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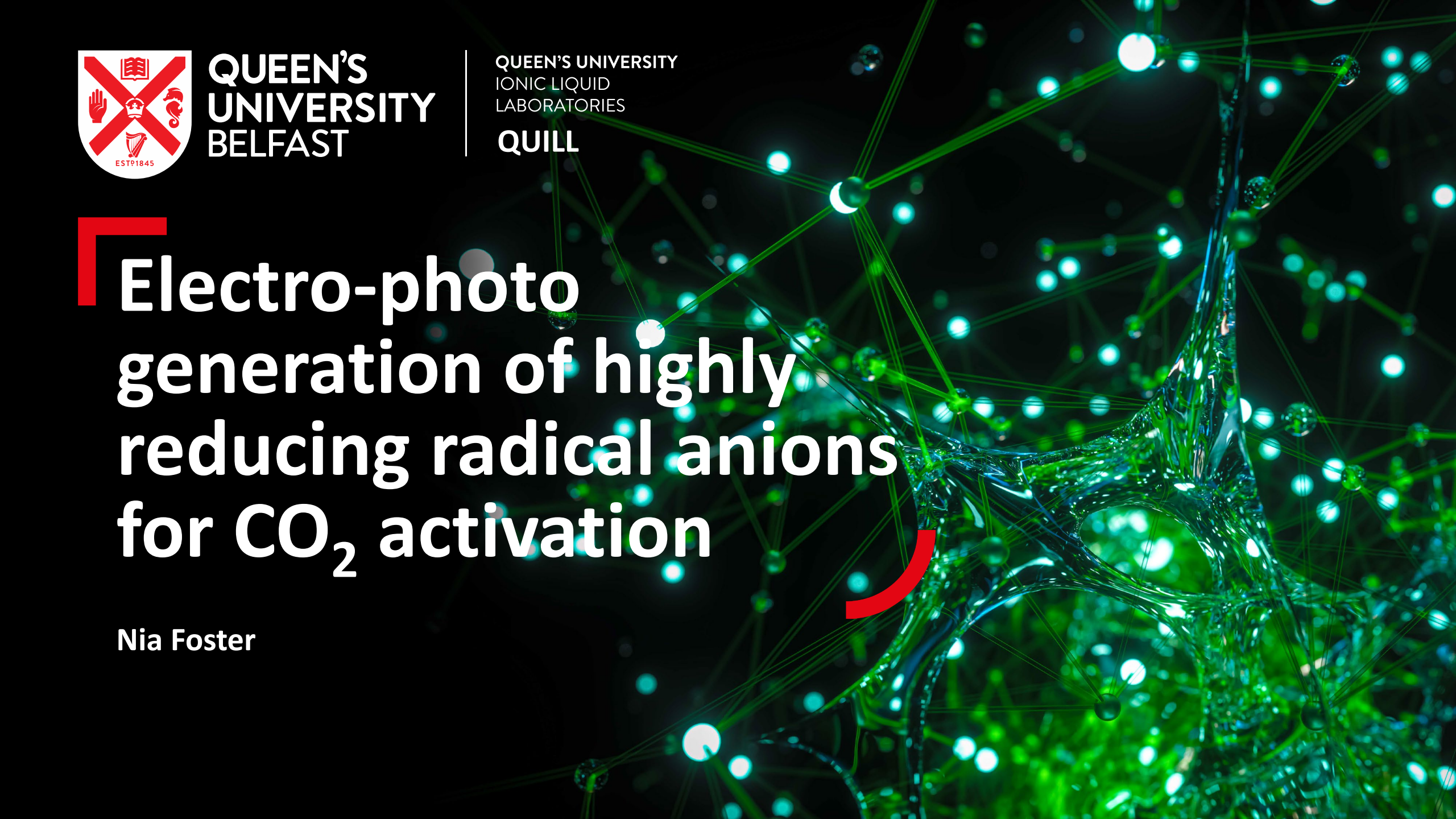
IONIC LIQUID
LABORATORIES

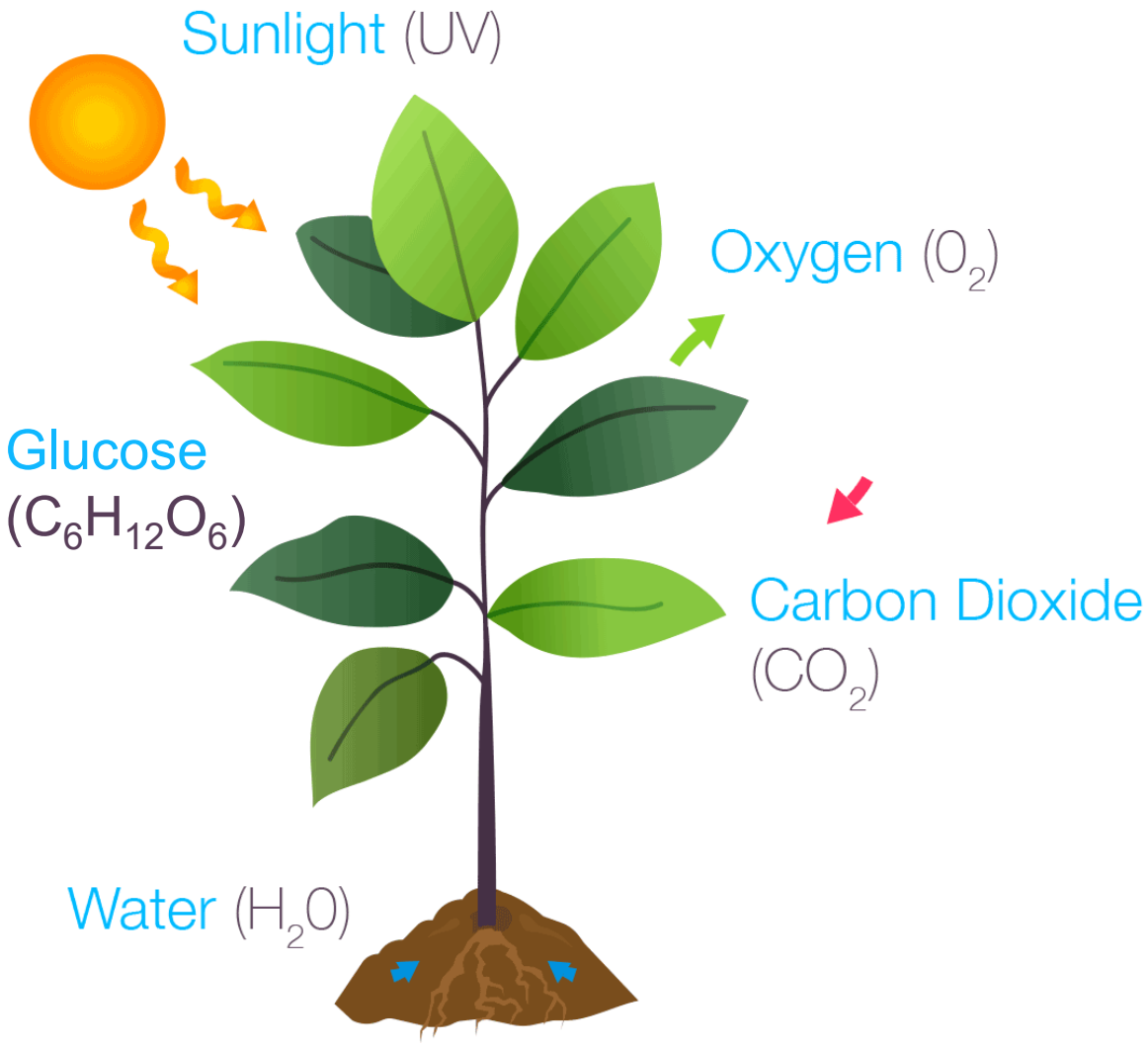
QUILL

Electro-photo generation of highly reducing radical anions for CO_2 activation

Nia Foster



Introduction



Difficulties with CO_2

- Stable and inert
- High activation energy
- Gas, difficult to control
- Solubility challenges
- Selectivity challenges
- Production of CO
- Catalyst deactivation

Introduction

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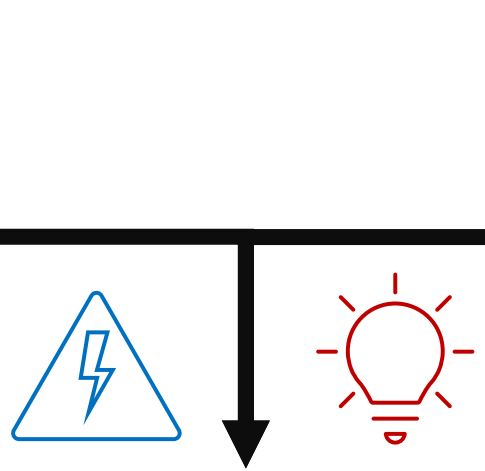
Electrochemical

Photochemical



Electrophotochemical

+ Can oxidise or reduce using electricity at the electrodes

- Not strong enough to activate more difficult substrates

- Compromised chemoselectivity

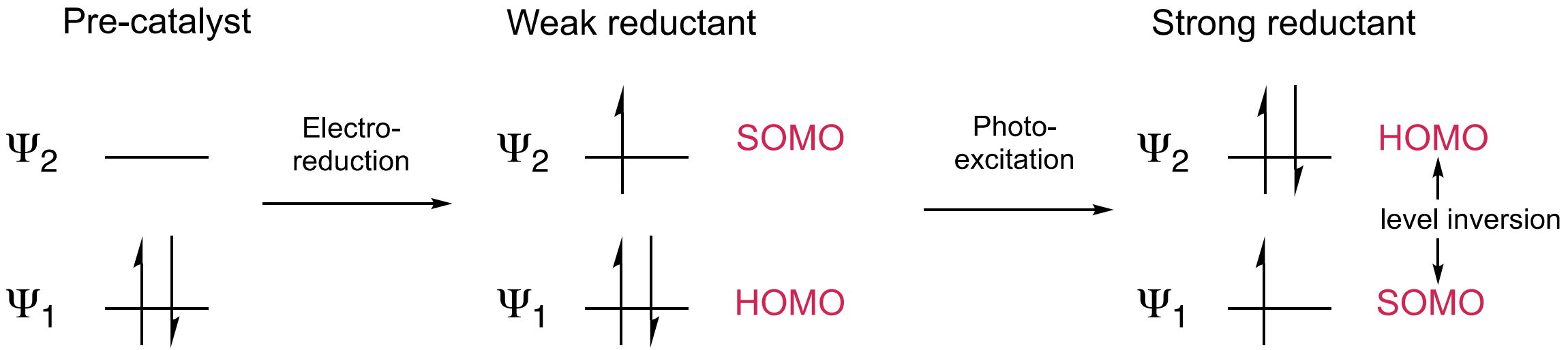
+ Excites electrons into a higher energy level using light

- Short lifetimes

- Specific wavelengths required

+++ highly oxidising or reducing radical ions that can oxidise or reduce a substrate, without the use of harsh chemicals

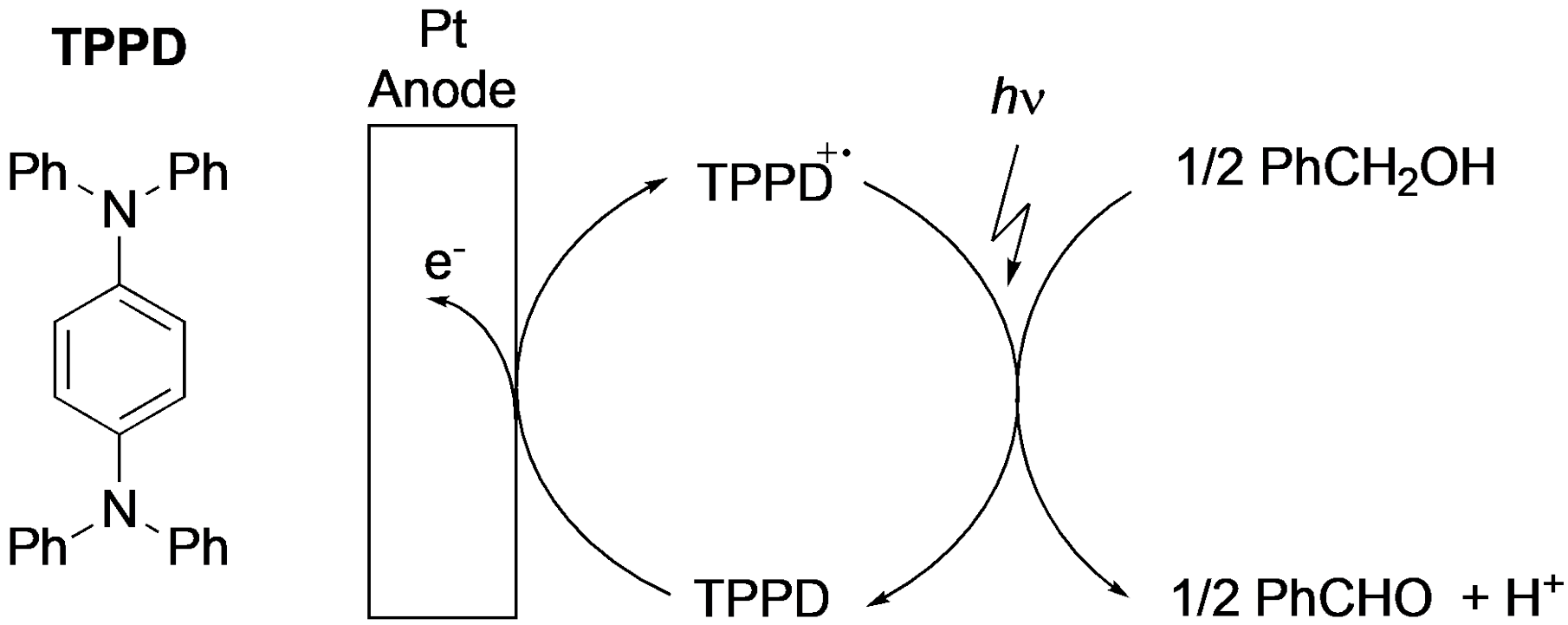
Introduction



C. Nuckolls and T. H. Lambert *et Al.*, *Angew. Chem. Int. Ed.*, 2019, **58**, 13318–13322.

Background

After their initial study on phenothiazine in 1979, Moutet and Revardy turned to N,N,N',N'-tetra-p-phenyl-p-phenylenediamine cation radical ($TPPD^{\bullet+}$) for use in alcohol oxidation reactions.



J.-C. Moutet and G. Reverdy,, *J. Chem. Soc., Chem. Commun*, 1982, 654–655.

Background

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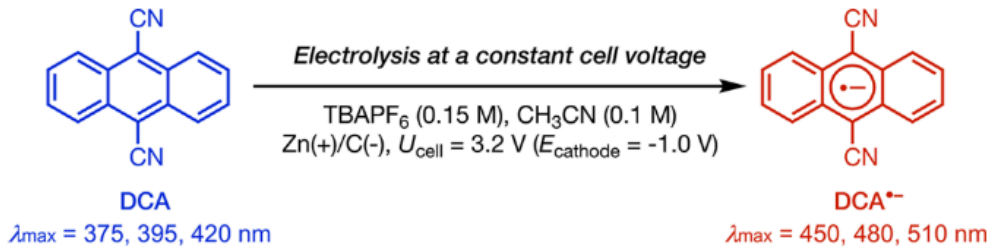
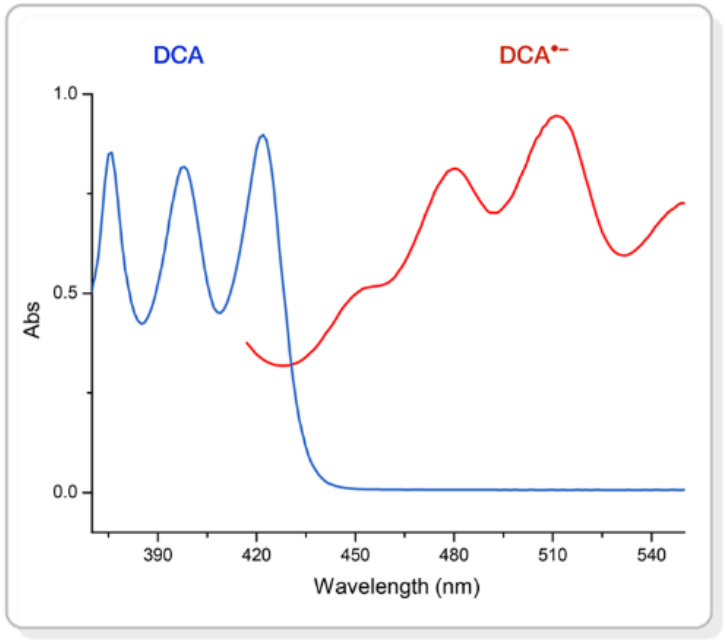
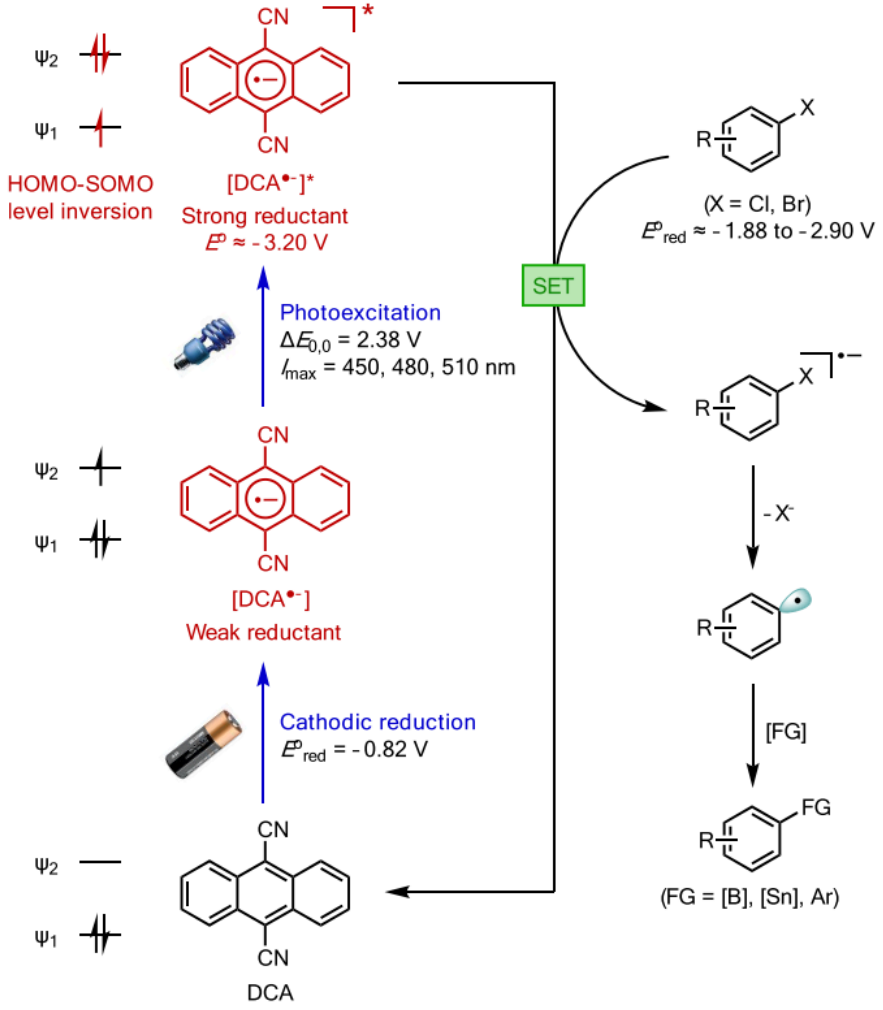
Dicyanoanthracene (DCA) has recently proven to successfully carry out electrophotochemical reductions:

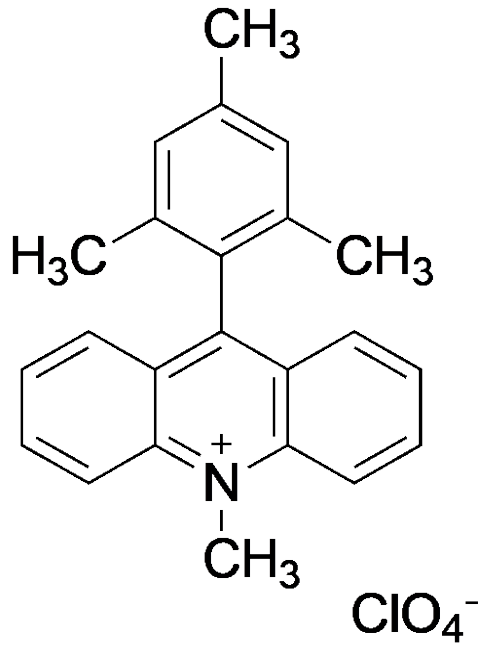






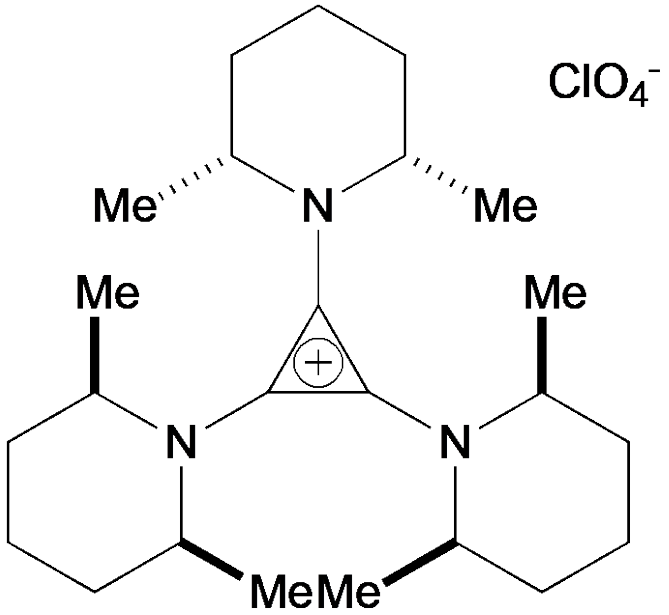
Lambert and Lin, *J. Am. Chem. Soc*, 2020, **142**, 2087–2092.

Background



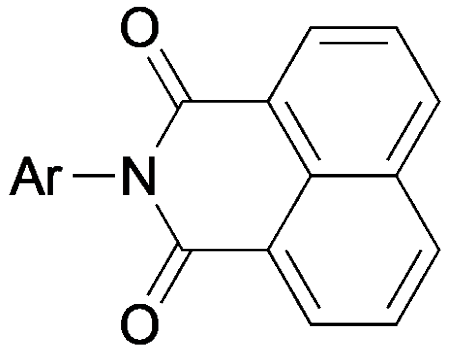
[Mes-Acr$^+$]ClO_4^-

H. Yan, Z. W. Hou and H. C. Xu, *Angew. Chem. Int. Ed.*, 2019, **58**, 4592–4595.



TAC

Nuckolls and Lambert, *Angew. Chem. Int. Ed.*, 2019, **58**, 13318–13322.



NpMI

Wickens et Al., *J. Am. Chem. Soc*. 2020, **142**, 2093−2099

Research Plan

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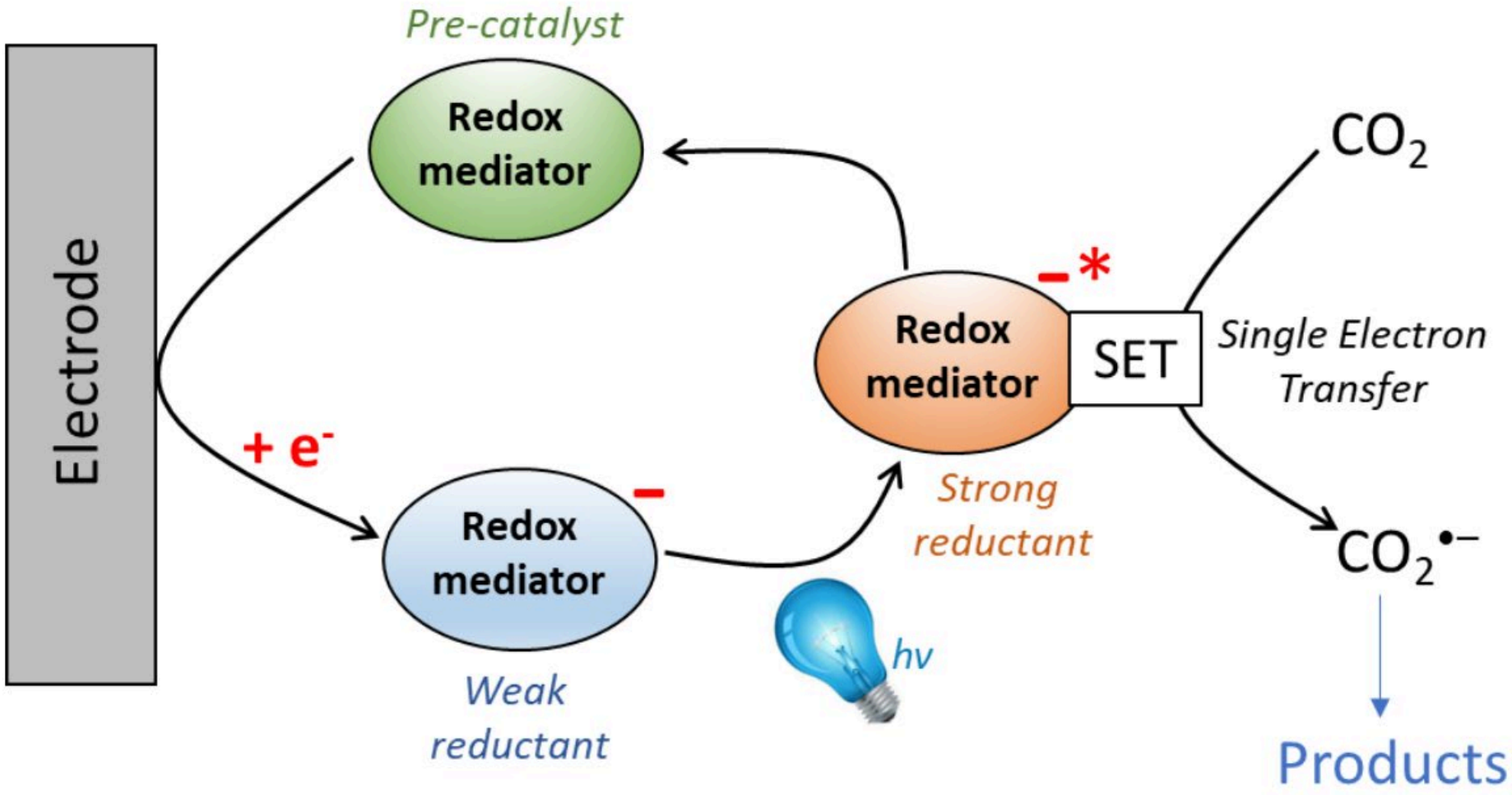

Research Plan

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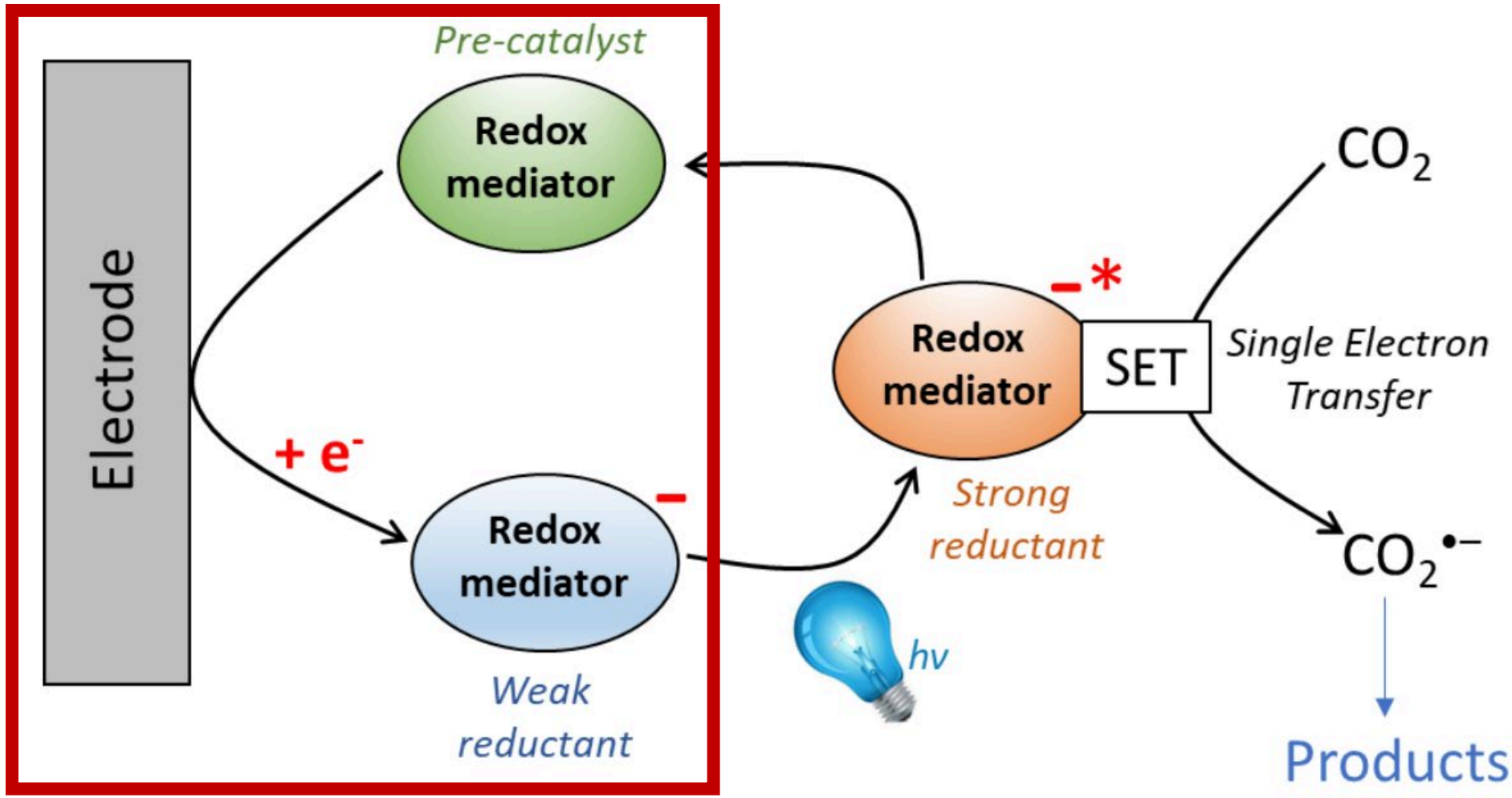

Initial Results

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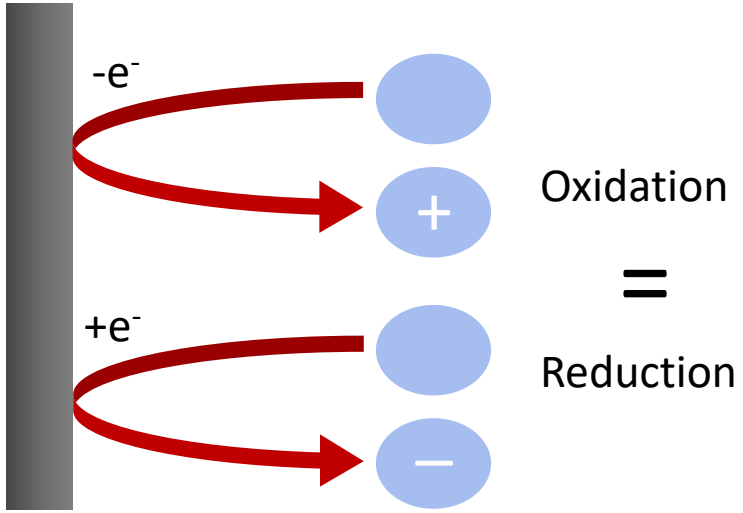
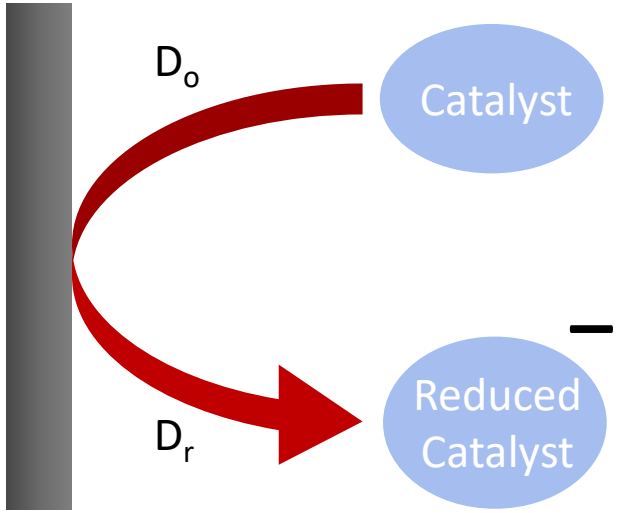
Redox potential
E^o (V)

The potential at which electrochemical oxidation and reduction are in equilibrium



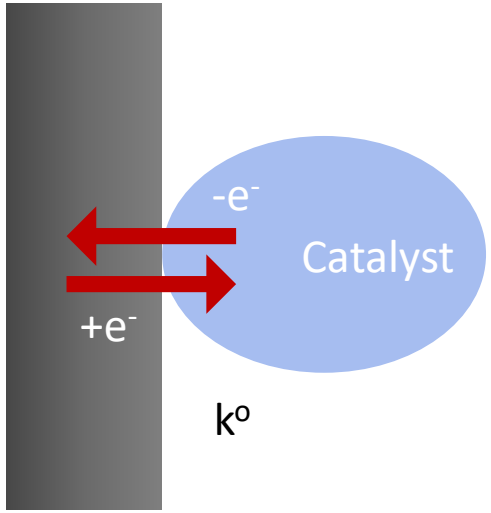
Diffusion co-efficient
D (cm^2s^{-1})

The speed at which the substrate diffuses through the solution to the electrode



Electron transfer constant
k^o (s^{-1})

The speed at which electrons can transfer across the surface of the electrode



Initial Results

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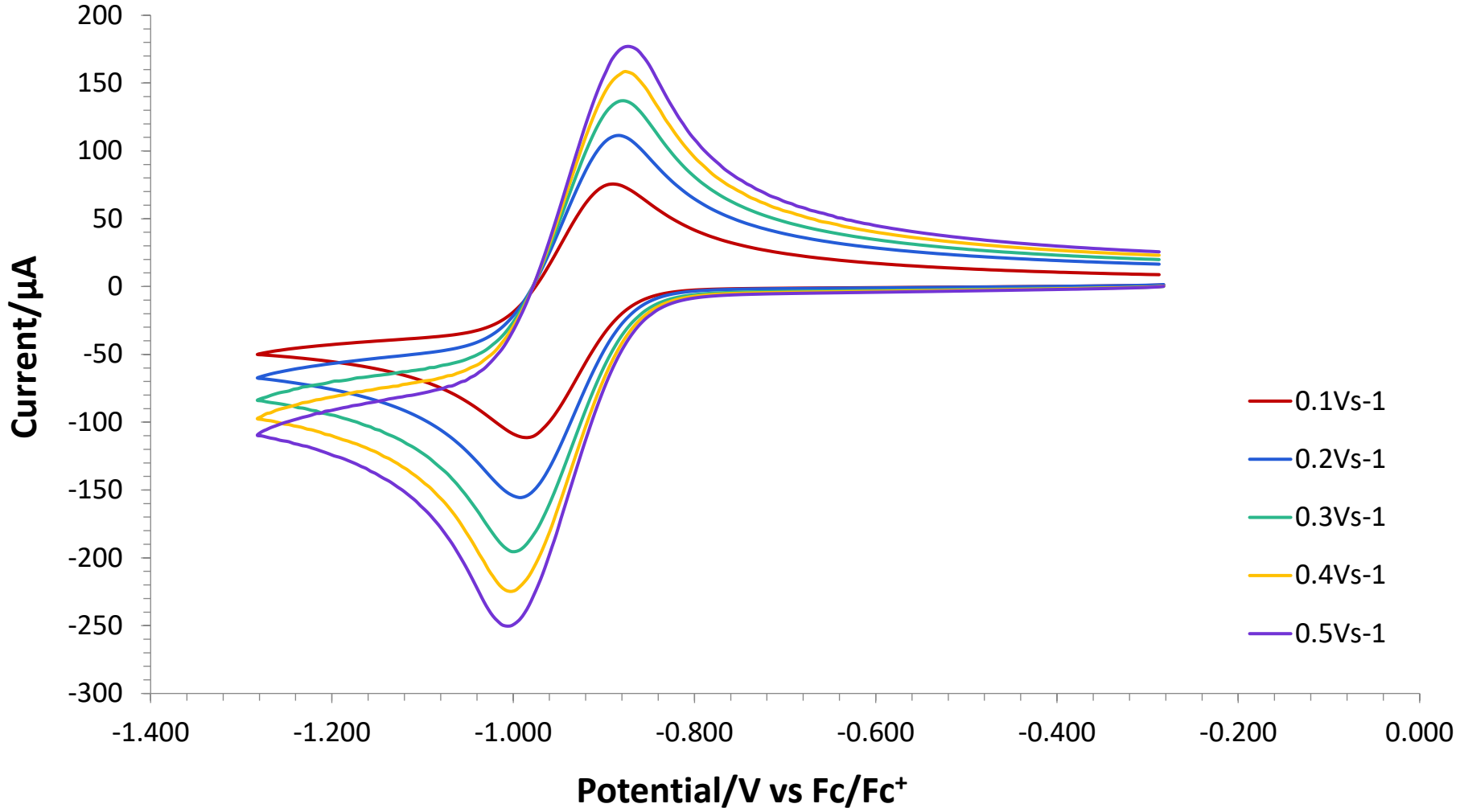

CV of Mes-Acr in an acetonitrile solvent with a $LiClO_4$ electrolyte

Initial Results

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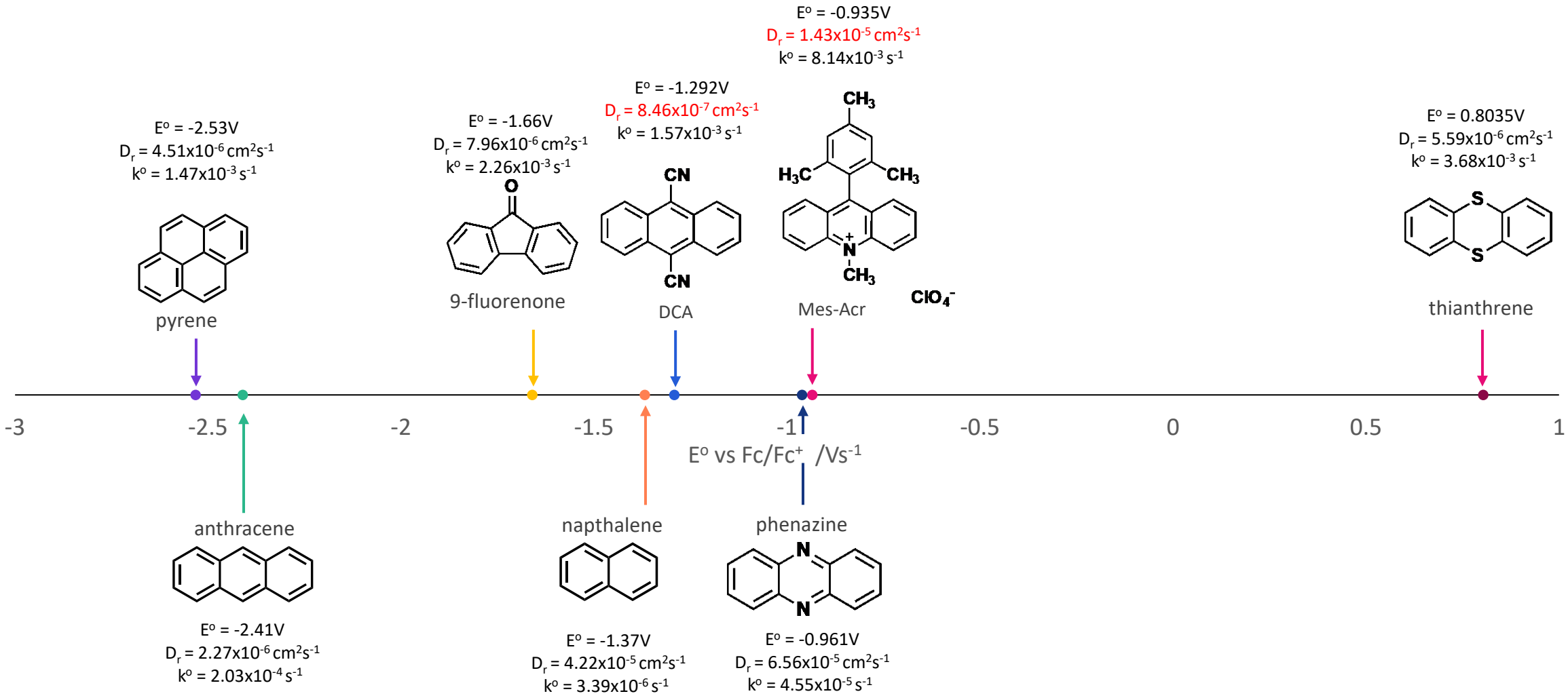

The more negative, the stronger the reducing power

The Next Steps

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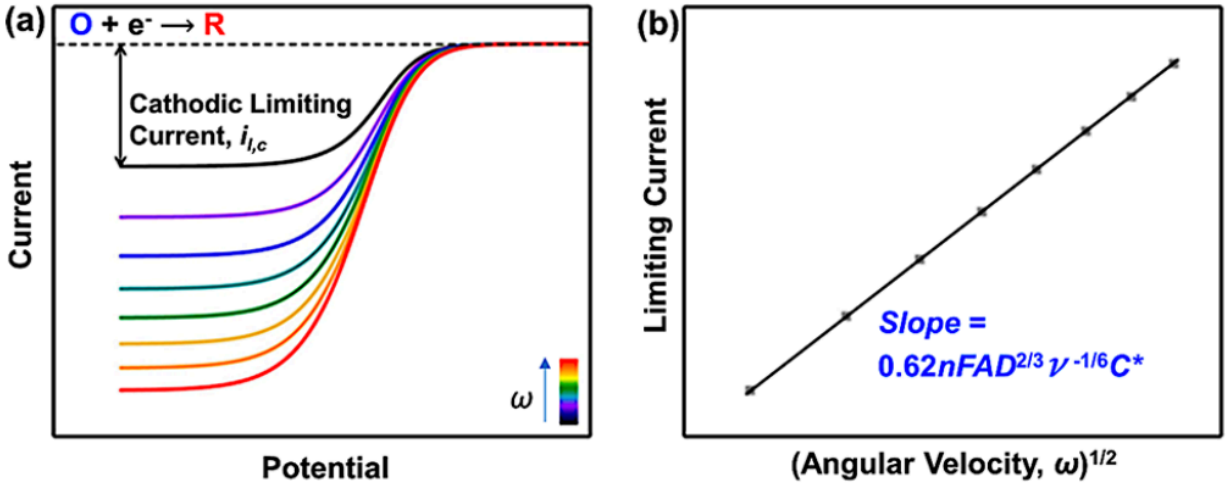
Rotating disk electrode (RDE) to determine the diffusion coefficient, D, for reversible, quasireversible, and irreversible redox systems



Levich-equation: Cathodic limiting current, $i_{l,c} = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C^*$, where ν is the kinematic viscosity of the fluid (measured in cm^2/s).

ACS Nano, (2020), 2575-2584, 14(3)

The Next Steps

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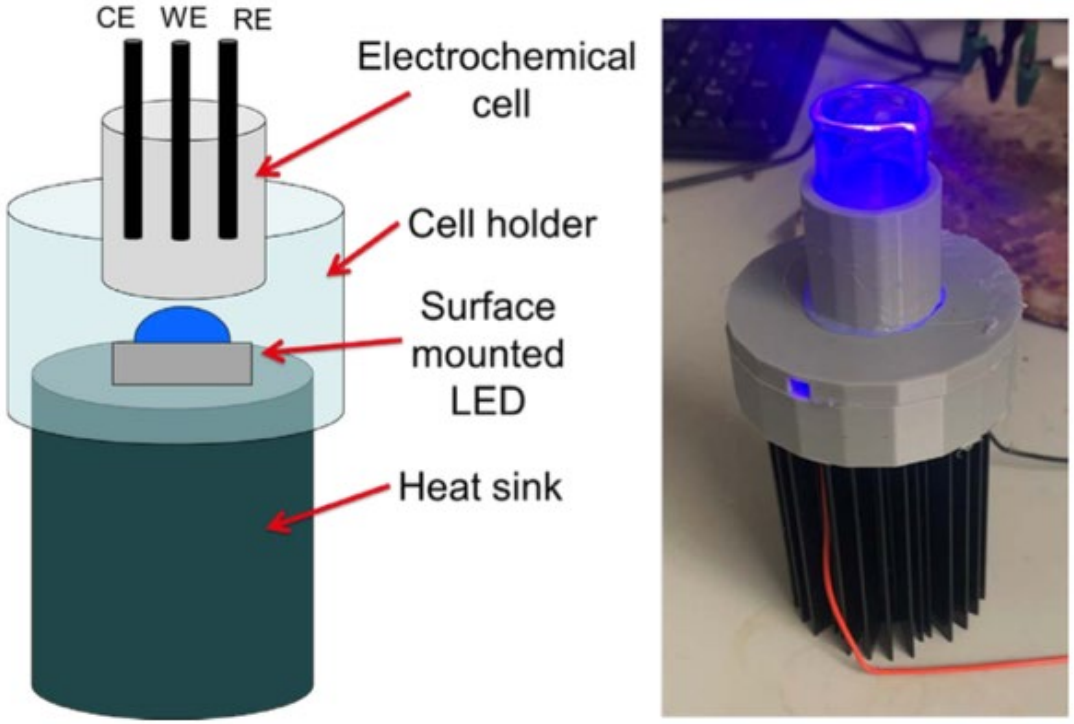
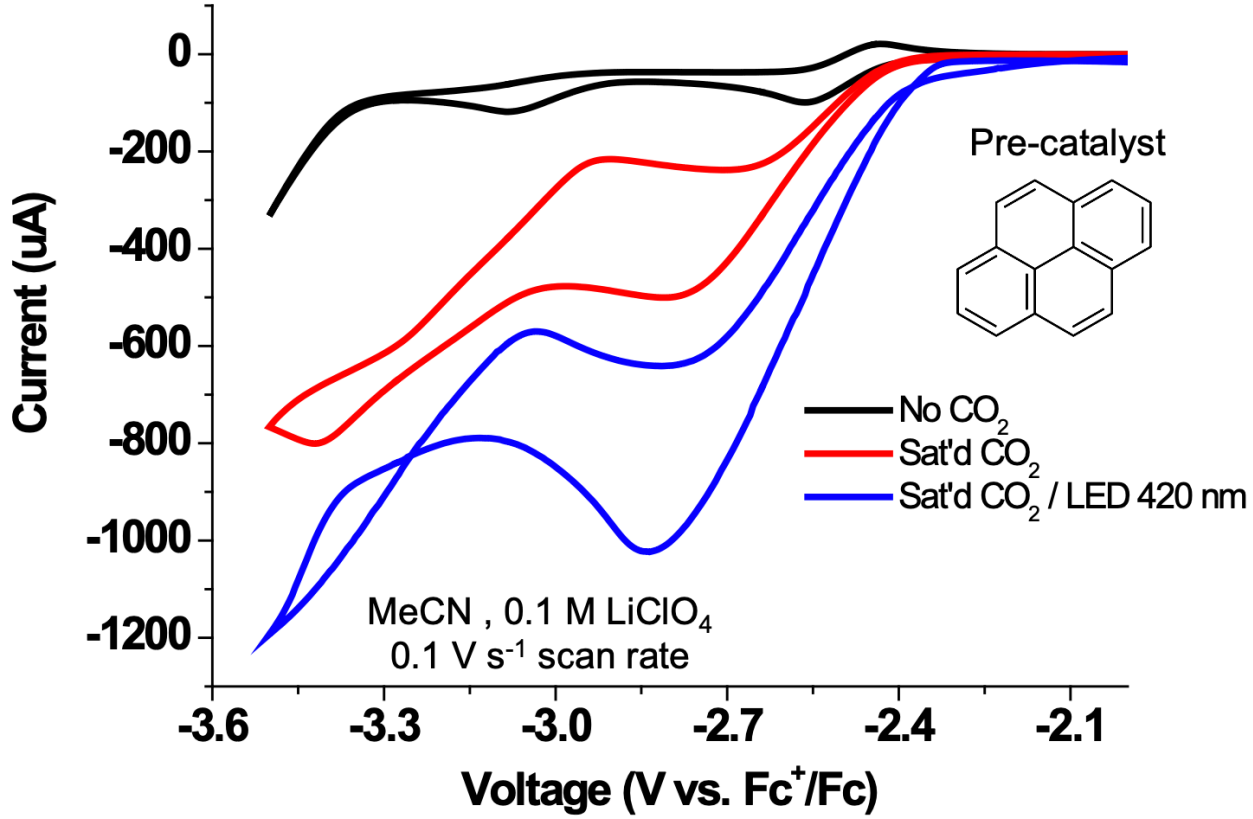
The catalysts will need to be tested under blue or UV light.





Acknowledgements

Thanks to my supervisors, Dr.Kavanagh and Prof.Robertson, and everyone at QUILL.