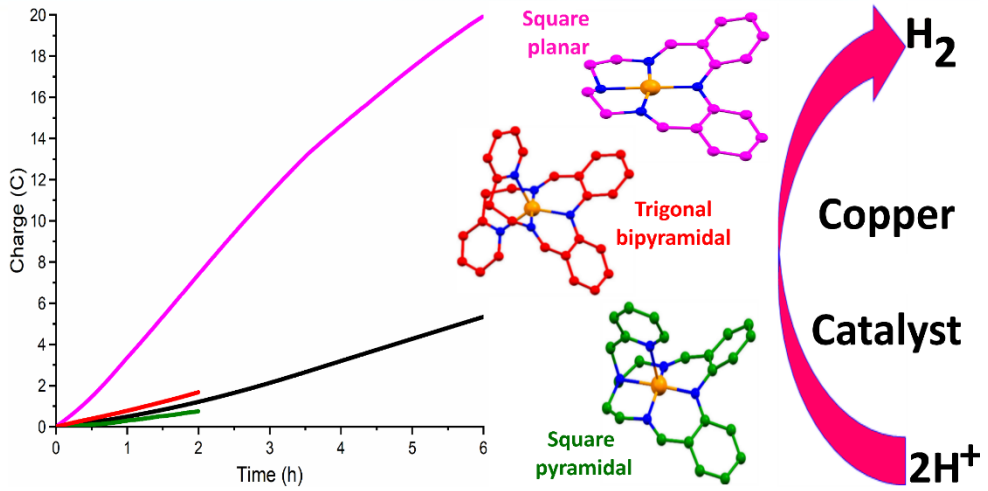
Copper Catalysts for Hydrogen Production

Otago Energy Research Centre



UNIVERSITY of OTAGO
Te Whare Wānanga o Otāgo
NEW ZEALAND
SAPERE AUDE

Abdullah Abudayyeh
Prof Sally Brooker

Significance of H_2

High Energy Density/ mass

$H_2 + ½ O_2 \rightleftharpoons H_2O + Energy$

$3/2H_2 + ½ N_2 \rightleftharpoons NH_3$

NH_3 Production

H_2

$2H_2 + CO \rightleftharpoons CH_3OH$

CH_3OH Production

Clean fuel

H_2 -fueled Cars

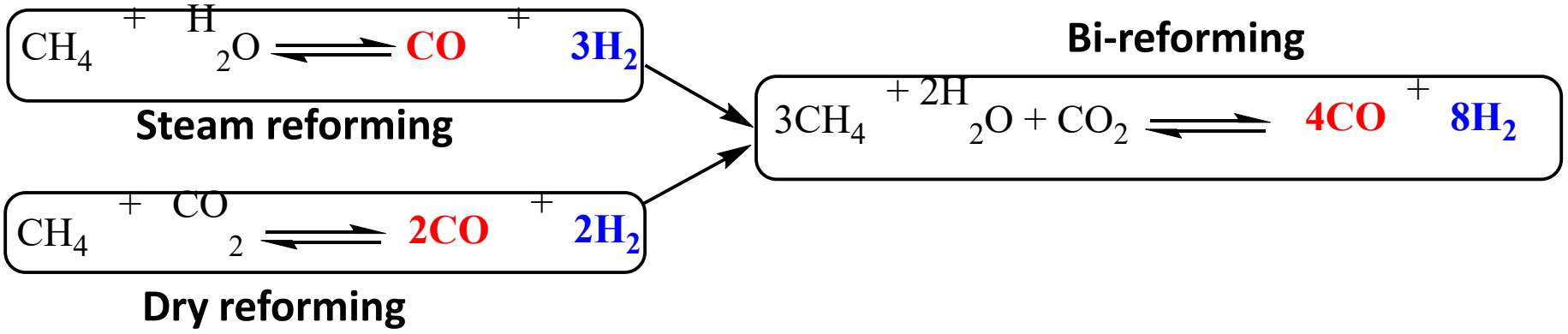
H_2 fuel cell

Space shuttle

Industrial Production of H_2

"Brown Hydrogen"

≥ 90%



All these processes require:

- Elevated temperature > 700 °C
- High pressure
- Rely on fossil fuel

- **Non sustainable**
- **Not green**
- **High carbon foot print**
- **Contributes to anthropogenic climate change**

Industrial Production of H_2

"green hydrogen"

≥ 10%

Other techniques:

Electrolysis of water

Electricity needed to drive the reaction

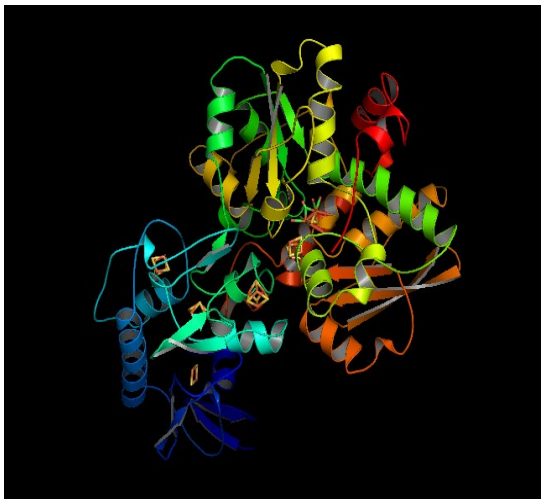
↓

Renewable → green H_2

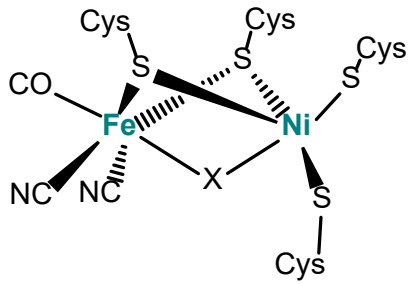
Natural production of H_2

Algae bioreactor for H_2 production

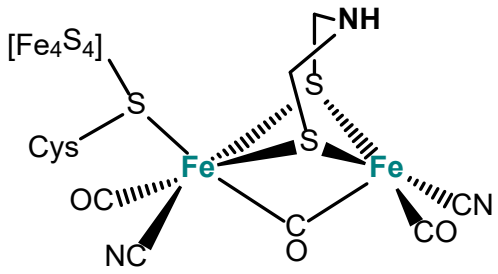
Cyanobacteria



[FeFe] hydrogenase



[FeNi] hydrogenase

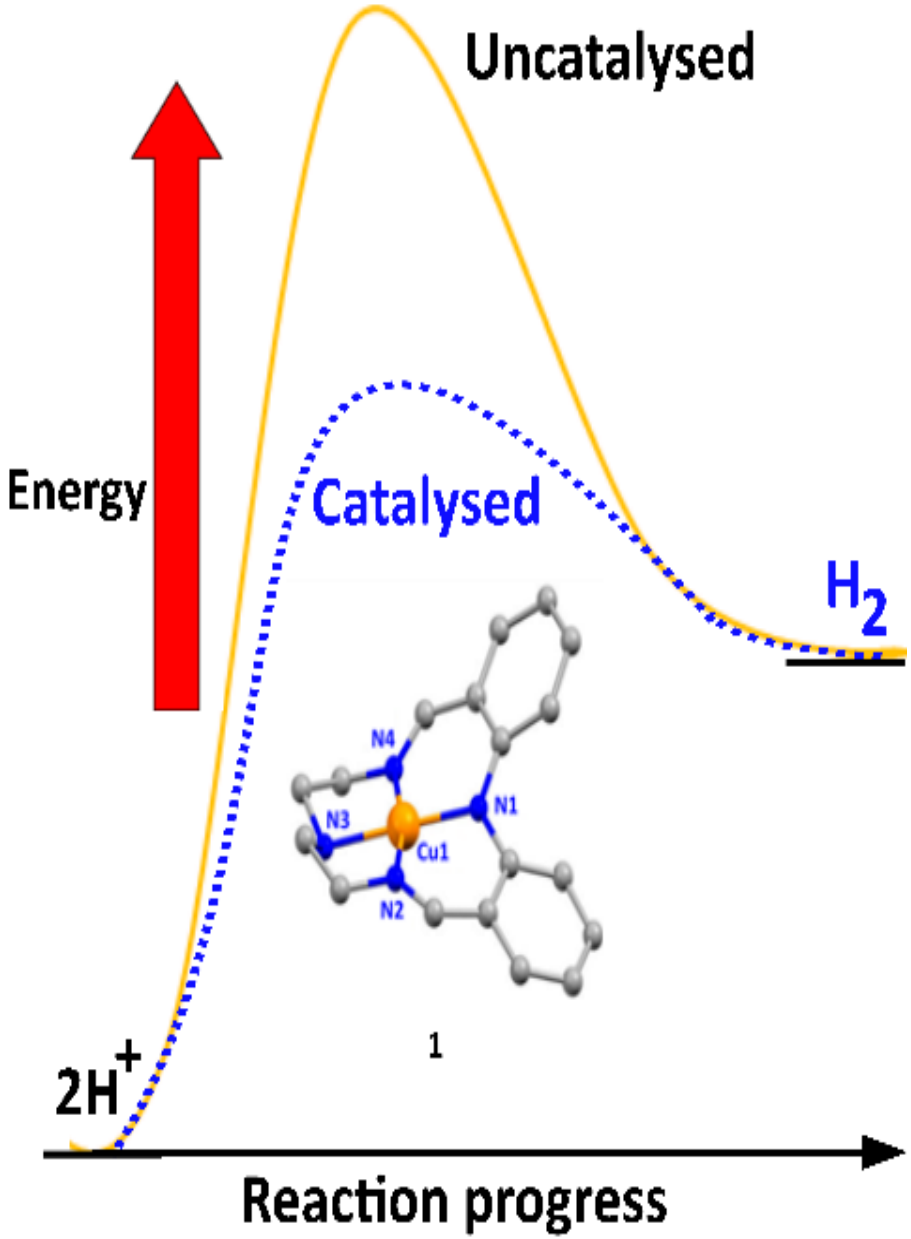


[FeFe] hydrogenase

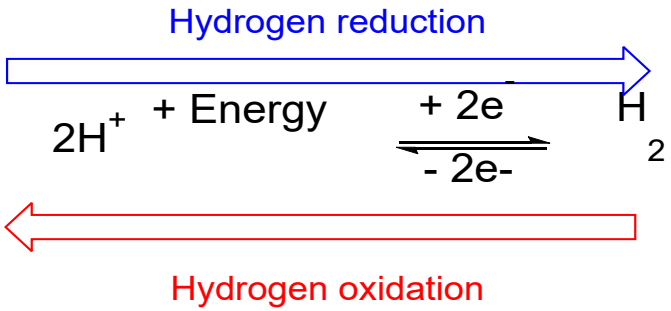
Nature uses earth abundant low toxicity 3d metal ions

Hemschemeier *et al, Photosynth. Res.* 2009, *102,* 523; W. Lubitz *et al, Chem. Rev*. 2014, *114*, 4081

Catalyzing H_2 production



Catalyst a substance that speeds up the process without itself being changed.



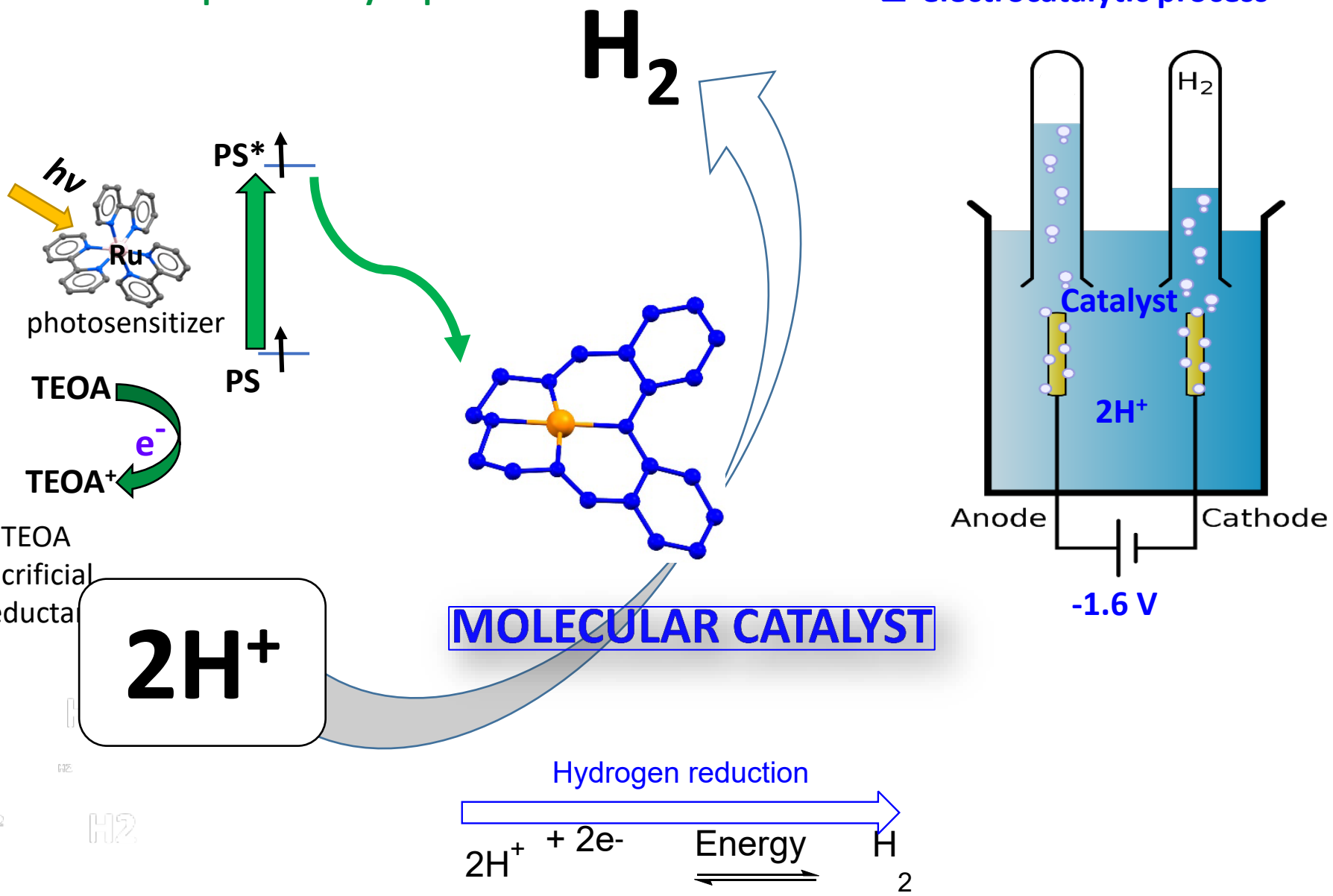
Driving force for the reaction could be:-

- ❑ Light = **photocatalytic process**
- ❑ Electricity = **electrocatalytic process**

Photo vs electro testing :

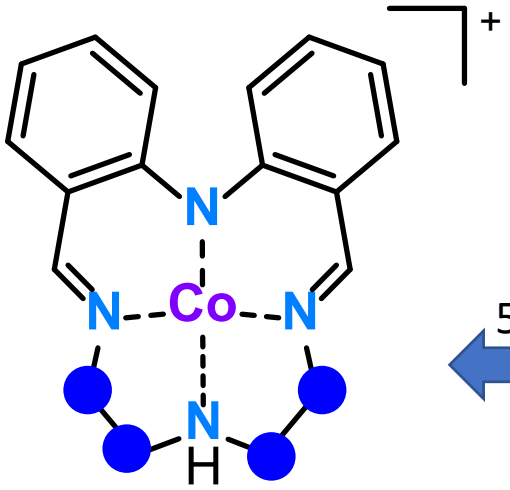
❑ photocatalytic process

❑ electrocatalytic process



Our reported molecular HER catalysts

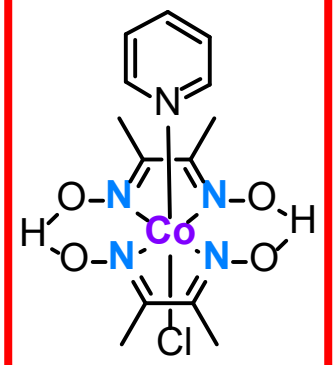
To date 17 cobalt complexes, including the following:



5 x better

TON = 130

Our best to date



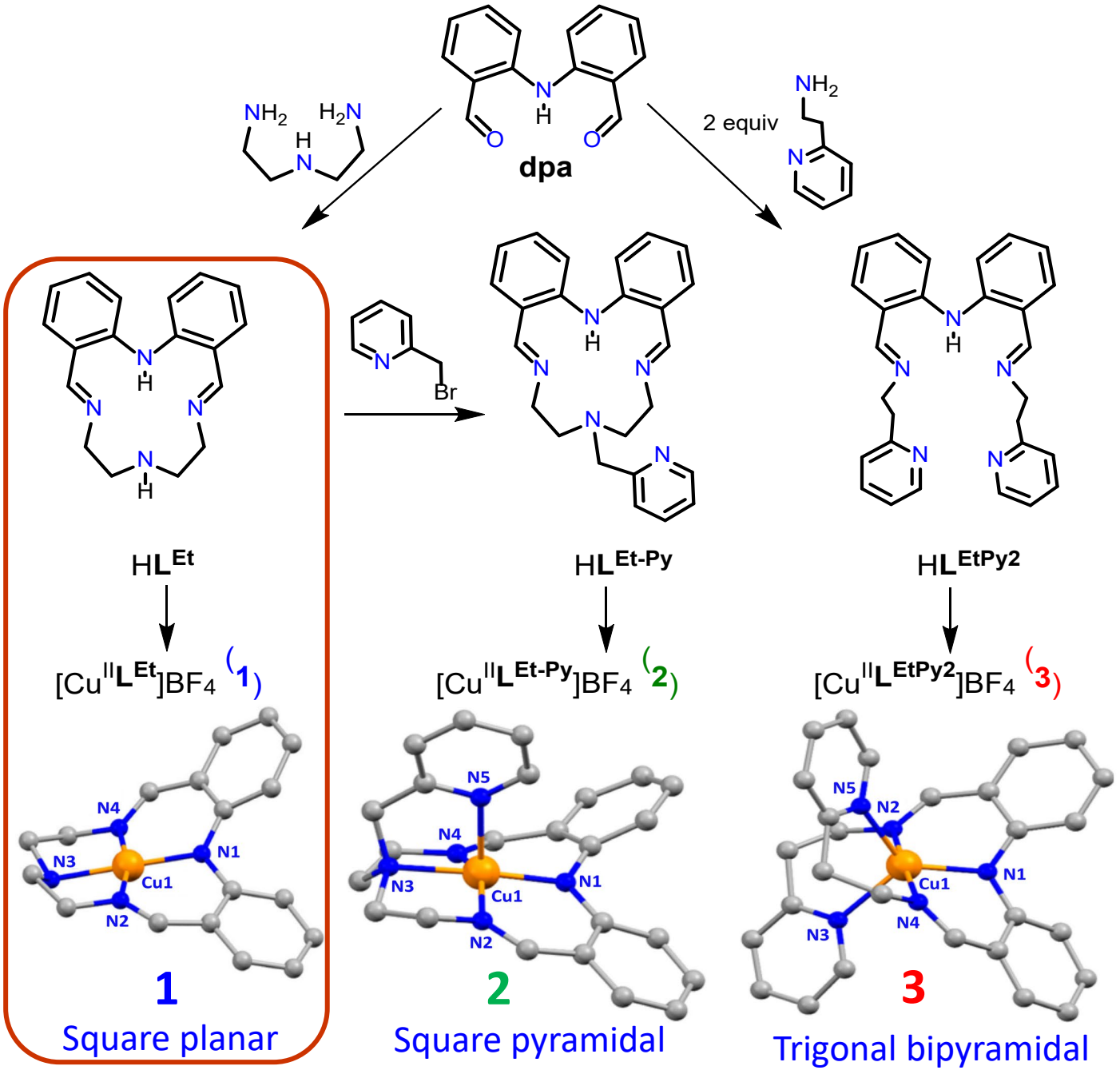
TON 25
Literature
benchmark

Photocatalytic conditions (blue light LED irradiation) in DMF or water;

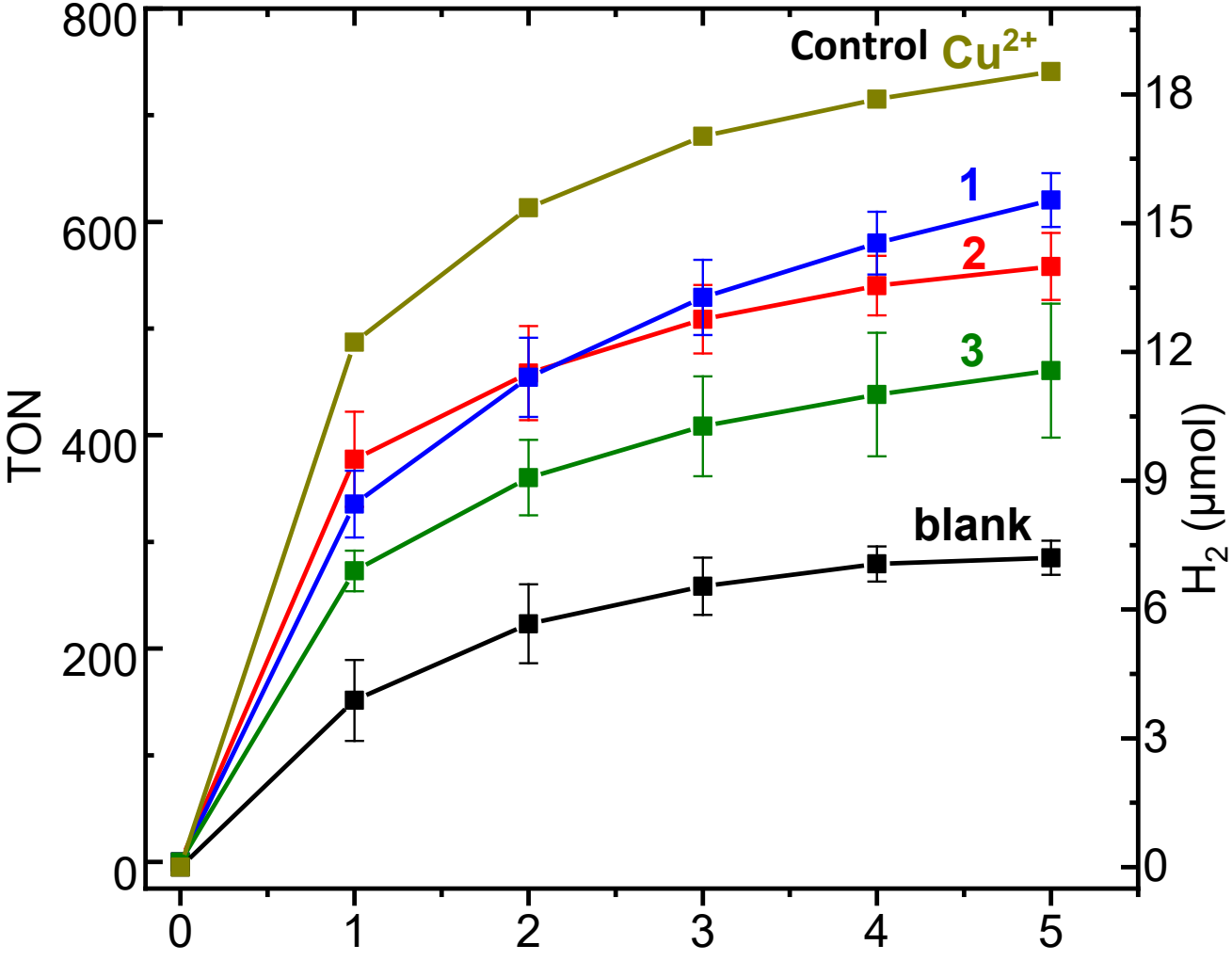
Sacrificial electron donor: TEAO or ascorbic acid; Photosensitiser: $[Ru(bipy)_3]^{2+}$

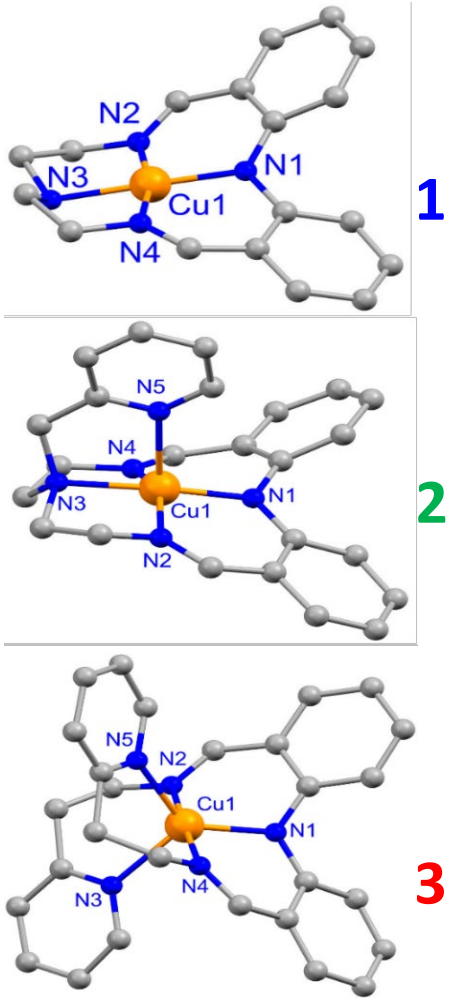
Brooker co-worker, Dalton Trans., **2011**, 40, 12277, *Chem. Eur. J.* **2018,** *24*, 9820

Copper complexes design



A. HER photocatalytic testing:

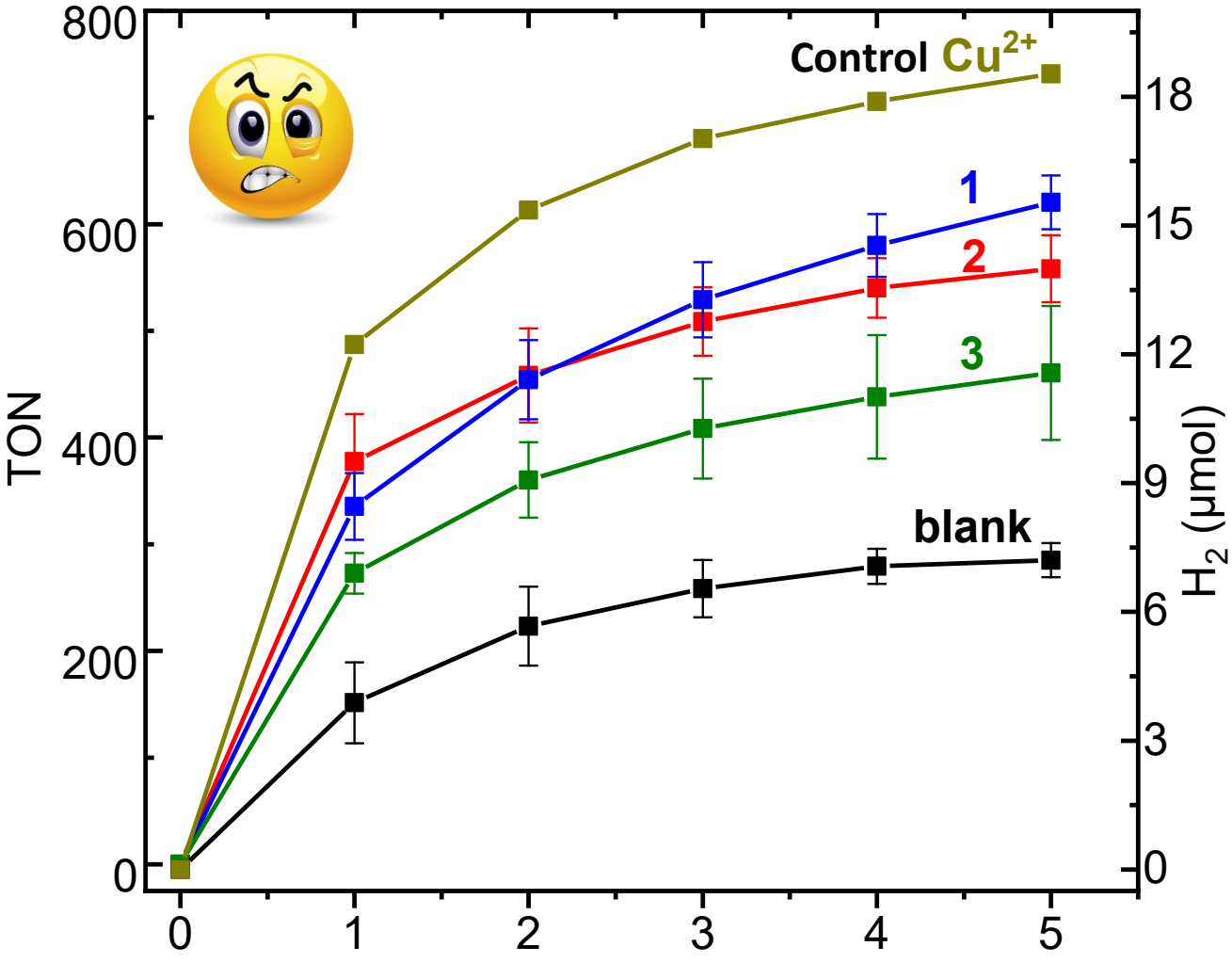


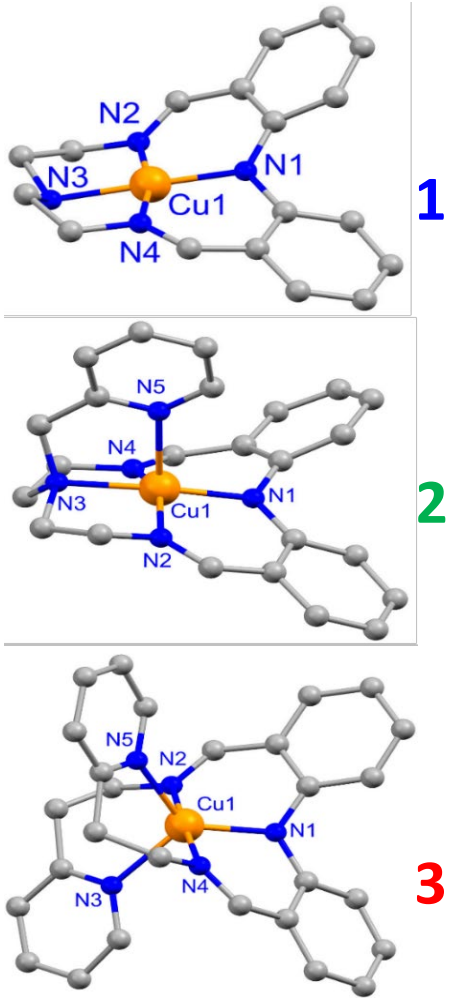


$2H^+ \xrightarrow[\text{Cu-Catalyst}]{\text{Blue LED}} H_2$

TEOA/Ru-PS

A. HER photocatalytic testing:

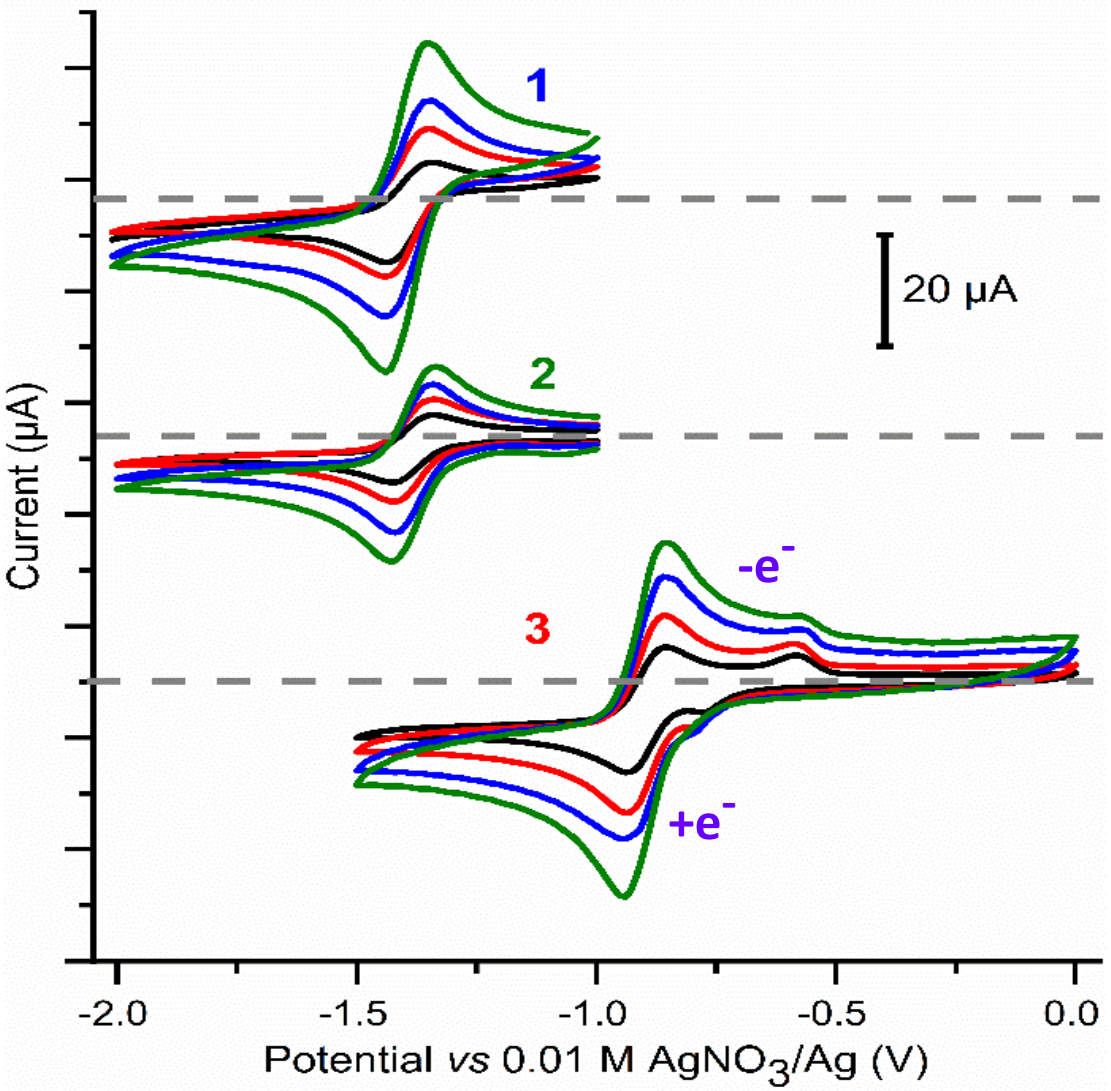


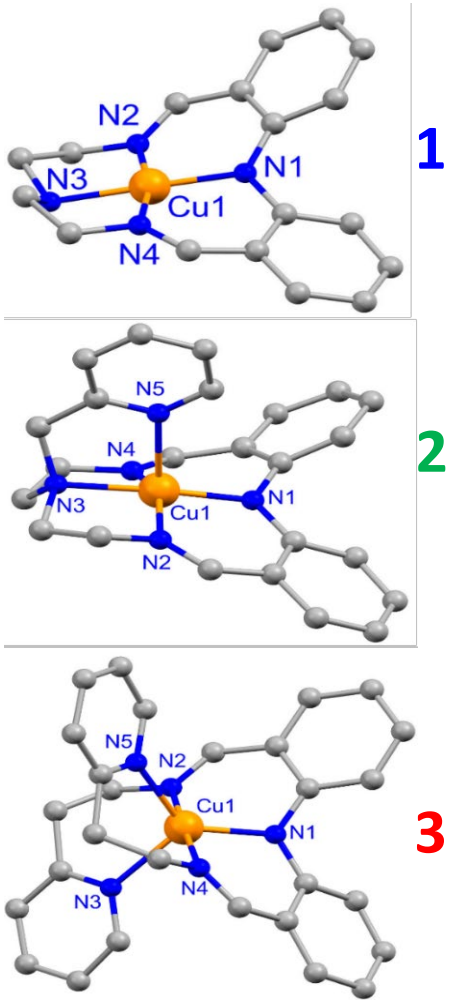


$$2H^+ \xrightarrow[\text{Cu-Catalyst}]{\text{Blue LED}} H_2$$

TEOA/Ru-PS

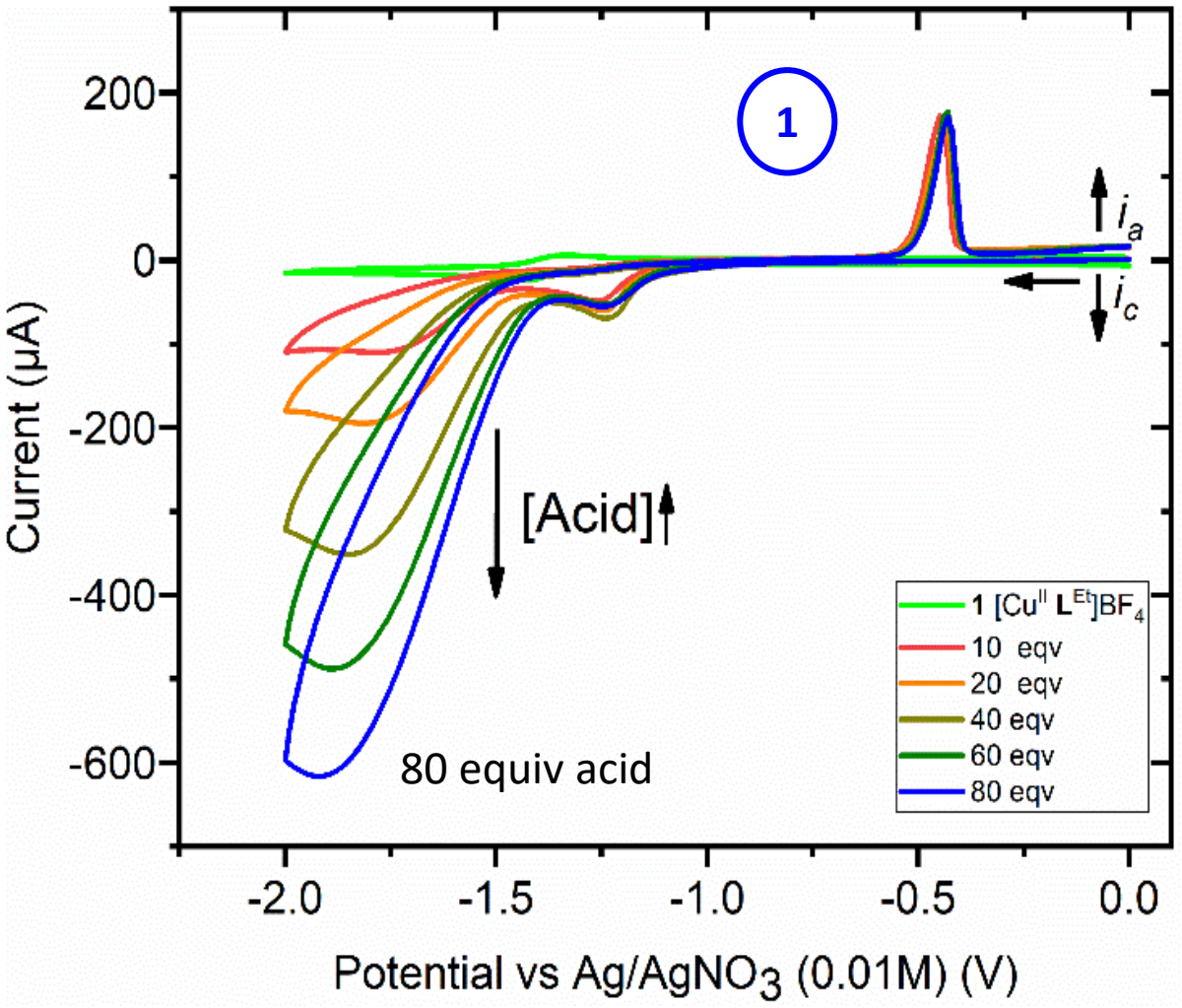
B. HER electrocatalytic testing:

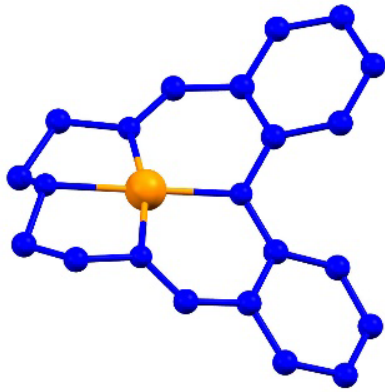




Cyclic voltammetry of the reversible redox processes: 1 mM MeCN, 0.1 M $(Bu_4N)PF_6$, glassy carbon working electrode (d = 3 mm, A = 0.071 cm^2), 293 K, vs 0.01 M $AgNO_3$/Ag.

B. HER electrocatalytic testing:



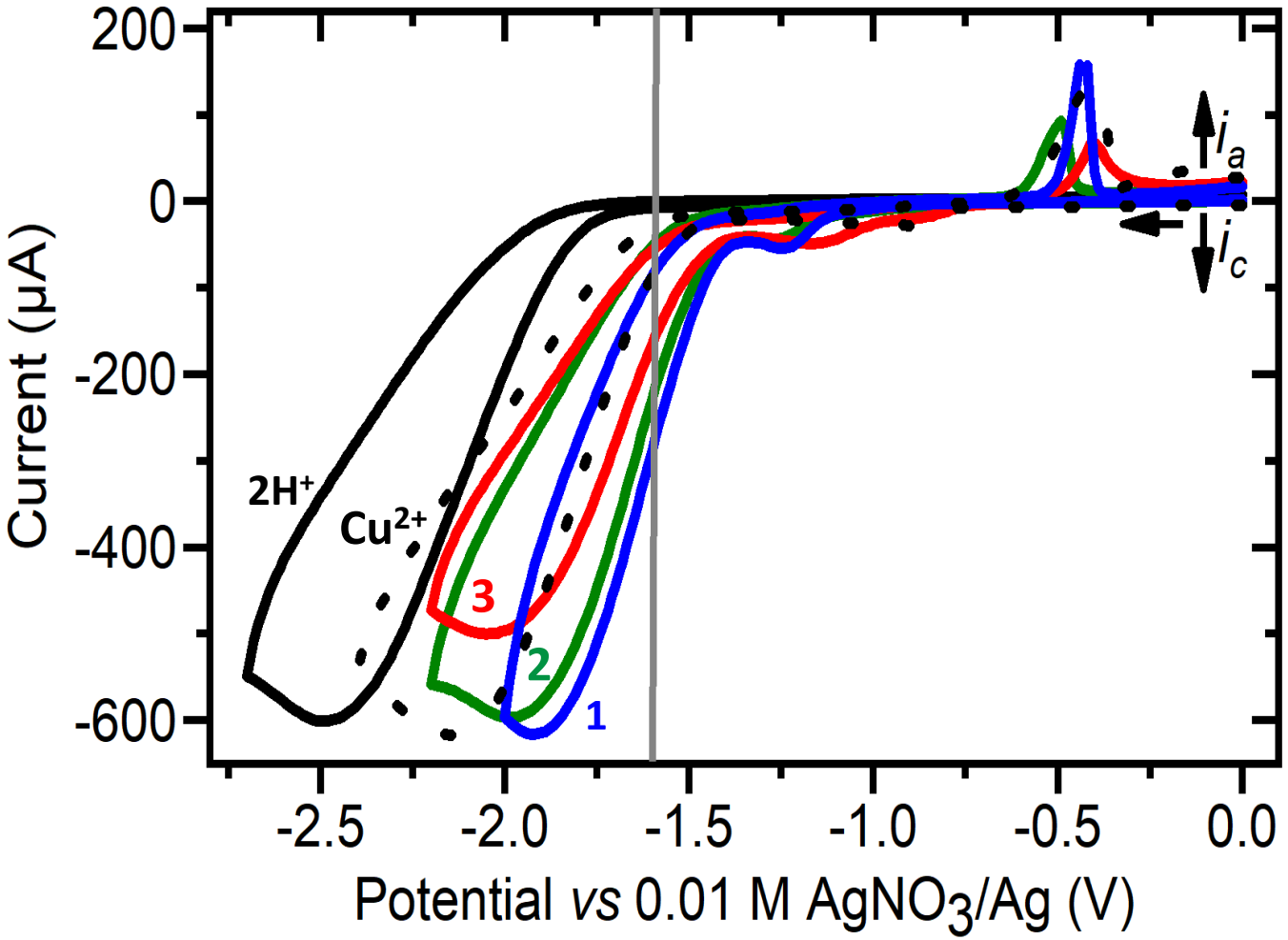


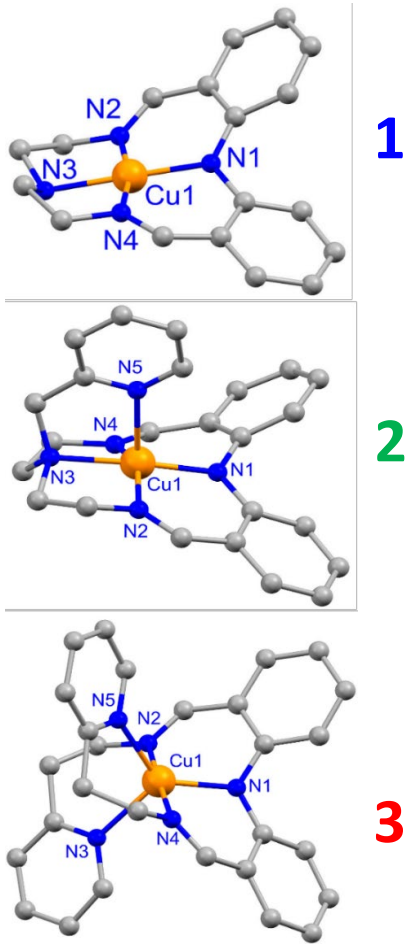
$[Cu^{II}\mathbf{L}^{Et}]^+$

1

Cyclic voltammetry, 0→ -2.0→ 0 V vs 0.01 M $AgNO_3$/Ag, for a 1 mM MeCN solution of **1** (light green, no acid), with successive additions of 10 or 20 equivalents of acetic acid

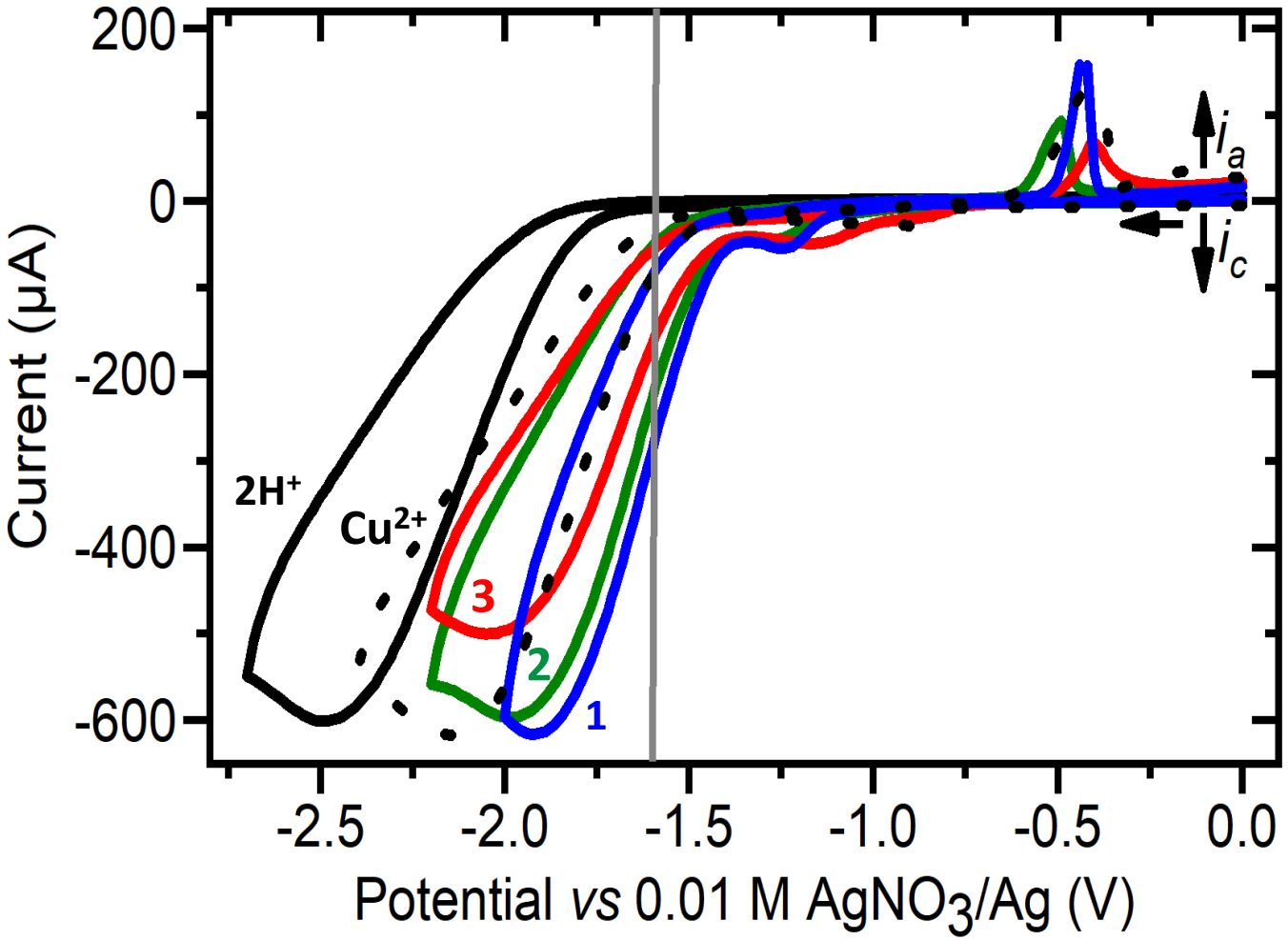
B. HER electrocatalytic testing:

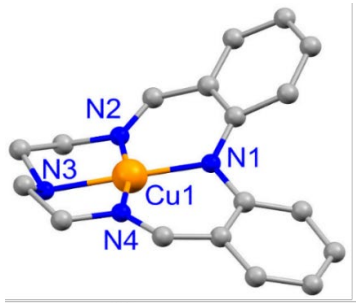




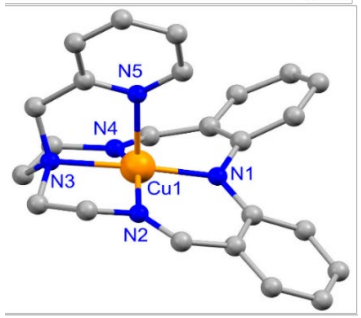
Cyclic voltammograms of 80 mM acetic acid in MeCN (control, black line) in the presence of 1 mM: $Cu^{II}(BF_4)_2 \cdot xH_2O$ (black dots), **2** (green), **3** (red) and **1** (blue).

B. HER electrocatalytic testing:





1



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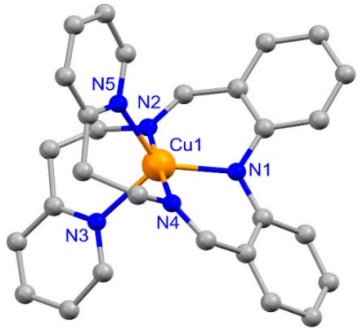
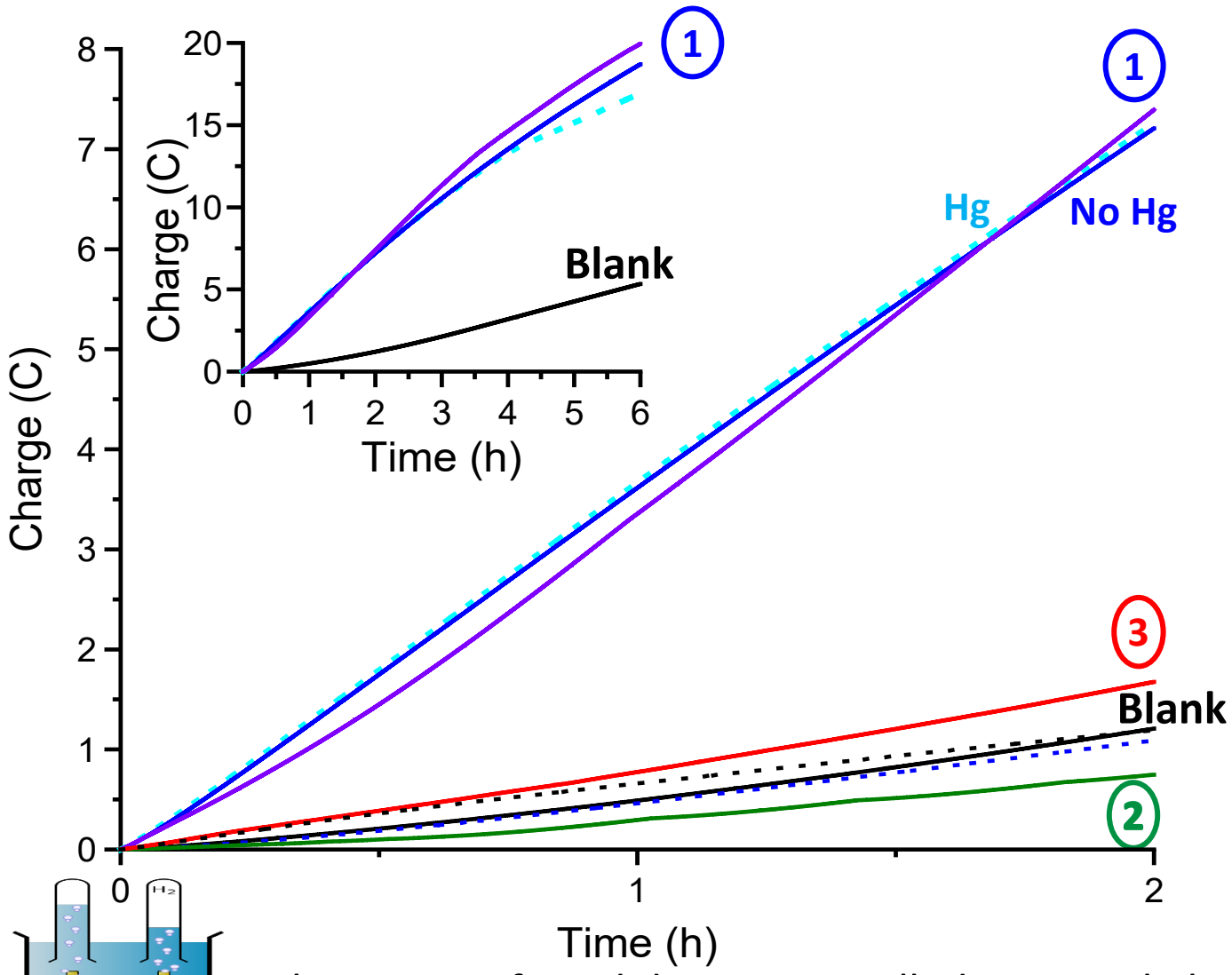


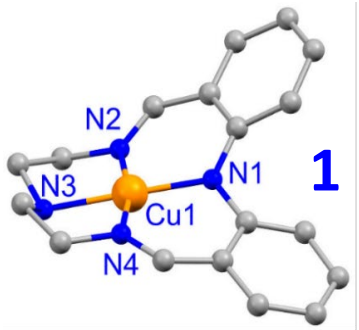
3

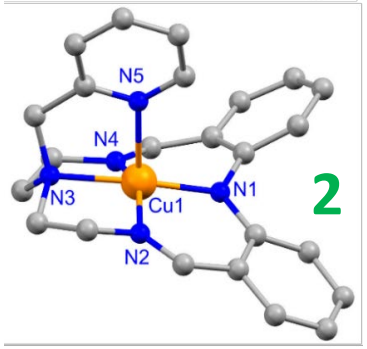
Cyclic voltammograms of 80 mM acetic acid in MeCN (control, black line) in the presence of 1 mM: $Cu^{II}(BF_4)_2 \cdot xH_2O$ (black dots), **2** (green), **3** (red) and **1** (blue).

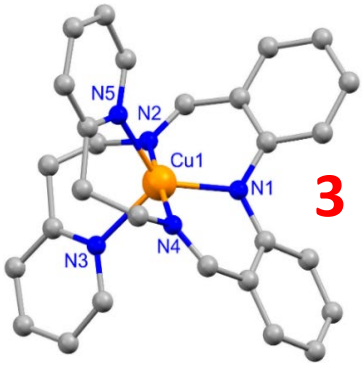
① promising catalyst

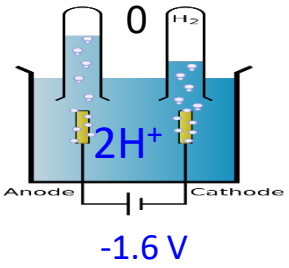
B. HER electrocatalytic testing:





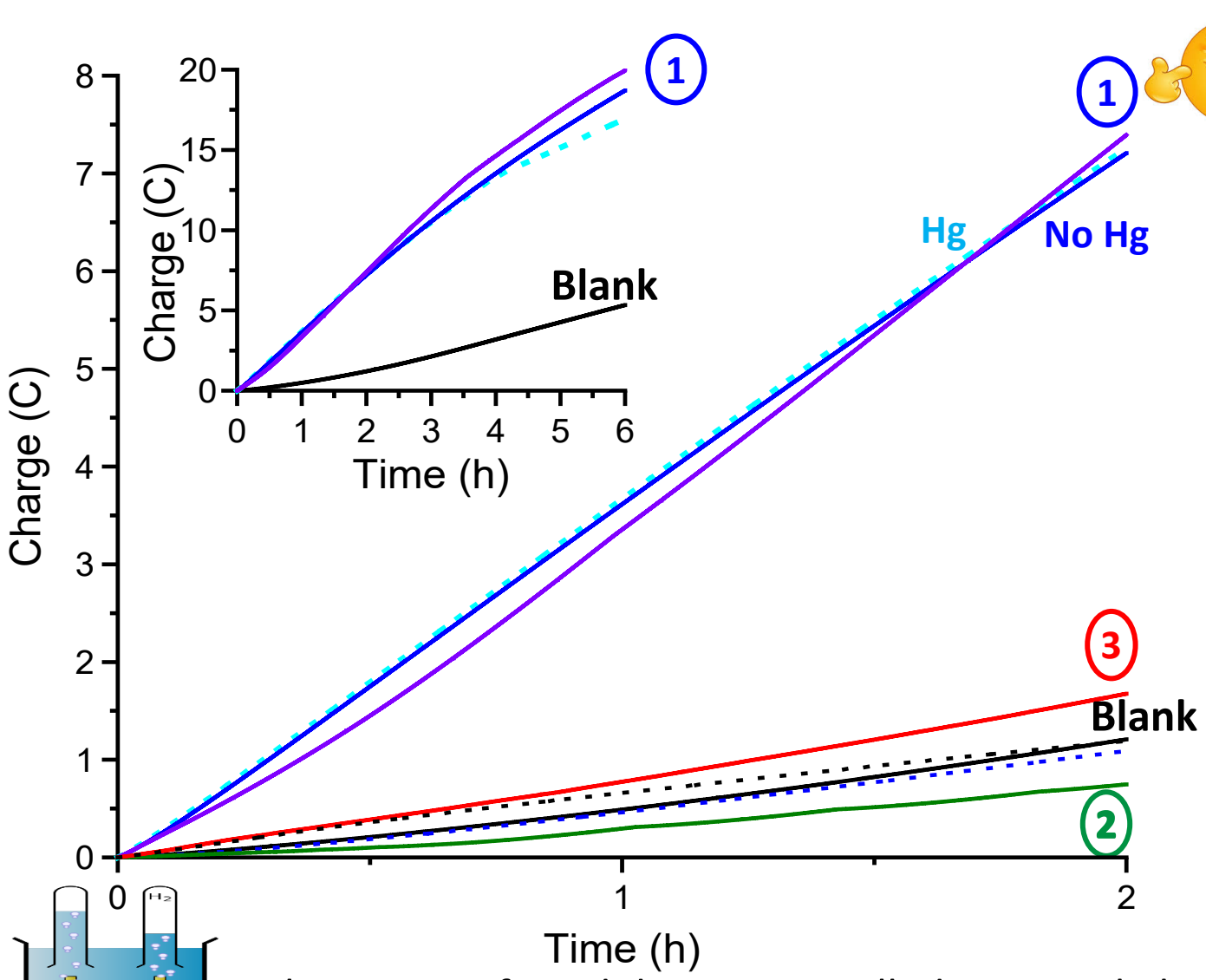




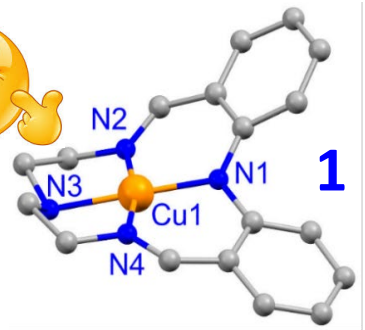


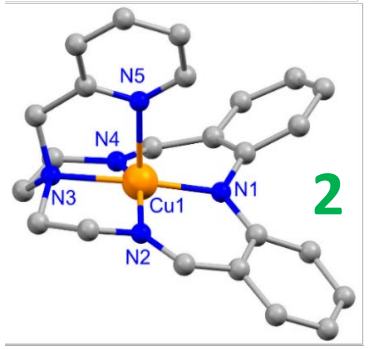
Charge transferred during controlled potential electrolysis at **-1.60 V** of an 8 mL solution of 80 mM acetic acid

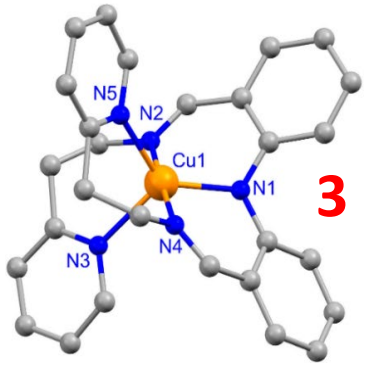
B. HER electrocatalytic testing:



acetic acid
-1.6 V







Charge transferred during controlled potential electrolysis at **-1.60 V** of an 8 mL solution of 80 mM acetic acid

B. HER electrocatalytic testing:

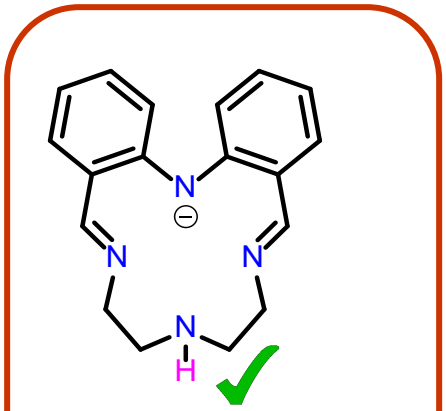
Electrochemical “H” cell (design details and training kindly provided in 1996 by Dr E. Bothe, MPI für Strahlenchemie, Mulheim an der Ruhr, Germany, to SB when she was there on sabbatical leave as a Humboldt Fellow) used for bulk electrolysis experiments

B. HER electrocatalytic testing:

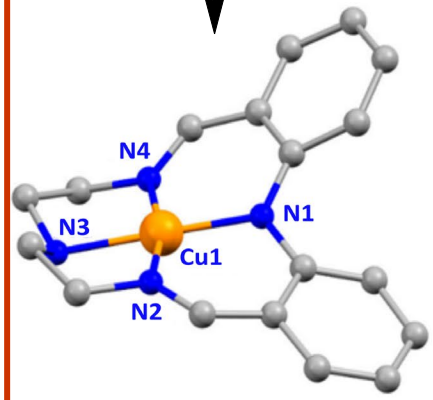
Summary of key data, including charge and e-equivalents transferred plus TON(H_2),

Description		Charge (C)	# of e's per 1	TON(H_2)
Run 1 (blue line)	2 hour	7.6	9.3	4.7
	6 hour	18.7	24.2	**12.1**
Run 2 (violet line)	2 hour	7.4	9.6	4.8
	6 hour	19.9	25.8	**12.9**
Run 3 - + mercury drop (sky blue line)	2 hour	7.2	9.3	4.7
	6 hour	17.0	22.0	**11.0**

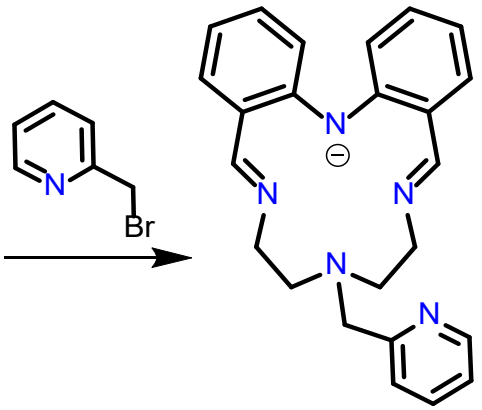
Copper complexes winning design



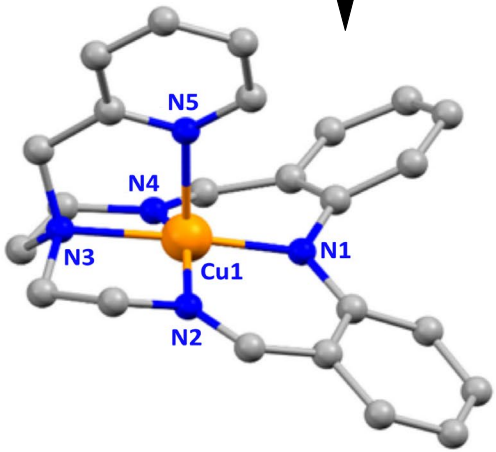
$(L^{Et})^-$



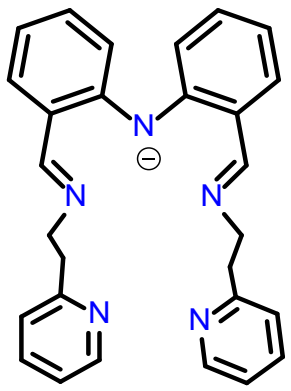
Square planar



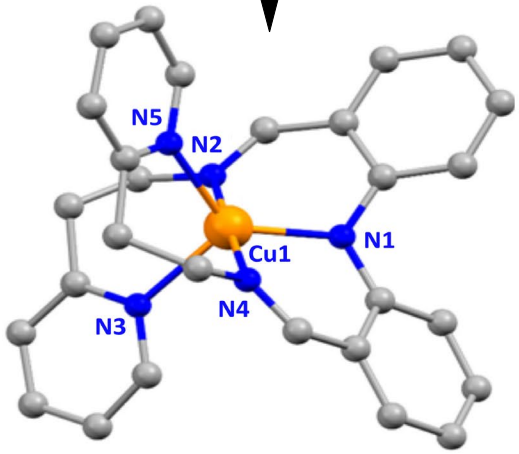
$(L^{Et\text{-}Py})^-$



Square pyramidal



$(L^{EtPy2})^-$



Trigonal bipyramidal

Conclusion

H_2 is the fuel of the future

Improved catalysts for hydrogen desired

Cu complexes 1-3 are poor HER photocatalysts

Cu complexes 1 is a promising HER electrocatalyst

Key design features NH and/or square planar

Testing in water is underway

Brookers Bunch

Acknowledgments

Supervisor: Prof. Sally Brooker
Dr. Humphrey L.C. Feltham
Prof. Garry S. Hanan
Olivier Schott

The Brooker Bunch

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- Sriram Sundaresan
- Sandhya Singh
- Luca Bondi
- Matt Robb
- Varinder Singh

Former PhDs

- Dr Santiago Rodriguez-Jimenez
- Dr Fabrice Karabulut

Research Assistant:

- Michael Bennington

Thank You