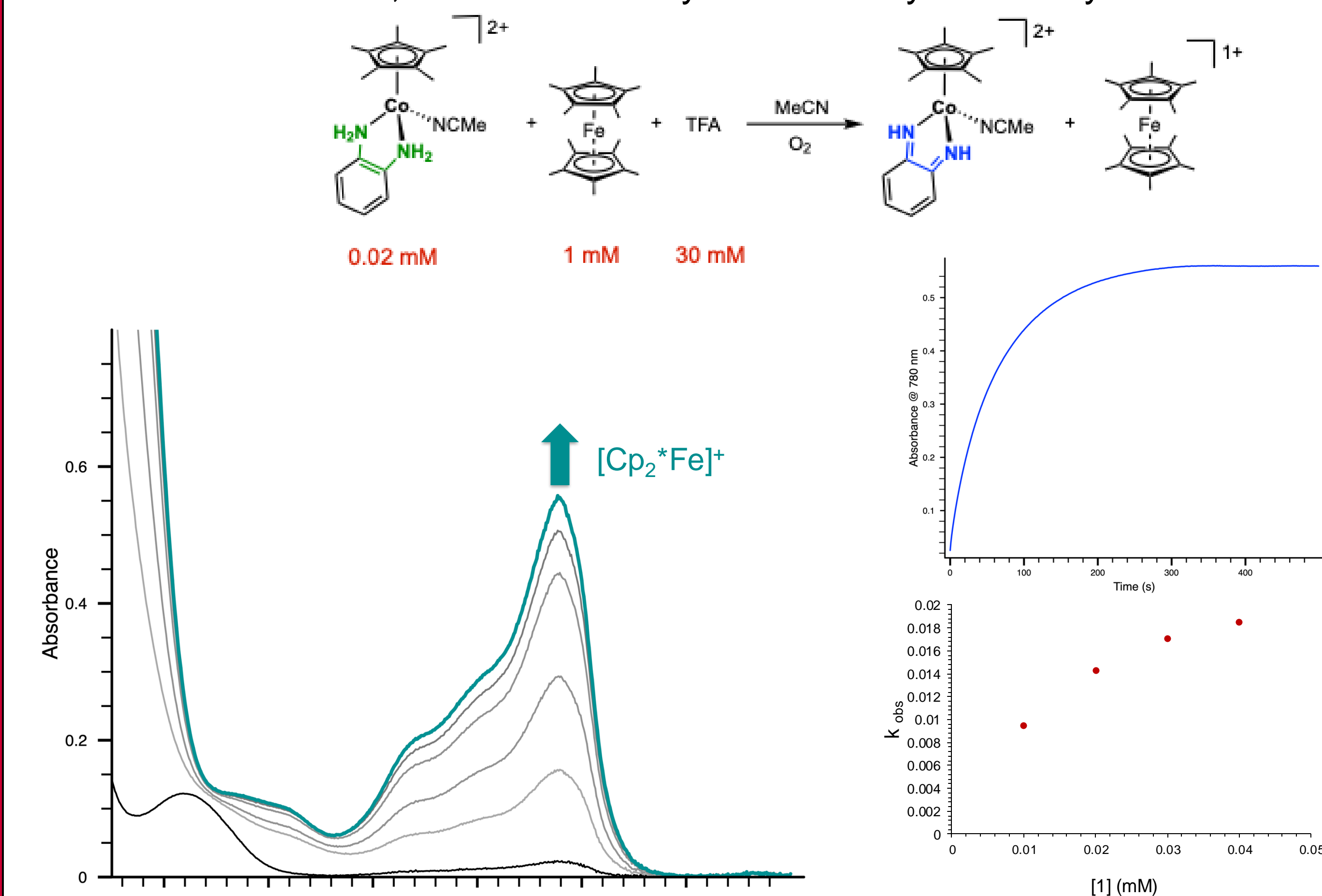


In the presence of trifluoroacetic acid (TFA; $pK_a(\text{MeCN}) = 12.65$)¹ as a Brønsted acid, a large increase in current is observed at an onset potential near -0.4 V vs. $Fc^{+/0}$, which is suggestive of electrocatalytic O₂ reduction by complex **1**.



Spectrochemical Studies

The catalytic activity of complex **1** for ORR was also studied under chemical conditions using stopped-flow UV-vis with Cp₂*Fe as a chemical reductant and TFA as the proton source. The growth of the absorbance at 780 nm is diagnostic for the [Cp₂*Fe]⁺ oxidation product.² Full conversion of Cp₂*Fe is reached within 300 s, and kinetic study are currently underway



References

- Rountree, E. S.; McCarthy, B. D.; Eisenhart, T. T.; Dempsey, J. L., *Inorg. Chem.* **2014**, 53 (19), 9983-10002.
- Wang, Y.-H.; Pegis, M. L.; Mayer, J. M.; Stahl, S. S., *J. Am. Chem. Soc.* **2017**, 139 (46), 16458-16461.
- Hooe, S. L.; Machan, C. W., *J. Am. Chem. Soc.* **2019**, 141 (10), 4379-4387.

Acknowledgement

We gratefully acknowledge financial supports from the ACS Petroleum Research Fund (65171-DN13) and Rutgers, The State University of New Jersey at New Brunswick. We acknowledge the Office of Advanced Research Computing (OARC) at Rutgers for providing access to the Amarel cluster and associated research computing resources that have contributed to the results reported here.