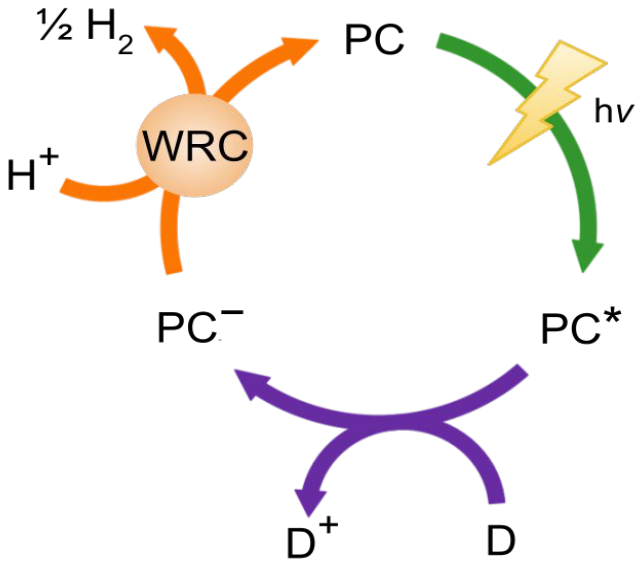
# MML Project Data

09/04/25

# Scientific Problem

- **Solar** $H_2$ generation as green solution towards mitigating the **energy crisis**
  - Energy dense
  - Clean oxidation products
  - Various methods to store and transport
- Current light-driven $H_2$ evolution systems are
  - **Expensive** and/or non earth abundant materials
  - **Inefficient** to be implemented industrially
- No effective methods to **predict what features will make good catalysts**
  - Systems are complex!




**PC** - photocatalyst

**D** - sacrificial electron donor

**WRC** - water reduction catalyst

# Homogenous hydrogen evolution using earth abundant materials in green solvent conditions (there is a decent amt of literature on this)

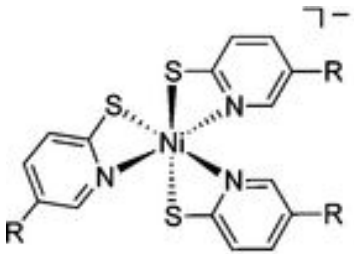
*System components:*

**Photosensitizer:** Fluorescein

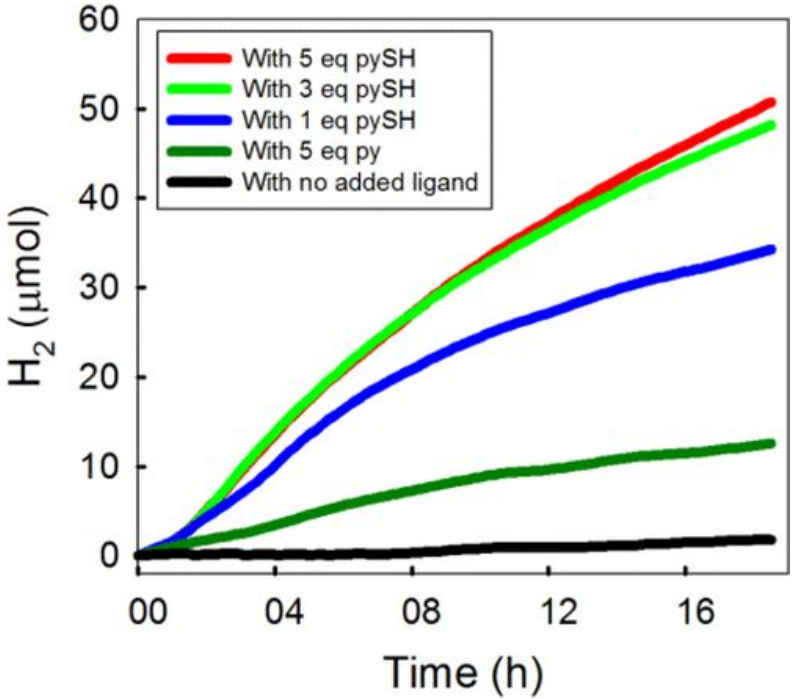
**Donor:** TEA

**Water Reduction Catalyst (WRC):** nickel pyridinethiolate complexes

**Solvent:** 1:1 water:ethanol

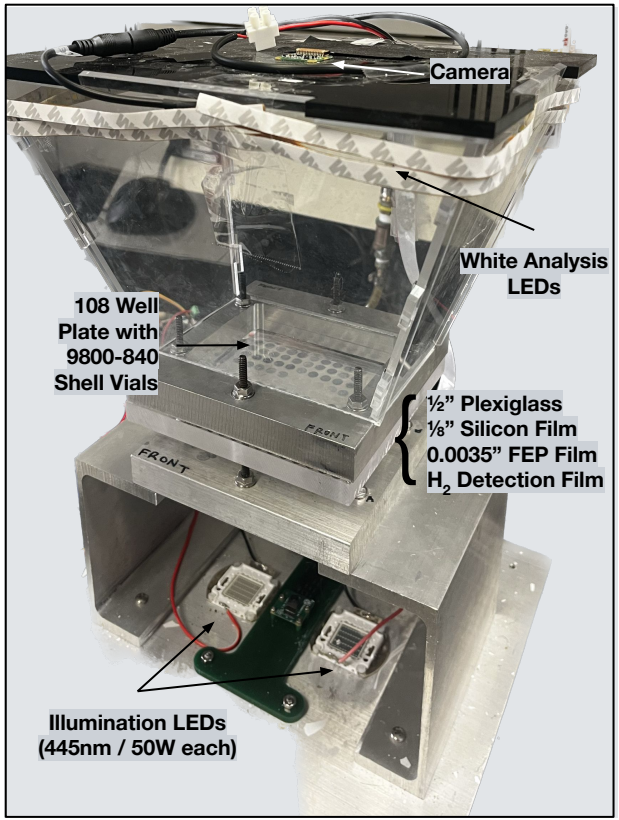


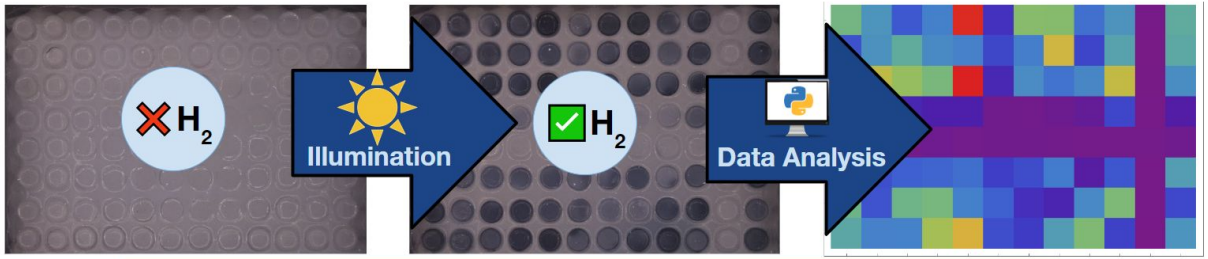

**Complexes can be made in situ!**



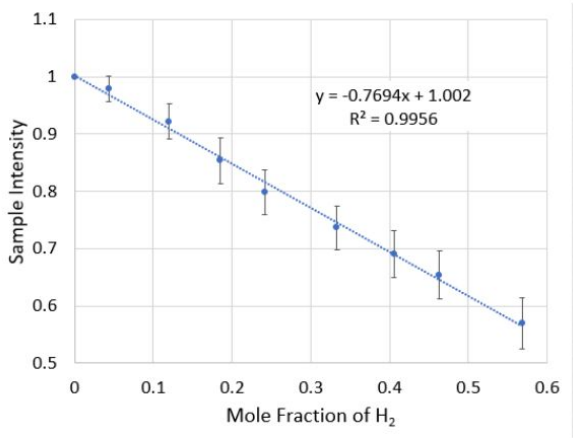

Source: *J. Am. Chem. Soc.* 2013, **135**, 39, 14659–14669

# High-throughput hydrogen evolution reaction configuration



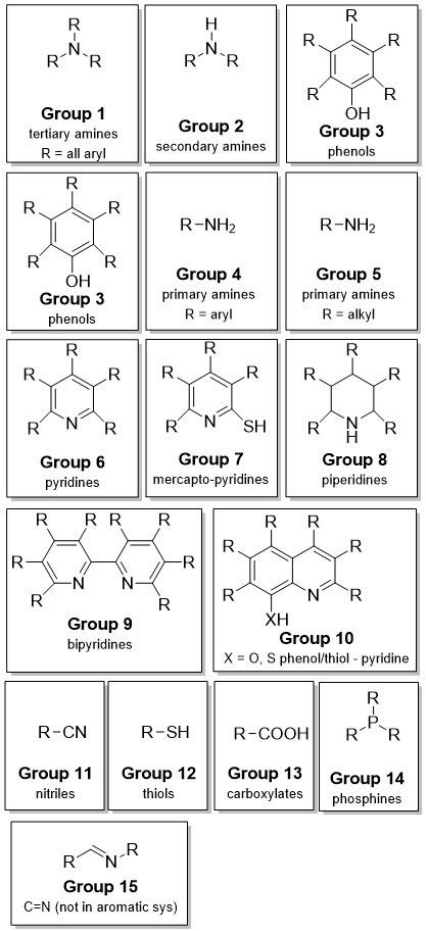

**Calibration Curve for $H_2$ Detection Films**




- 108 multiwell plate sealed with colorimetric detection films
- Plates are illuminated on photoreactors that take images of plate (top and bottom)
- Python script processes images to correlate film darkness to amt of $H_2$ generated

Source: *Digital Discovery,* 2024, **3**, 1430-1440

# Current Dataset




- Fluorescein as the PS, TEOA as the D
- Two metals
  - Ni
  - Co
- 56 ligands
  - At eight different concentrations
- 56 * 2 * 8 = 896 data points (technically thousands more if you consider the whole kinetic trace of each)
- Previous investigation with this project involved binary classification of the data (1 - h2 producer, 2 - no h2)
  - Ligands were featurized with molformer, but minimal success was achieved -> need more intentional featurization and maybe a more specific dataset

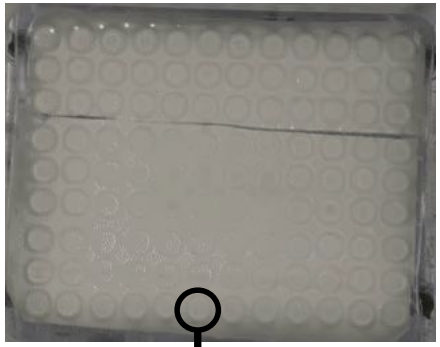
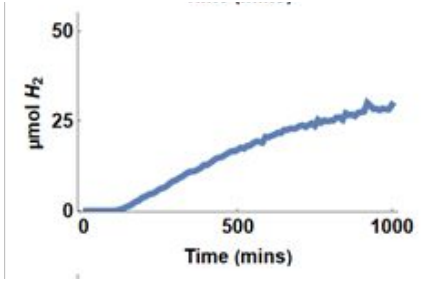


Image processing



# Direction of the Proposal

**Experimental Goals/Work**

- Find a way to see if we are actually making the complexes
  - HTP MS? Gabe has one i think
  - NMR (need a cheaper solvent to NMR)
- Extract Features from experiment besides final H2 measurement
  - Incubation time
  - Plateau time
  - Rates
  - Does a precipitate form
- Conformation w/ GC to ensure the films are giving accurate results
- Once we have a model working we can validate by running additional experiments with new ligands

**Computational Goals/Work**

- Some method to compute functionals for the ligands we are screening
  - Extract relevant features
  - Build a model that can use the features/determine feature importance to predict ligand behavior
- Find a database of ligands to use as test/train data

GOAL:

- Predict whether or not a ligand (feed in a SMILES) when chelated to a metal will afford a hydrogen evolution catalyst

# Mechanism: CECE (C -> chemical step, E-> electrochemical step)

Step 1: Chemical (C) – Protonation

- The nickel complex undergoes protonation at the pyridyl nitrogen, which is accompanied by ligand dechelation.
- This step is reversible and supported by NMR and UV-vis data showing color and spectral changes upon acid/base addition.

Step 2: Electrochemical (E) – Reduction

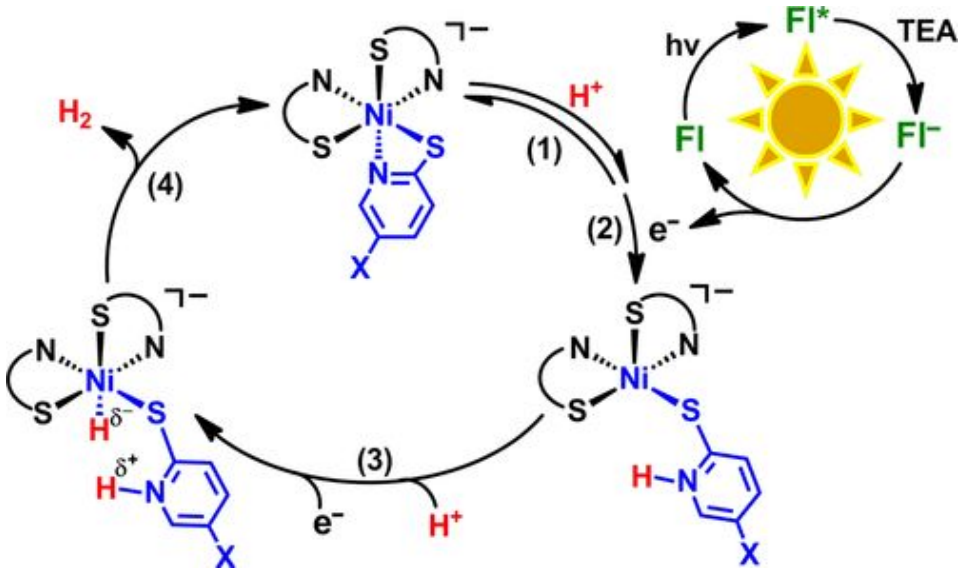
- The protonated complex is reduced, likely forming a Ni(I) species.
- Cyclic voltammetry (CV) shows a new reduction wave upon acid addition, assigned to a Ni(II)–H / Ni(I)–H couple.

Step 3: Chemical (C) – Second Protonation

- A second protonation occurs, likely at the Ni–H intermediate, forming a $Ni–H^-$ / $N–H^+$ species.
- This step sets up the heterocoupling needed to form $H_2$.

Step 4: Electrochemical (E) – Second Reduction

- A second electron transfer reduces the intermediate further, facilitating H–H bond formation.
- This is proposed to be the turnover-limiting step (TOLS) of the cycle.



# Ideas for descriptors

Hydride binding energy