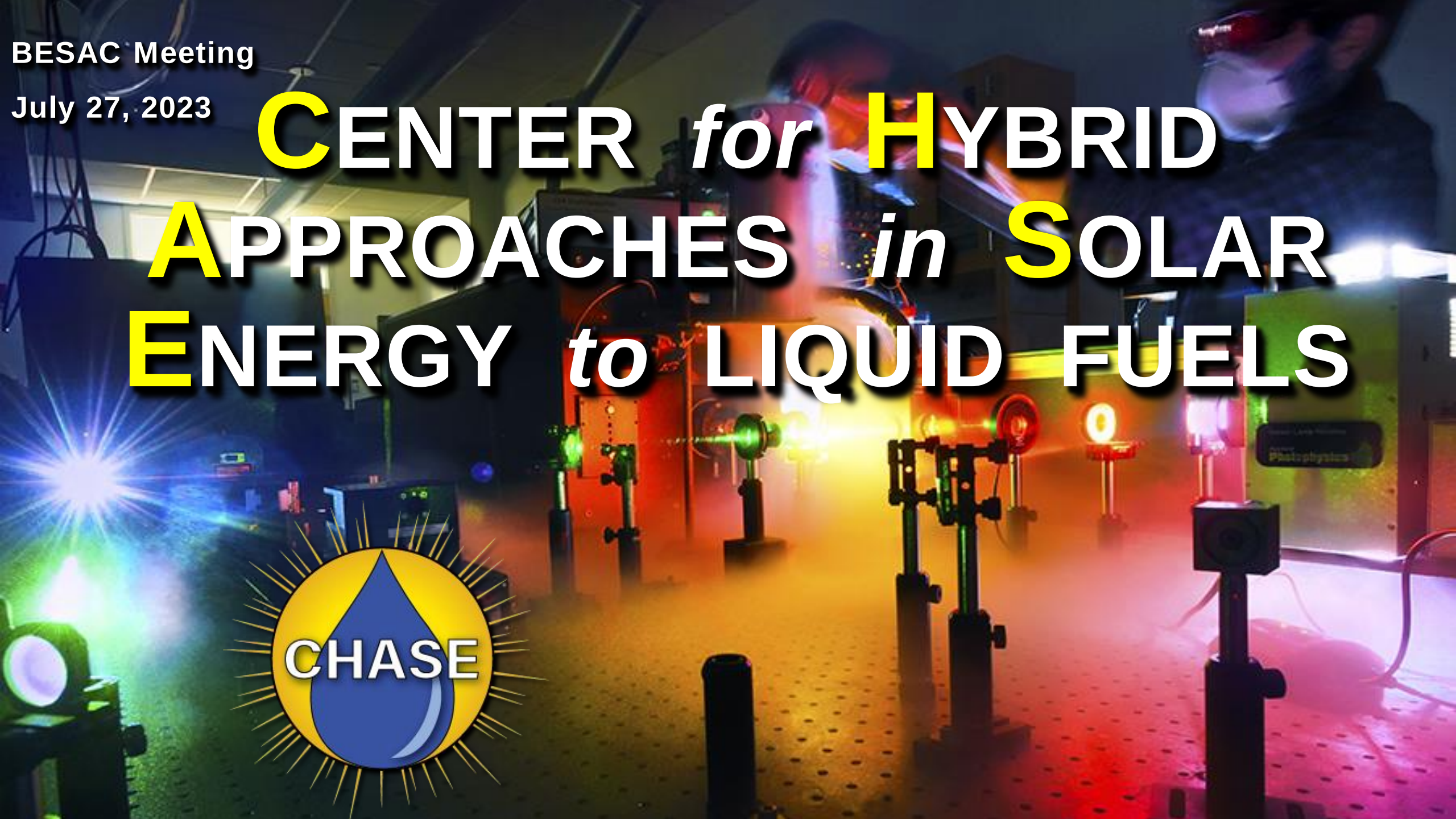
BESAC Meeting

July 27, 2023

CENTER *for* HYBRID APPROACHES *in* SOLAR ENERGY *to* LIQUID FUELS

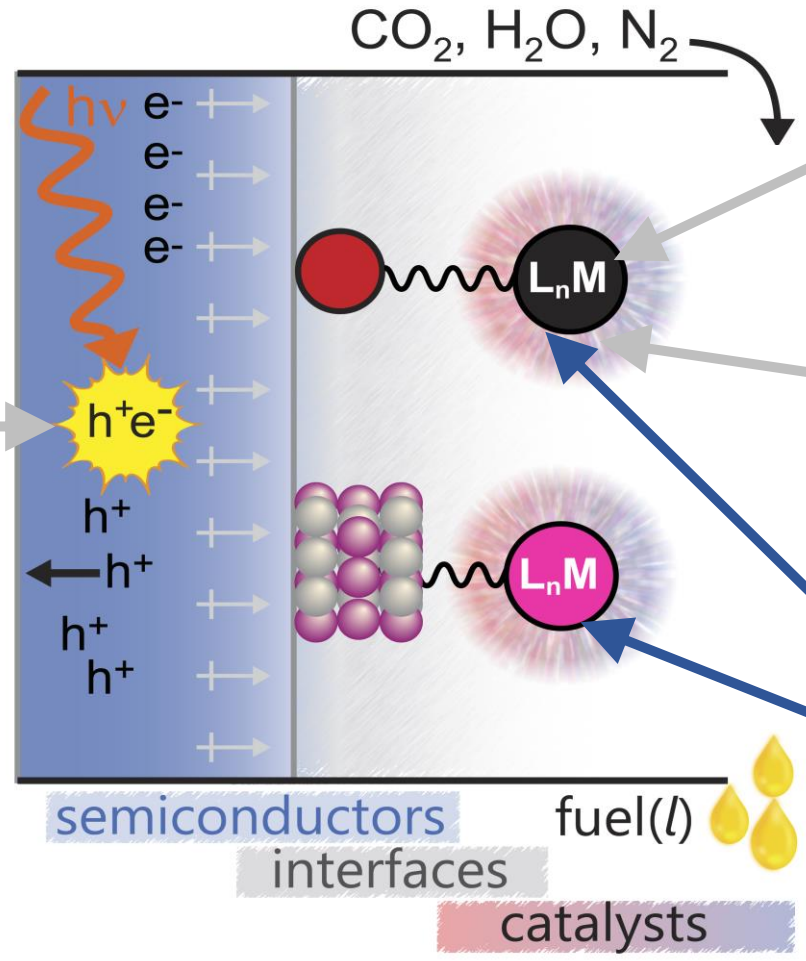


The CHASE Strategy

CHASE
Center for Hybrid Approaches in Solar Energy to Liquid Fuels

FIVE-YEAR RESEARCH GOAL

To develop a fundamental molecular level understanding of how *hybrid photoelectrodes, comprised of molecular catalysts with tailored microenvironments* integrated with semiconducting light absorbers, couple single photon absorptions to the multi-electron/multi-proton chemical transformations necessary to generate liquid solar fuels



semiconductors absorb light and separate charge

molecular catalysts generate fuels

tailored microenvironments enhance catalyst selectivity and durability

cooperative interactions of catalysts enable cascade production of high value liquid fuels

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CHASE Vision

Liquid fuels can be generated using the small molecules found in air as the only chemical feedstocks and sunlight as the only energy source.

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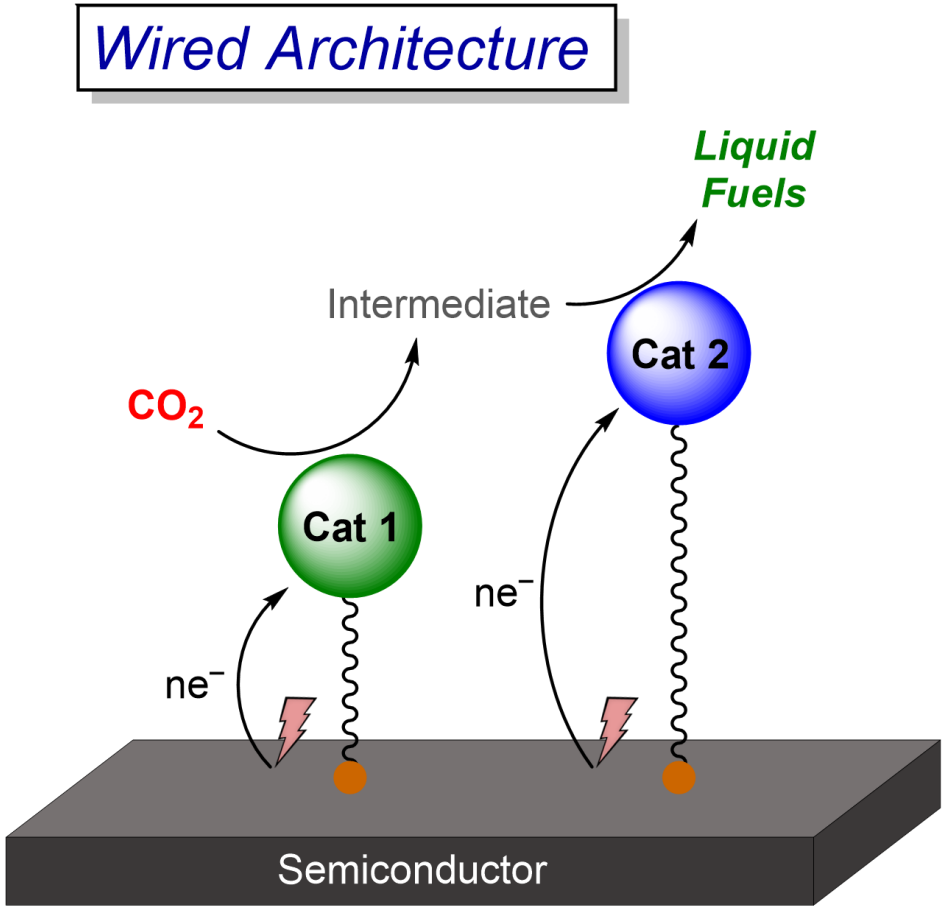
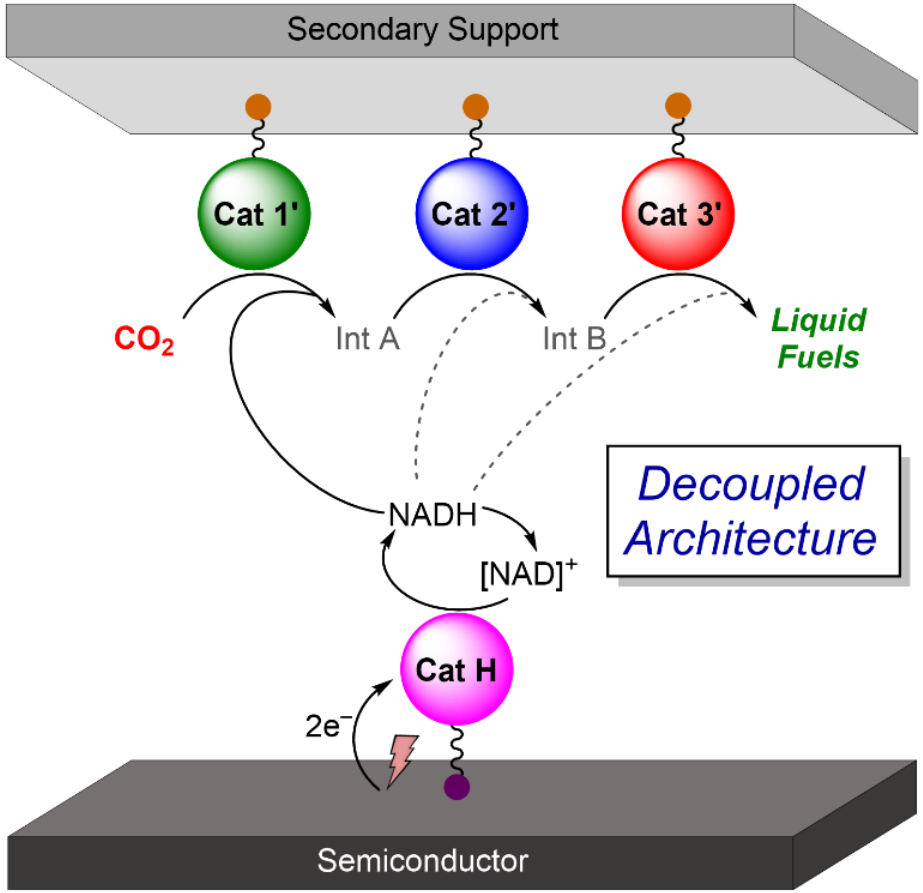
The challenge of practical liquid solar fuel production can only be met through the *cooperative interactions of molecules and materials.*

Two Newly Proposed "Architectures"



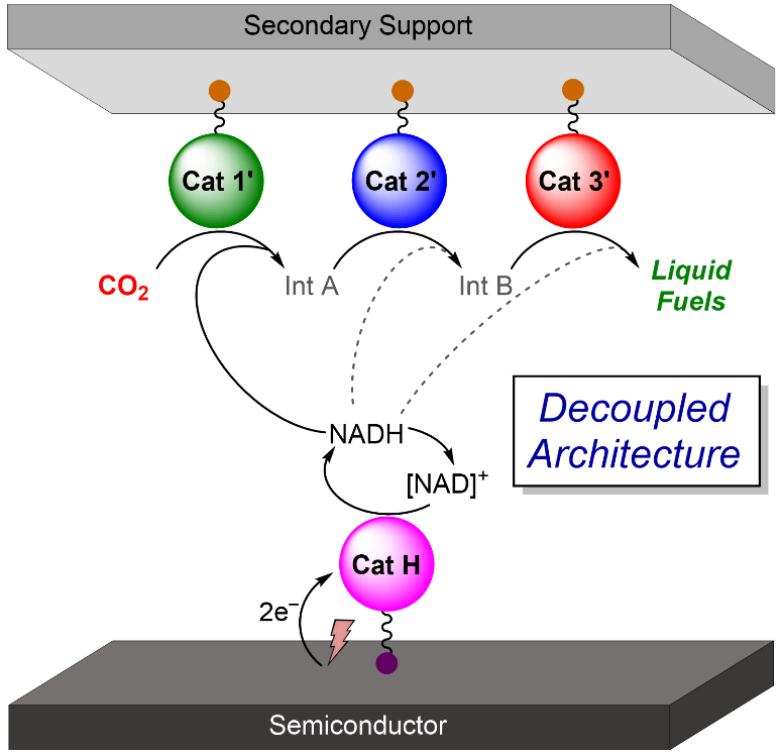


Decoupled Architecture

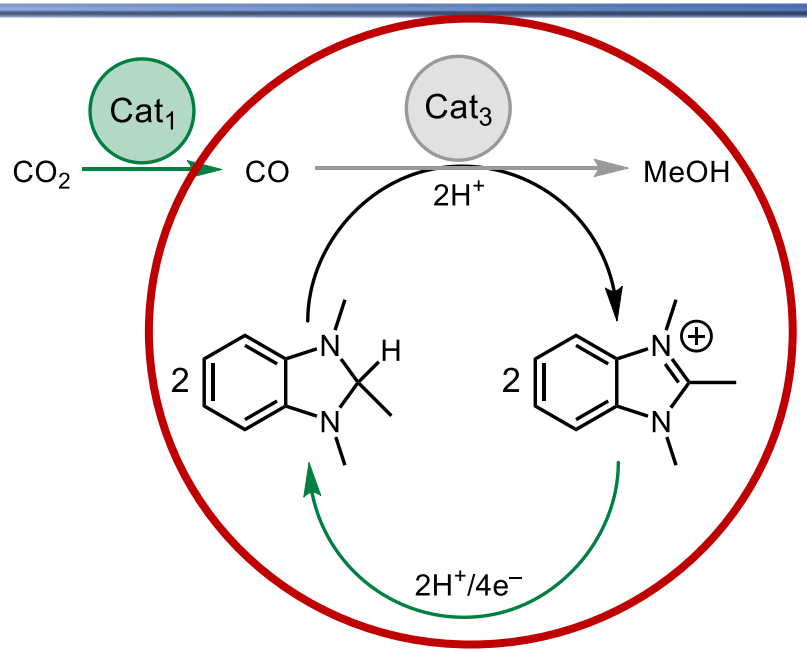
Key, defining features

- Catalysis occurs remote to the light absorbing semiconducting hybrid photoelectrode.
- Hydride reagents mediate catalysis and are subsequently regenerated at an illuminated hybrid photoelectrode.

Cascade catalysis occurs on a secondary support, driven by renewable hydride donors that are regenerated at a semiconductor surface.



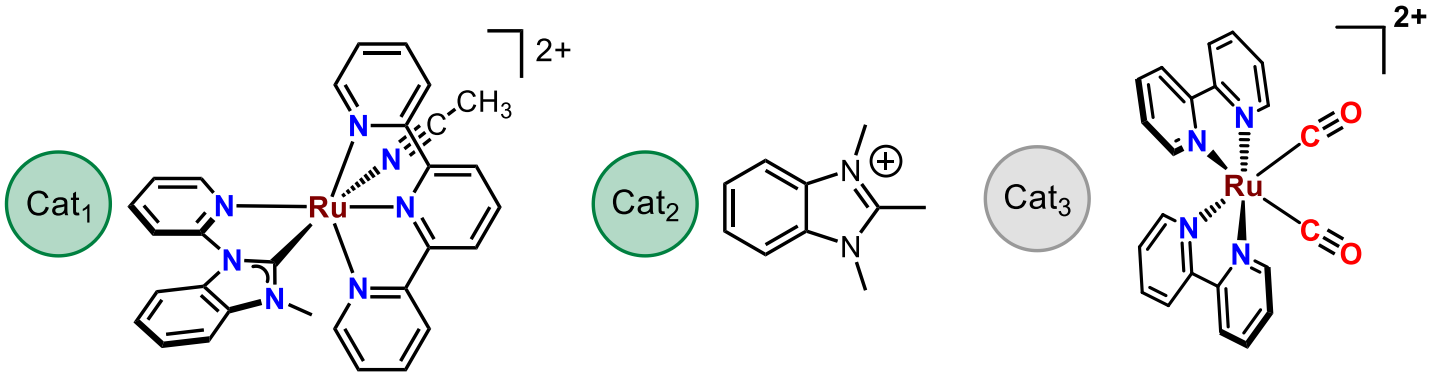
CO_2 → CO → MeOH Cascade Mechanistic Studies



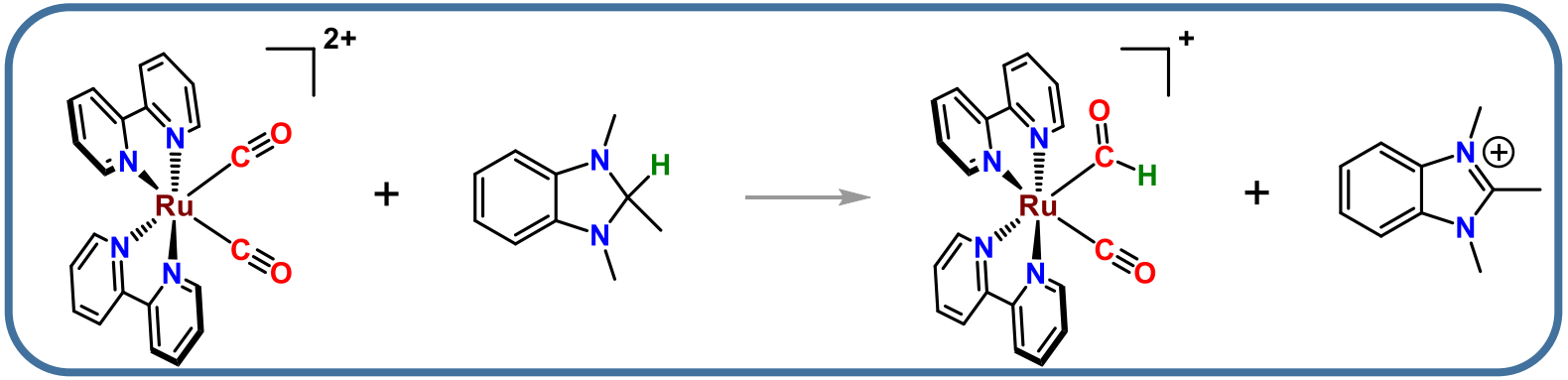
Catalysts for light reactions

Catalyst for dark reactions

Challenge:
Required chemistry remains unknown or poorly developed.



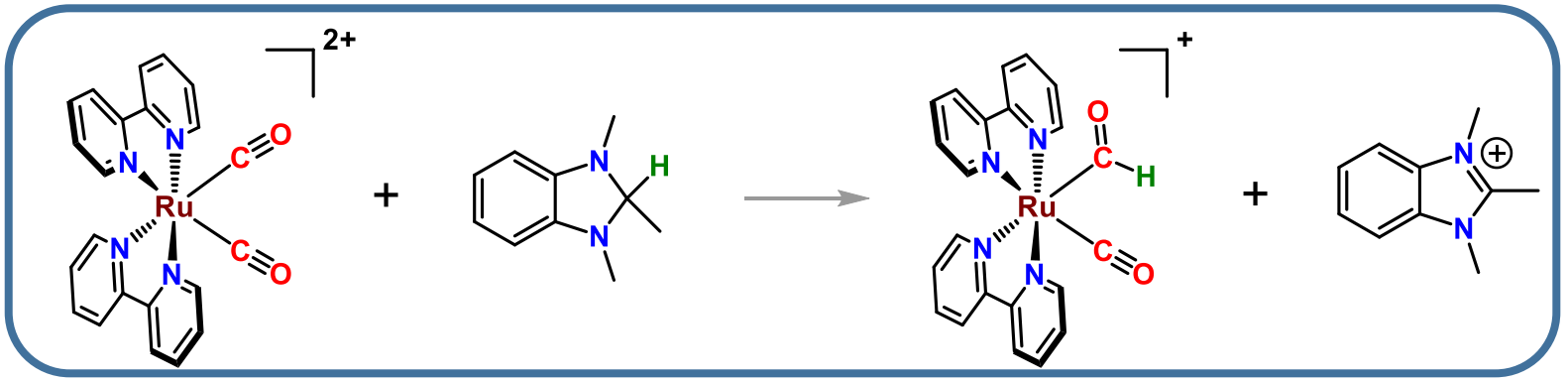
Mechanistic Studies



Step 1 : Formyl

- Quantitative reaction
- KIE = 72
- ET-HAT Mechanism

Cascade Reactions and Mechanistic Studies



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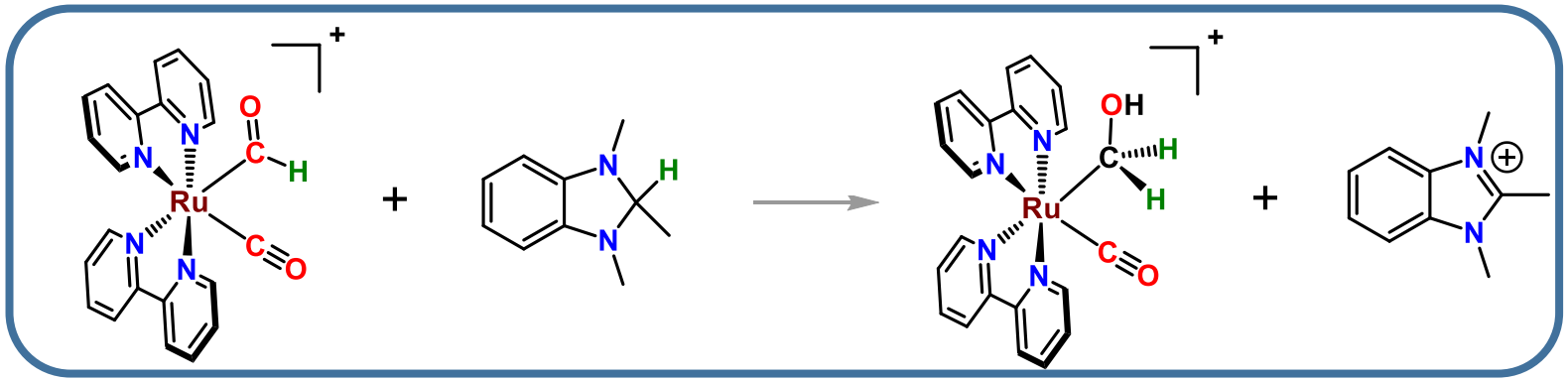
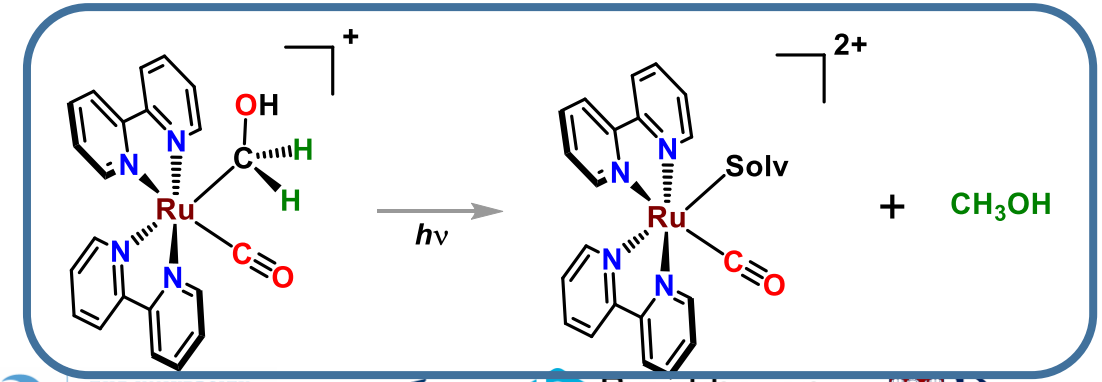
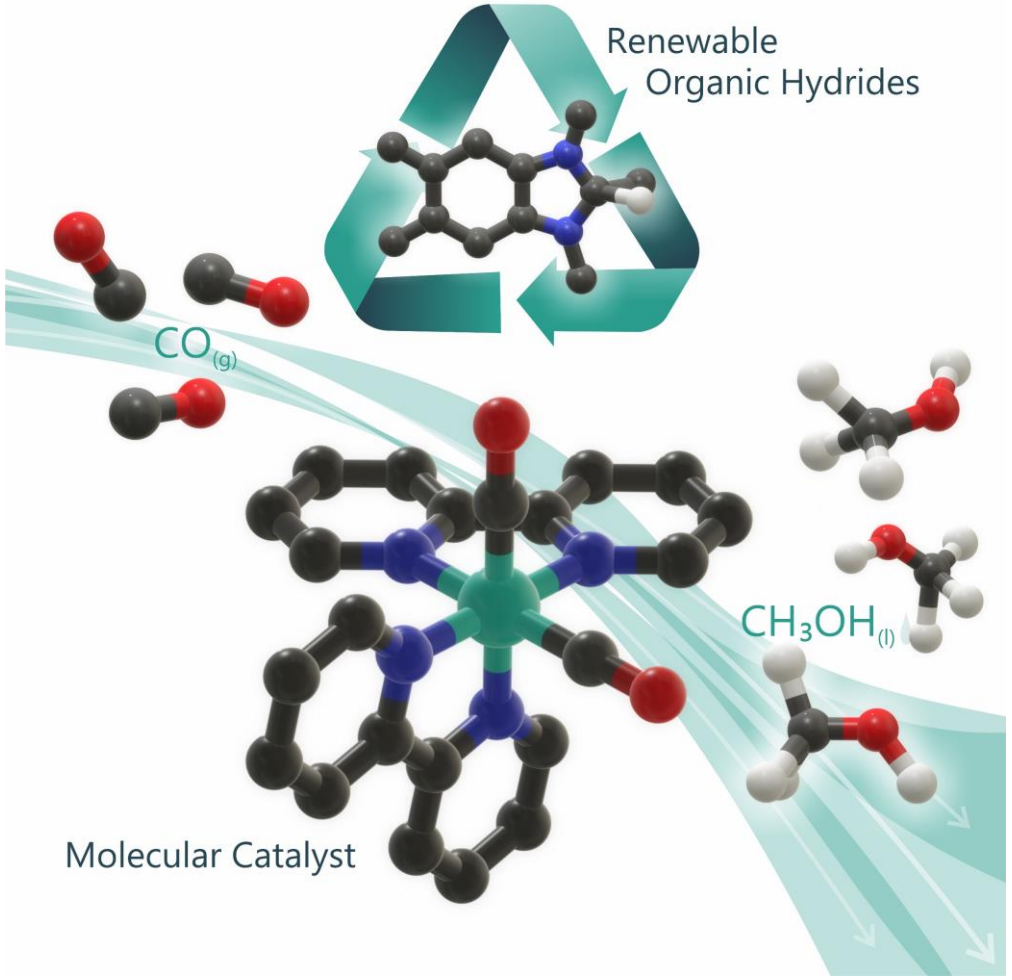


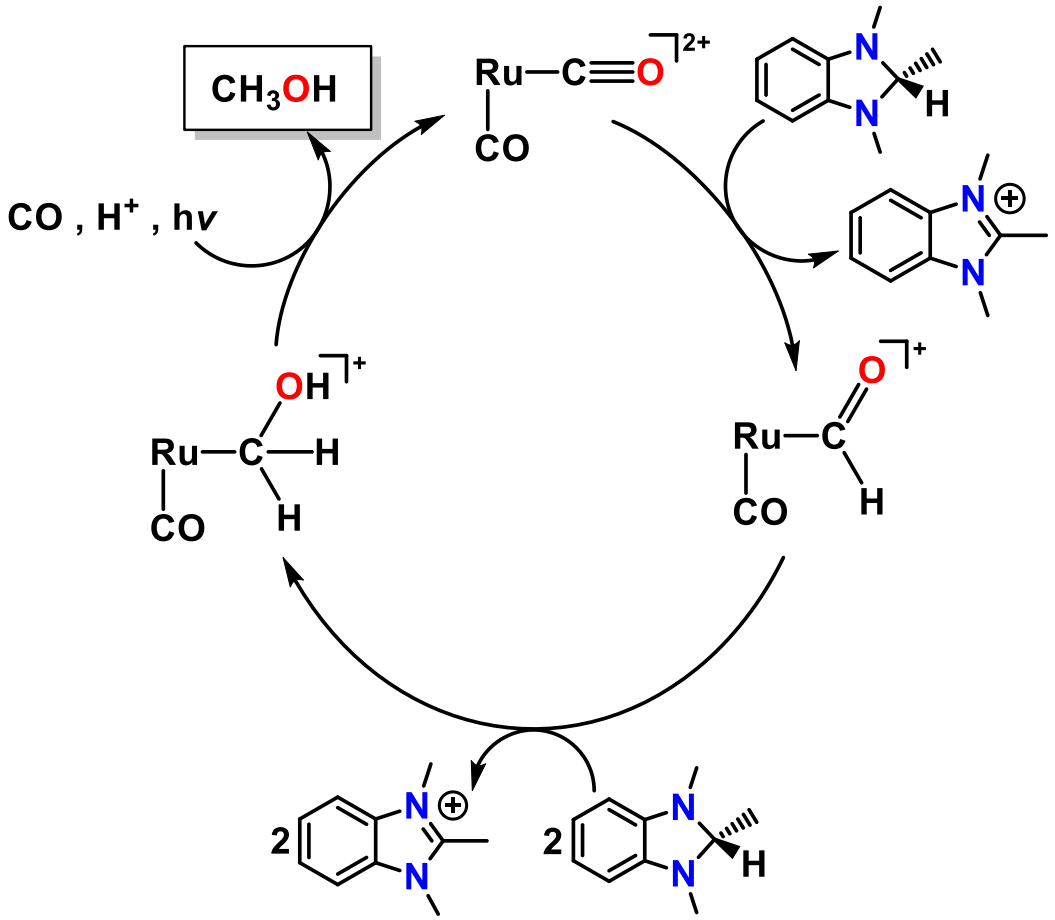
Step 2 : Hydroxymethyl
- Quantitative reaction
- Stoichiometry?



Step 3 : Methanol photorelease

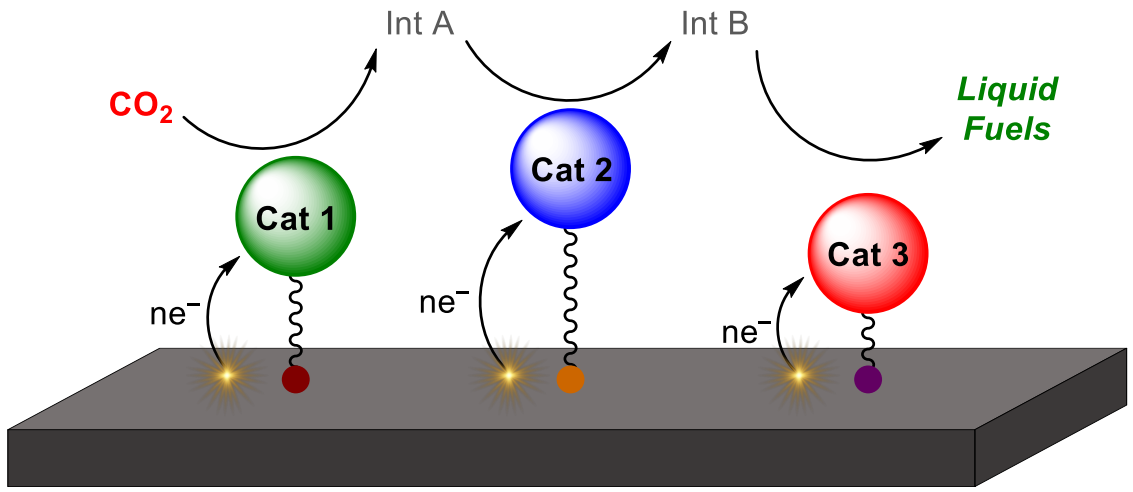
Catalytic Cycle for Methanol Production





Wired Architecture

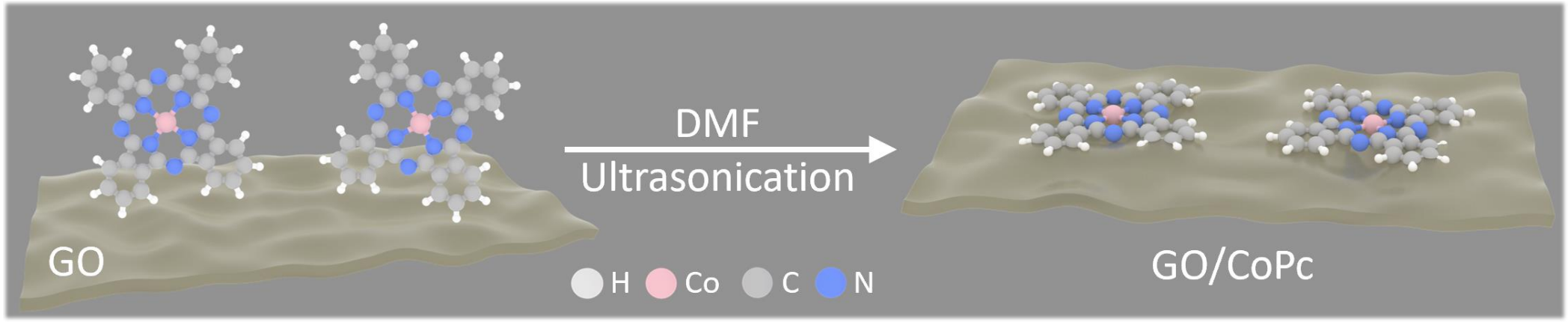
Cascade reactions on a single hybrid photoelectrode using integrated catalysts to reduce CO_2 to a liquid fuel.

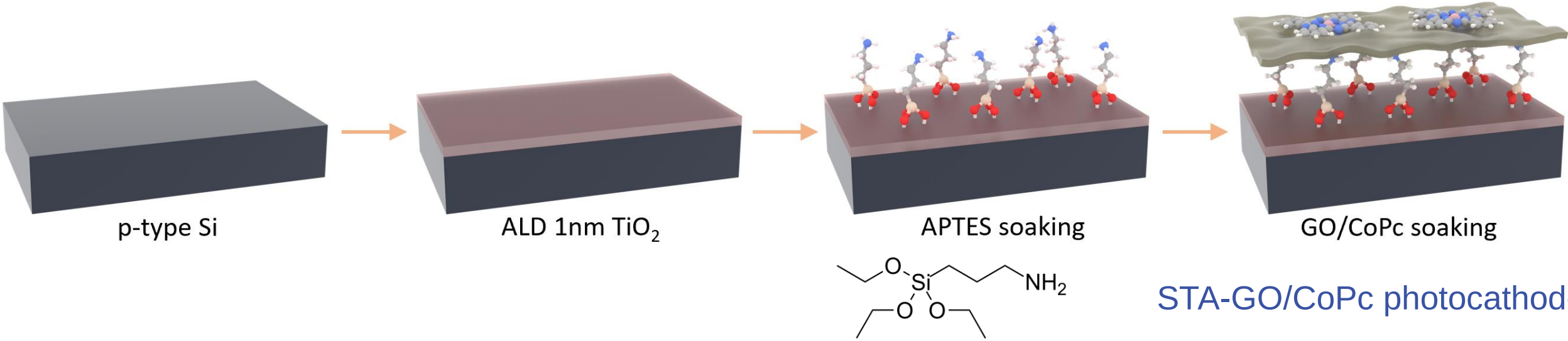


Key, defining features

- Each catalyst in the cascade is integrated into a single hybrid photoelectrode
- The illuminated semiconductor transfers electrons directly to the molecular catalysts.

CoPc Integration with p-Type Silicon





STA-GO/CoPc photocathode

Solar to Methanol Performance

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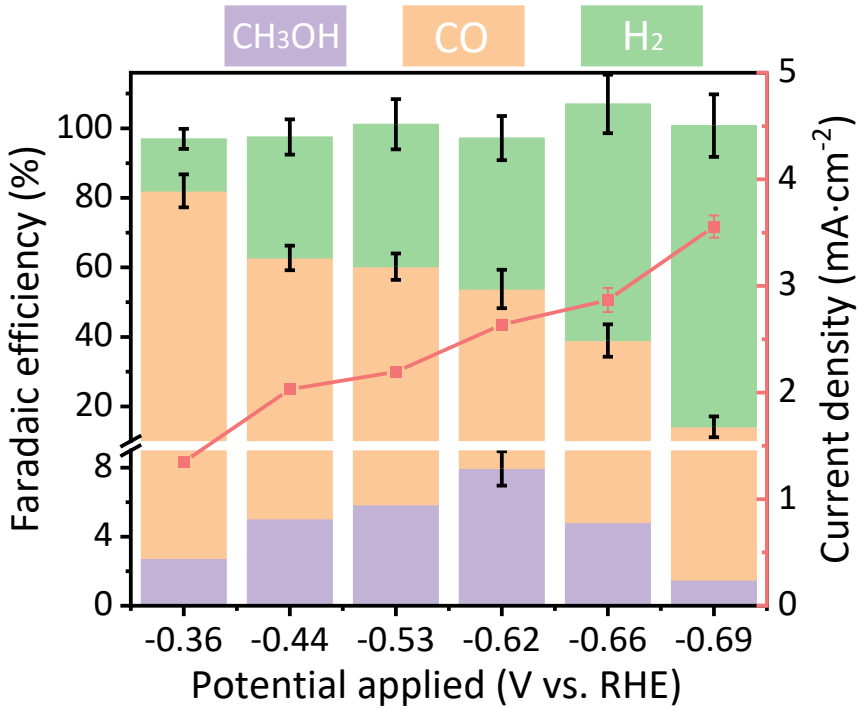
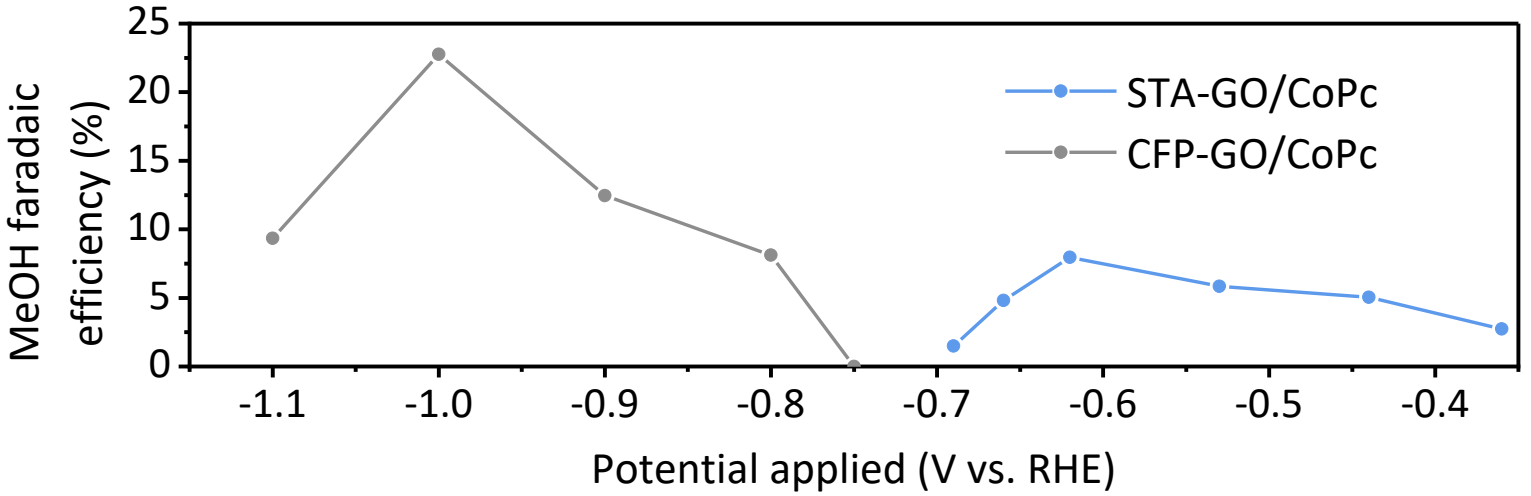


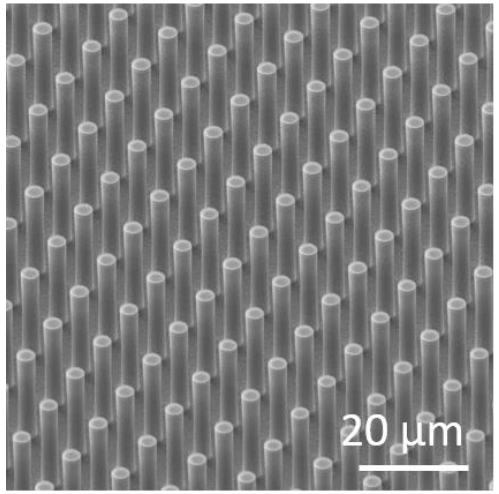


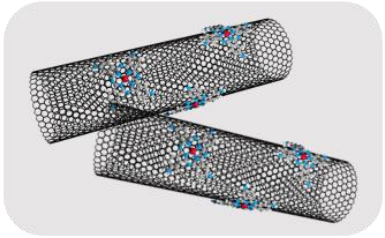
First molecular CO_2-to-methanol photoelectrode:

- ~400 mV photovoltage
- Photocurrent density 2.5 mA/cm^2
- Methanol FE = 8%

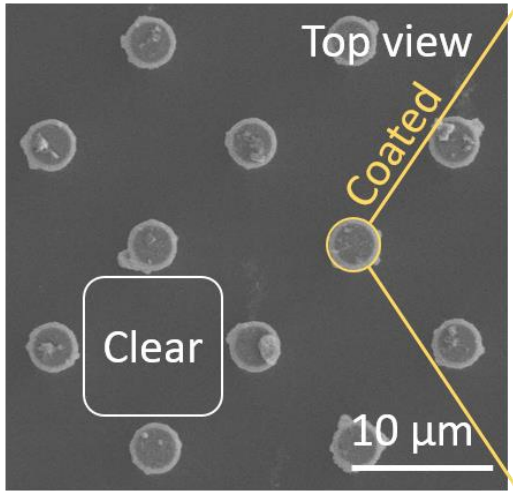
Shang, Rooney, Gallagher, Wang, Krayev, Shema, Leitner, Harmon, Xiao, Sheehan, Bottum, Gross, Cahoon, Mallouk, Wang. *Angew. Chem. Int. Ed.* **2023**, *62*, e202215213

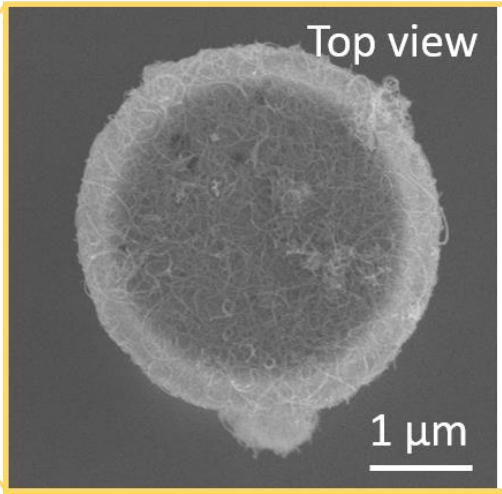
Silicon Pillar CoPc Photoelectrode

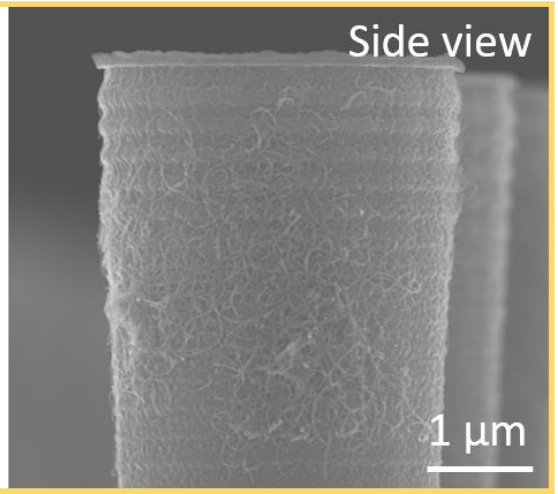




CNT/CoPc-NH_2







Manuscript in preparation

Silicon Pillar CoPc Photoelectrode

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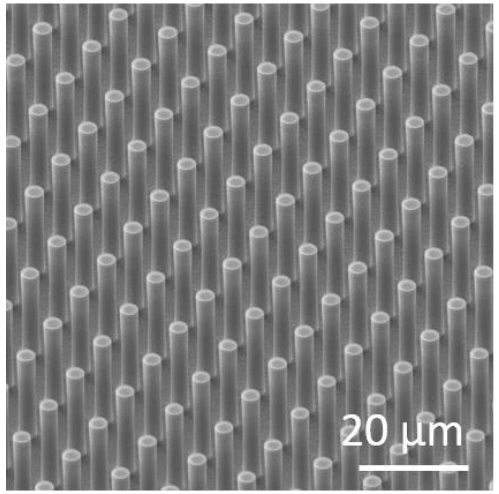
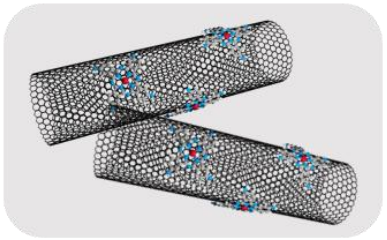
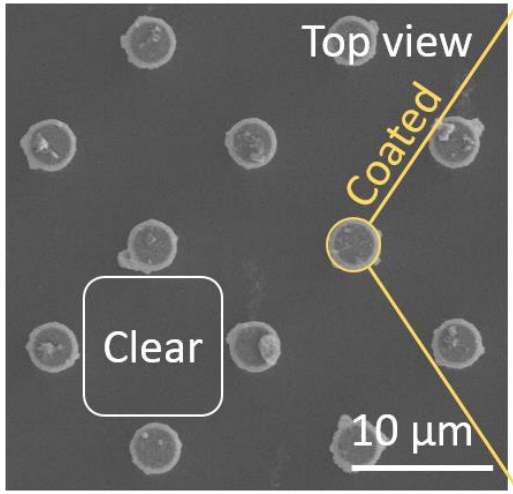
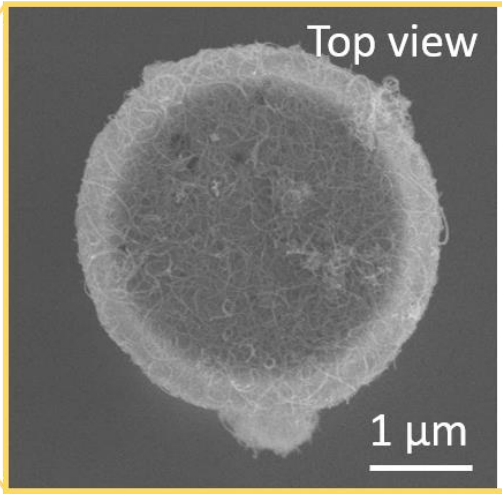
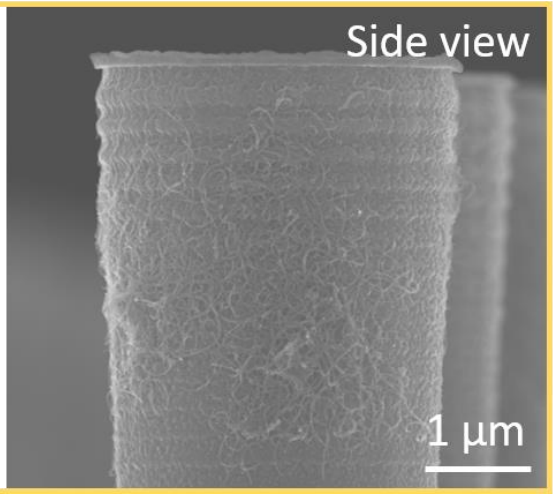


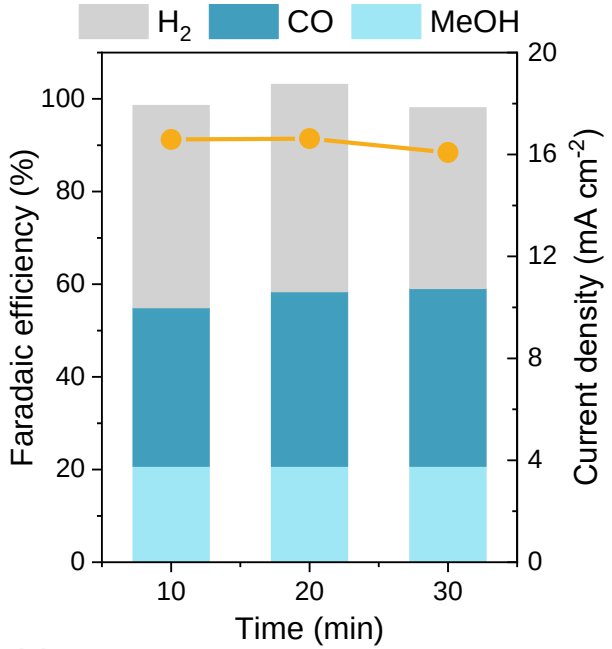


CNT/CoPc-NH_2









- FE: 8% → 20%
- j_{total}: 2.5 → 16 mA/cm^2
- Stable operation for 2 h

Manuscript in preparation

Acknowledgement to the Whole CHASE Team!

CHASE
Center for Hybrid Approaches in Solar Energy to Liquid Fuels

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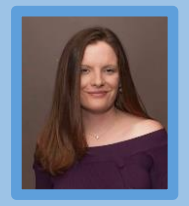
Director & IC

Jillian Dempsey
Deputy Director



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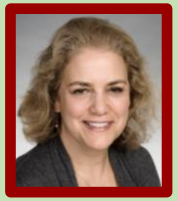
Thrust Co-Leaders



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Eric Stach
TC: SC Synth & Surf

Yosuke Kanai
TC: Theory/Modeling

Tim Lian
TC: Surface kinetics

IC = Institution Coordinator

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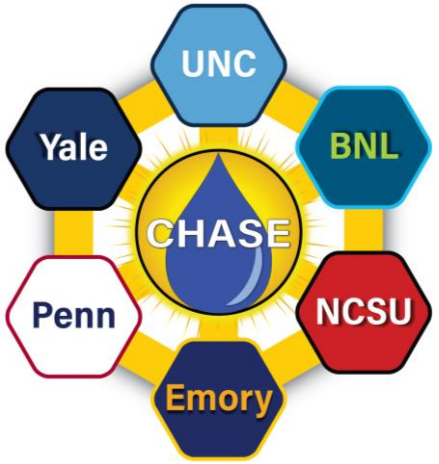
Holland – Yale
Concepcion – BNL
Goldberg – Penn
Castellano – NCSU
Lian – Emory



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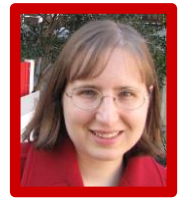

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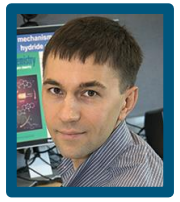

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Confidential Information

Center for Hybrid Approaches in Solar Energy to Liquid Fuels

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