QUEEN'S UNIVERSITY BELFAST

QUEEN'S UNIVERSITY
IONIC LIQUID
LABORATORIES
QUILL

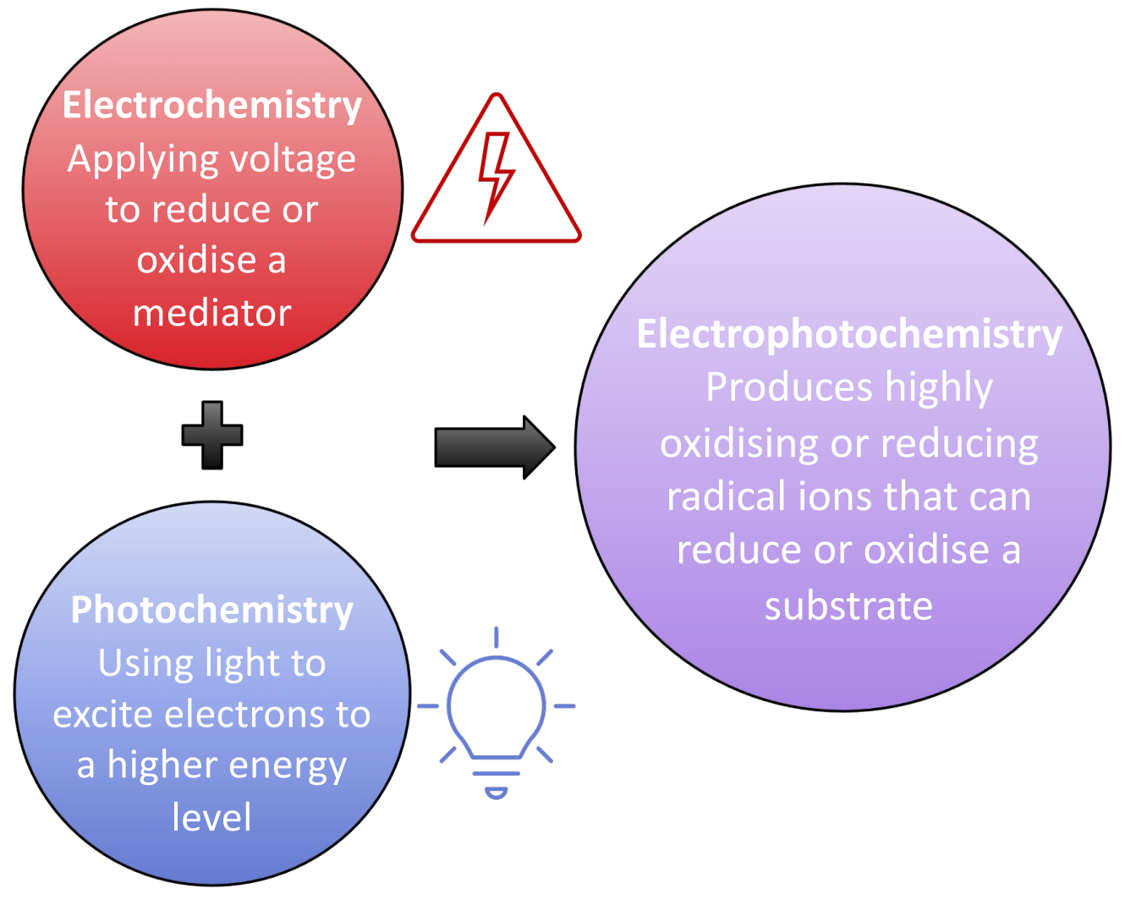
Electro-photo generation of highly reducing radical anions for CO2 activation

Nia Foster, Peter Robertson and Paul Kavanagh

What is electrophotochemistry?

Redox reactions such as the reduction of CO_2 and N_2 have proven to be very difficult in the past, using harsh chemicals and conditions.

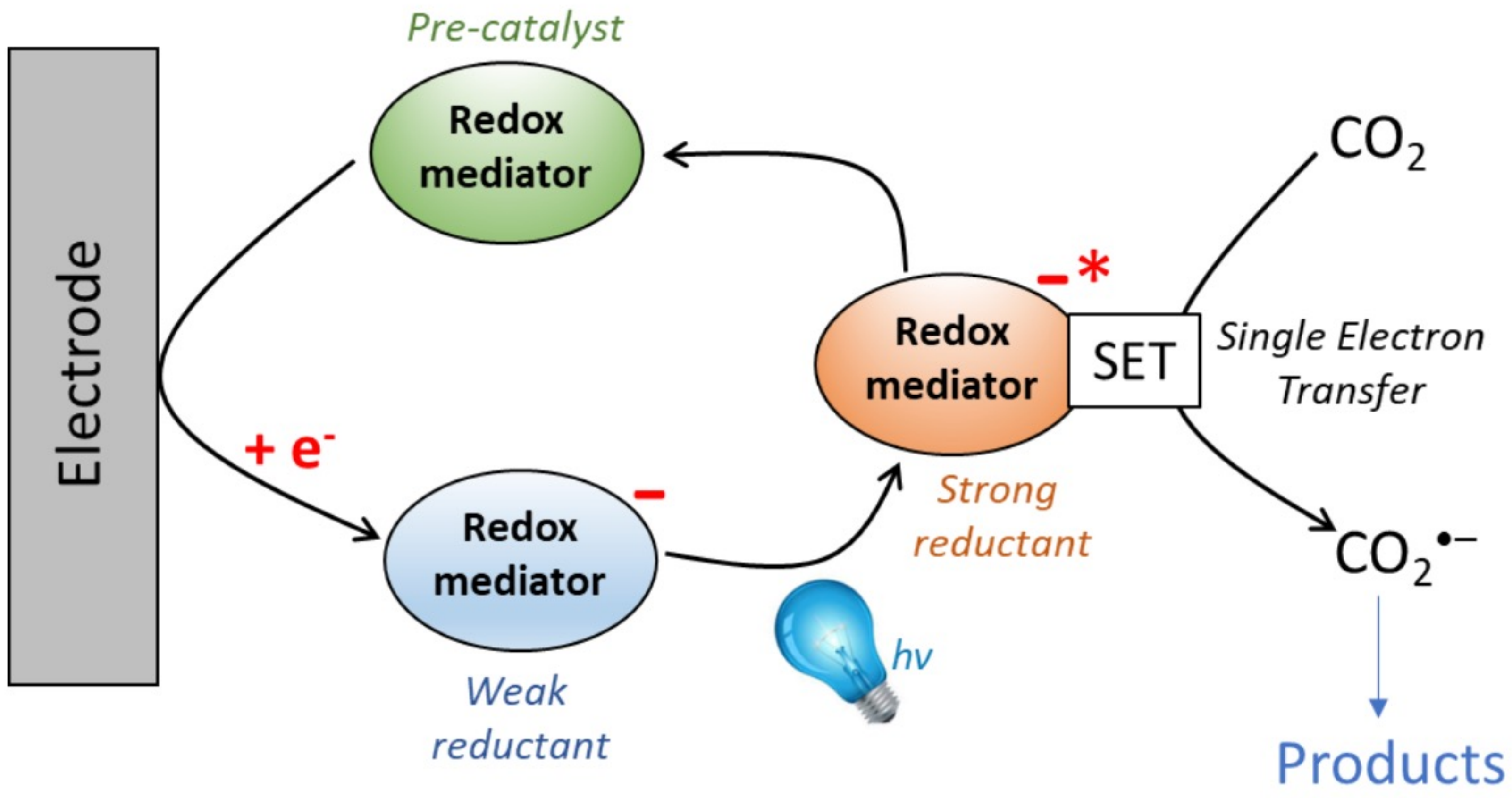
Recent research has shown that by utilising electrophotochemistry, highly oxidising or reducing catalysts can be formed that can activate these more difficult substrates.



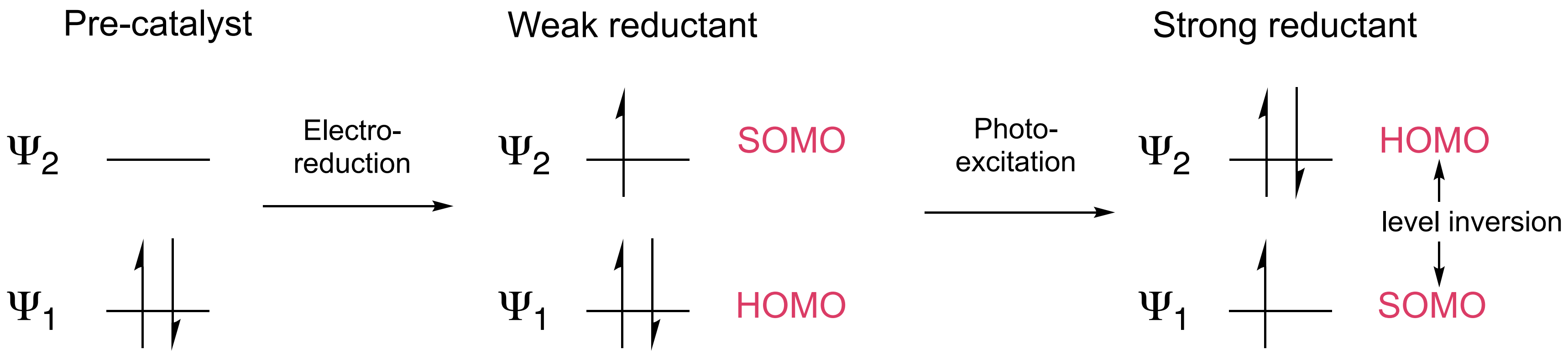
Electrochemistry Applying voltage to reduce or oxidise a mediator

Photochemistry Using light to excite electrons to a higher energy level

Electrophotochemistry Produces highly oxidising or reducing radical ions that can reduce or oxidise a substrate

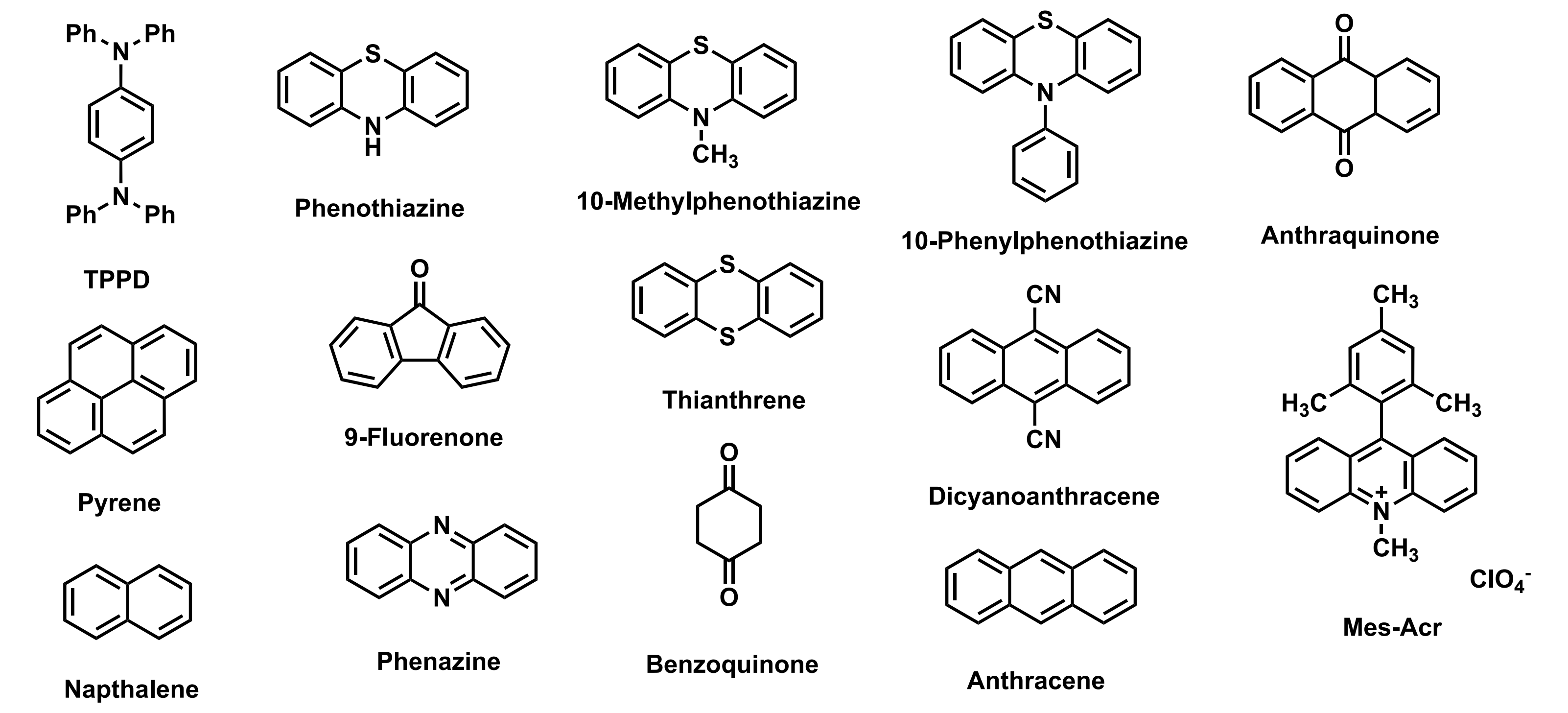


The catalyst is first oxidised or reduced at the electrode, then excited to a radical state using light. The reason why the catalyst becomes much stronger after the irradiation is due to a HOMO-SOMO level inversion occurring[1]:

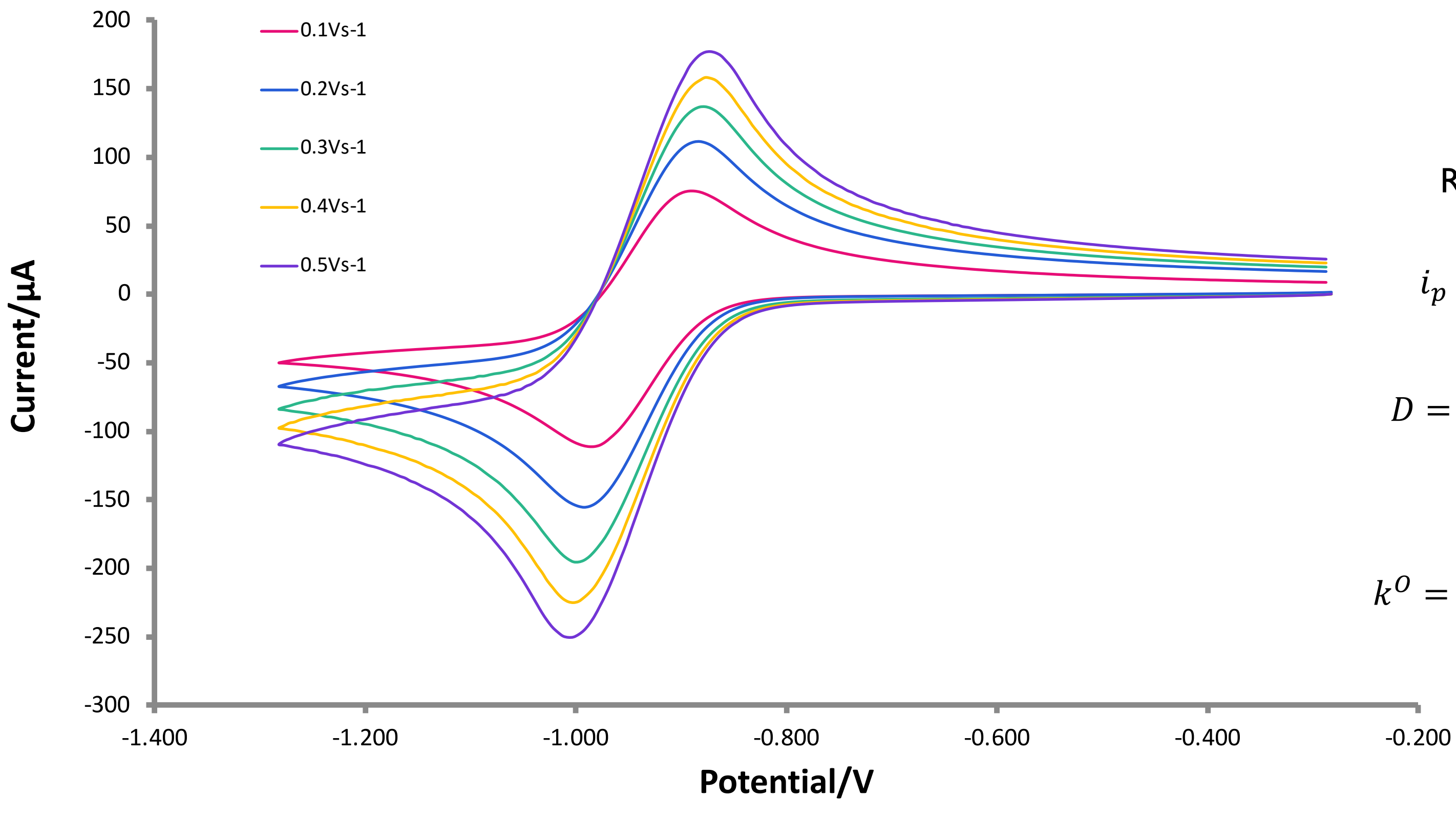


Initial Study

The first study carried out was categorising a series of heterogeneous redox electrophotocatalysts that have previously been mentioned in papers:



CV readings were taken for each catalyst at five different scan rates, and the redox potential (E°), diffusion co-efficient (D) and electron transfer constant (k°) were calculated.



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

Equations used:

$$E^\circ = \frac{E_{pa} + E_{pc}}{2}$$

Randles-Sevcik equation:

$$i_p = 0.4463\, nFAC \left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$

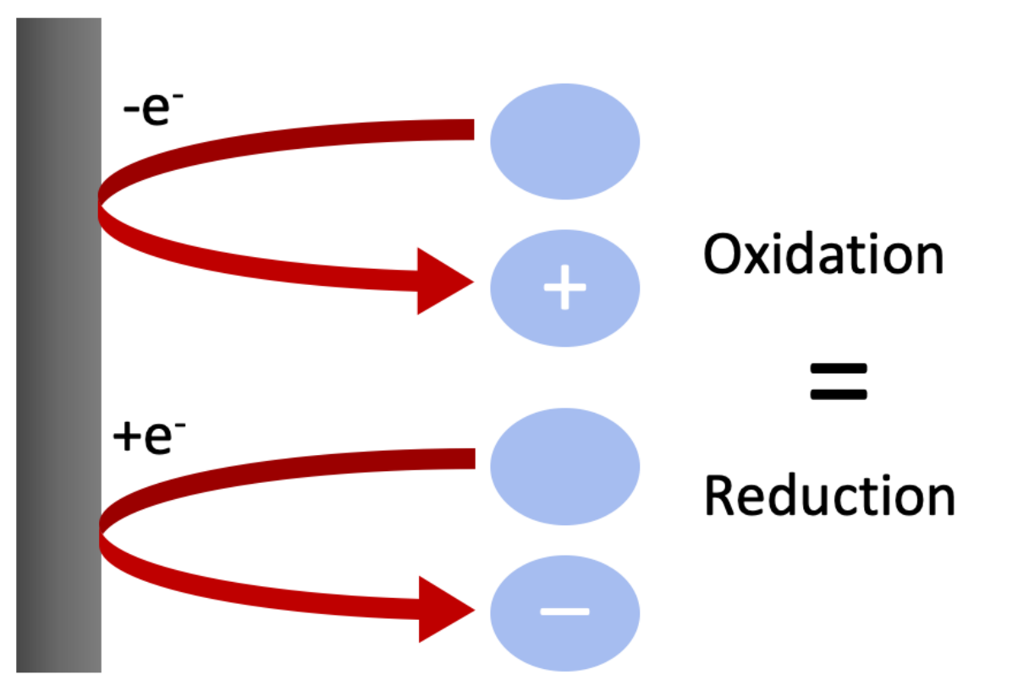
$$D = \frac{(slope)^2}{n^3\,(2.69 \times 10^5\, A\, C^*)^2}$$

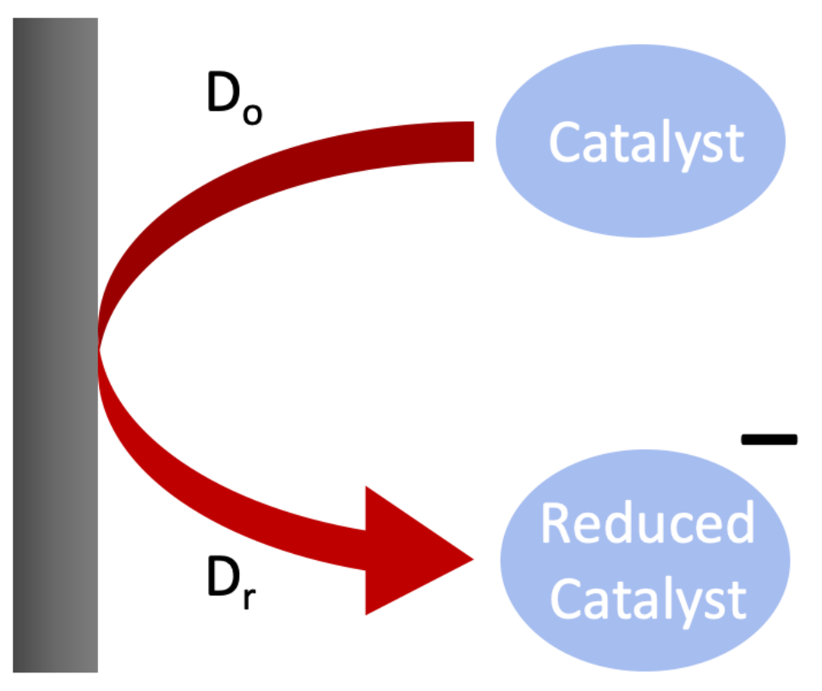
$$k^o = \frac{slope \times \left[\left[\left(\frac{nF}{RT}\right)\pi D_r\right]^{\frac{1}{2}}\right]}{\left(\frac{D_r}{D_o}\right)^{1/4}}$$

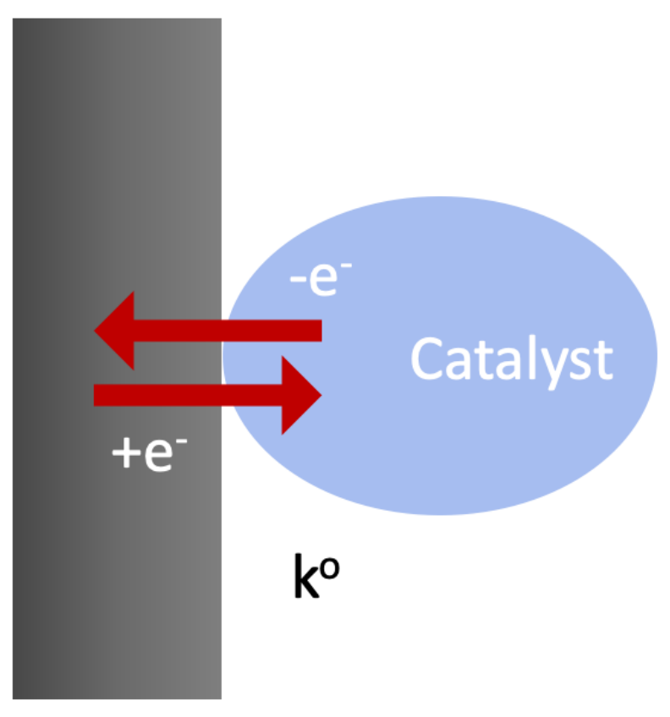
Redox potential (E°)
electrochemical oxidation and reduction are in equilibrium

Diffusion co-efficient (D)
speed at which the substrate diffuses through the solution

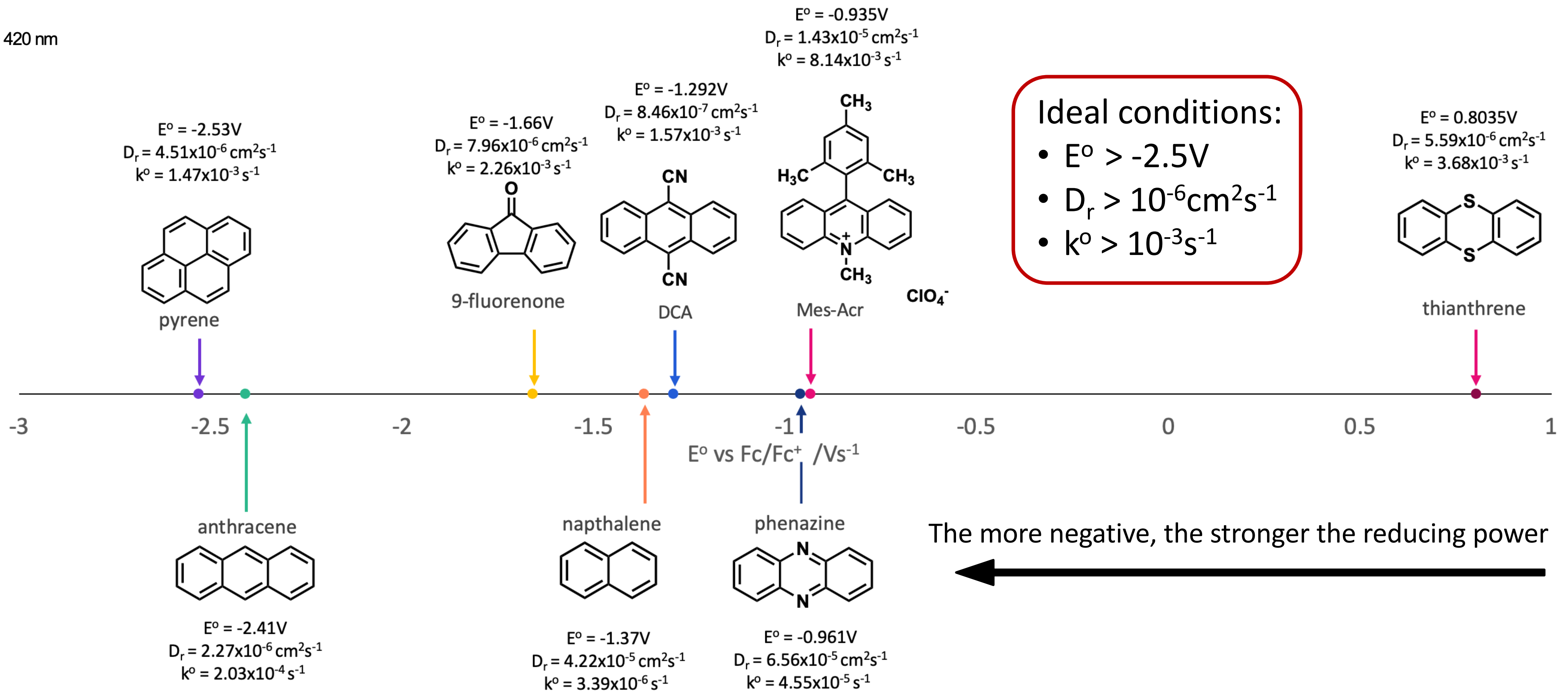
Electron transfer constant (k°)
speed at which electrons can transfer across the surface of the electrode







Below are a series of catalysts plotted by their redox potential along with their diffusion coefficient and electron transfer constant values:

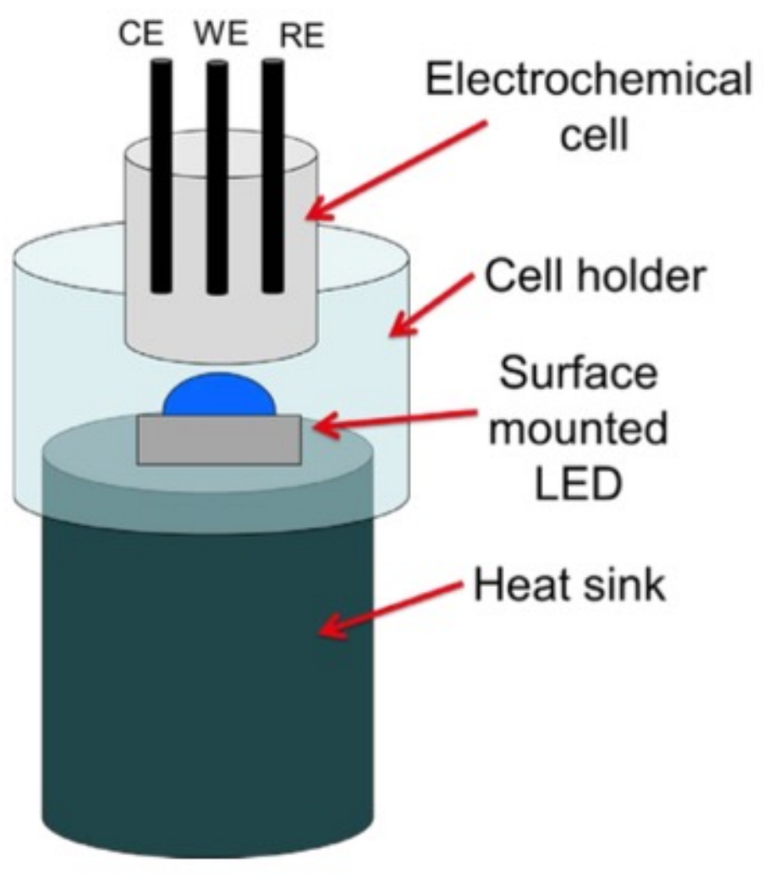


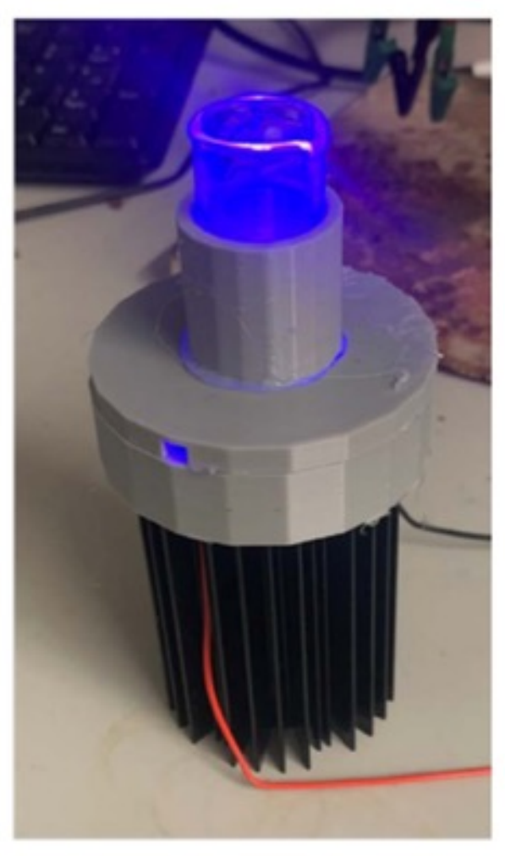
Ideal conditions:
- $E^o > -2.5V$
- $D_r > 10^{-6} cm^2s^{-1}$
- $k^o > 10^{-3}s^{-1}$

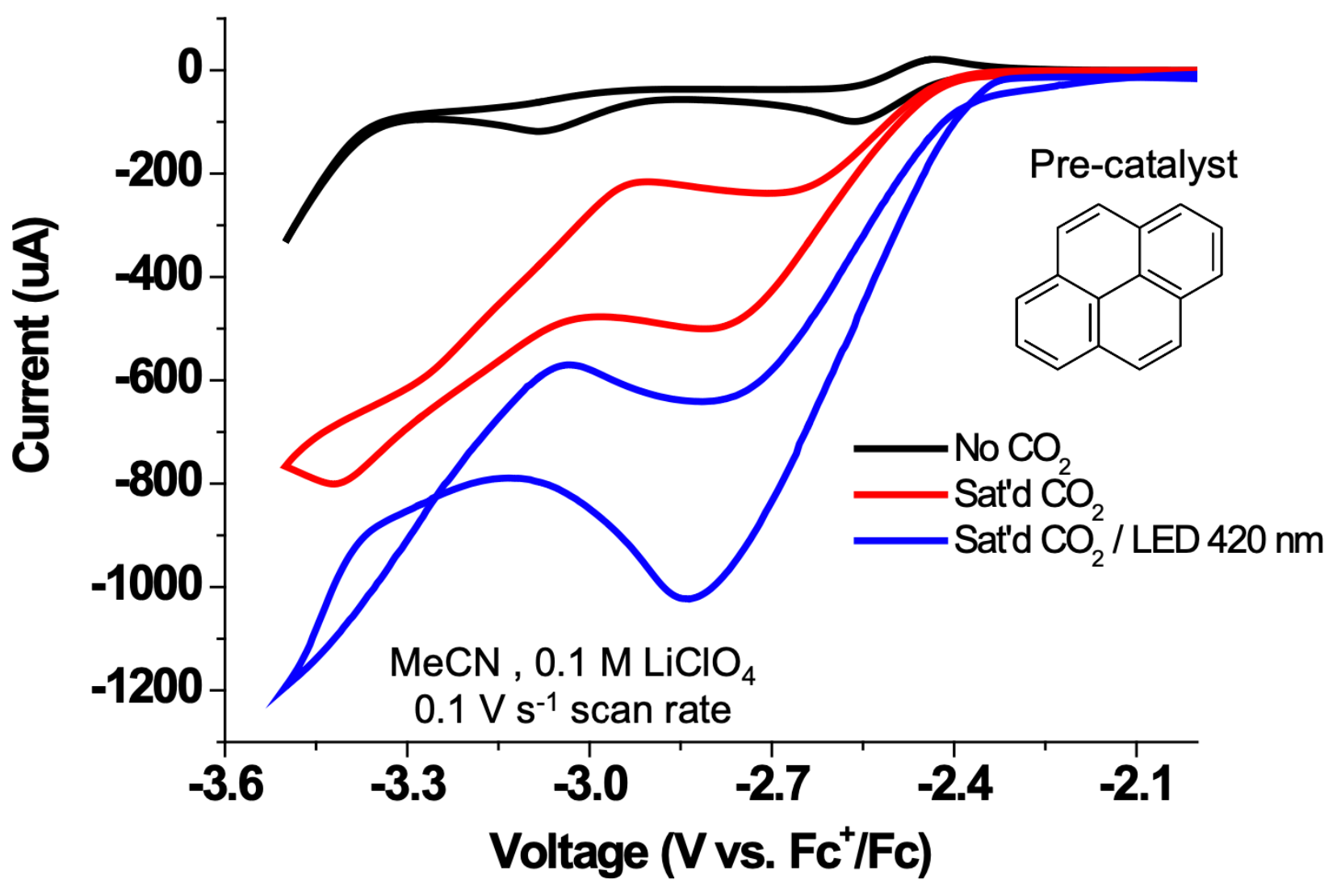
The more negative, the stronger the reducing power

Future Plans

Catalysts will be tested under UV light to observe their photoactivity. The setup below will be used, with the electrochemical cell being held in position with an LED below.
These are some preliminary results for reducing carbon dioxide using an electrophotocatalytic system.







References:

1. Nuckolls and Lambert et al. *Angew. Chem. Int. Ed.*, 2019, **58**, 13318–13322.
2. Moutet and Reverdy, *Chem. Commun*, 1982, 654–655.
3. Lambert and Lin, *J. Am. Chem. Soc*, 2020, **142**, 2087–2092.

Acknowledgements

Department for the Economy

Funding from the Department of Economy, Northern Ireland is gratefully appreciated