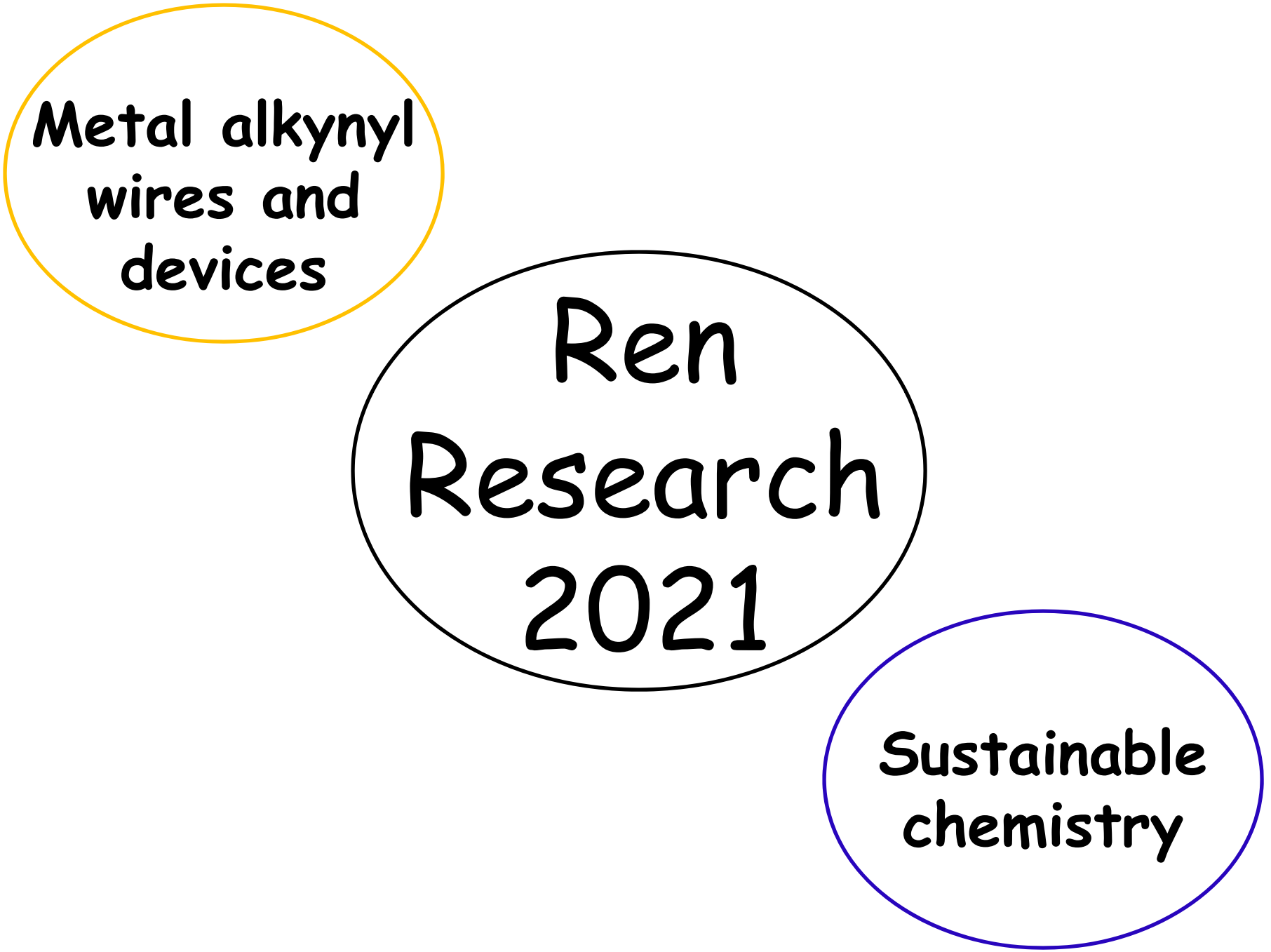
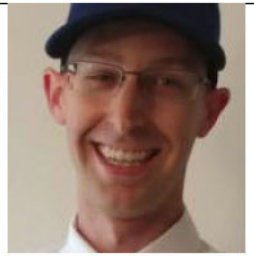
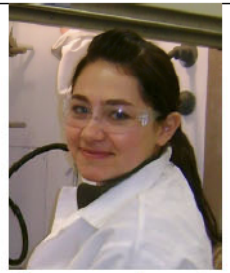
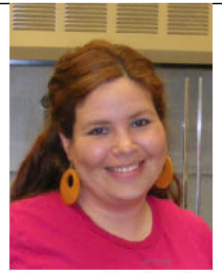
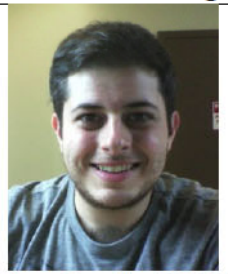
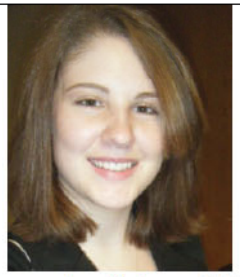
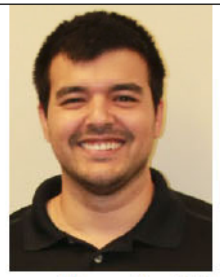

Metal alkynyl wires and devices
Ren Research 2021
Sustainable chemistry

State of the Ren Lab

- 4 graduate students
- Publications: 140+ since 2005
- Current Support (ca. $350k/yr)
  - NSF CHE-1764347: Sustainable Metal Alkynyl Chemistry
  - NSF CHE-1609151: Photo-electro CO_2 fixation
  - Discretional Funds
- Looking for 2 new students

Currently: Four graduate students, two undergrads and one progressive radical

Recent Ph.D.s (2010 -)

 Darryl Boyd, 2010 Scientist, Naval Res Lab	 Steven Cummings, 2012, Faculty, Howard Univ	 Will Forrest, 2012 Scientist, Merck	 Julia Savchenko, 2013; Scientist, Urban Mining	 Leslie Villallobos, 2013; Faculty, Broward Coll.
 Yang Zhang, 2013 Scientist, Saint-Gobain	 Zhi Cao, 2014 Faculty, Chin. Acad Sci.	 Dylan Thompson, 2014; Faculty, Concordia Univ	 Tim Cook, 2016 Faculty, Wabash Coll.	 Sarah Robey, 2017 Sr. Engineer, Intel
 Eileen Judkins, 2017 Analyst, Northrop Grumman	 Sean Natoli, 2017 Scientist; Proctor & Gamble	 Susie Banziger, 2019 Scientist, Corteva	 Adharsh Raghavan, 2020, Postdoc, Univ Pennsylvania	

Spotlights on Recent Ph.D.s

Darryl Boyd

2016 – NOBCChE Ferguson Young Scientist Award

2018 ACS Talented 12

2020 Purdue Distinguished Early Career Alumni

Sean Natoli

2018 Burroughs Wellcome Fund Award

2019 CAS Future Leaders

Susie Banziger

2016 Arthur Kelly Teaching Award

2018 Cagiantas Fellowship

Area I: Sustainable Organometallics as (Opto)-Electronic Materials

- Monodisperse oligo(Ru_2-alkynyl) as electronic wires
- Metal-cyclam acetylide compounds as photonic wires
- Active materials for molecular devices
- Photoactive dendrimers & bio-markers

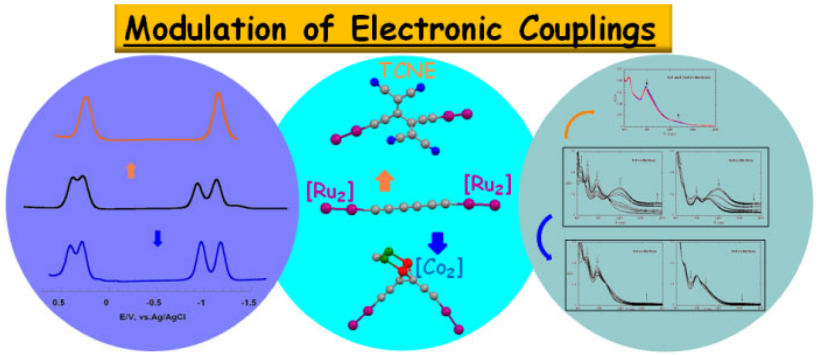
Ashley Schumann

Lyndsy Miller

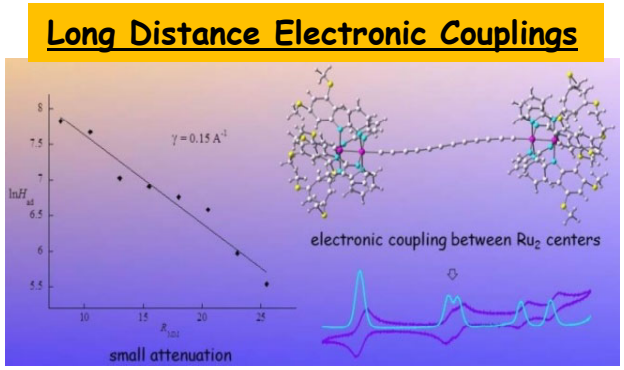
Reese Clendening

Leo Rodriguez

Area I: Selected (old) Examples



Successful modulation of electronic coupling within Ru_2-C_6-Ru_2 systems through insertion of organic and organometallic fragments. (*JACS*, **2011**, *133*, 15094)



Electronic couplings within Ru_2-C_{2m}-Ru_2 systems have been determined using voltammetry and spectroelectrochemistry, and a small attenuation constant (γ) determined. (*JACS*, **2014**, *136*, 12174)

Other readings

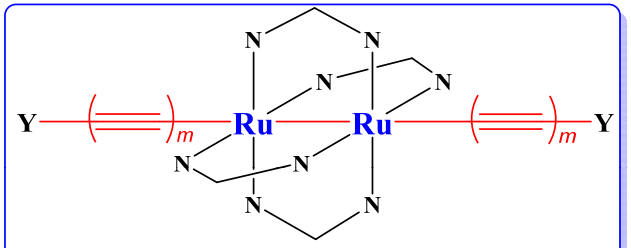
(1) Ren, T., *Organometallics* ***2005,*** *24,* 4854.

(2) Xu, G.-L.; Crutchley, R. J.; DeRosa, M. C.; Pan, Q.-J.; Zhang, H.-X.; Wang, X.; Ren, T., *J. Am. Chem. Soc.* ***2005****, 127*, 13354.

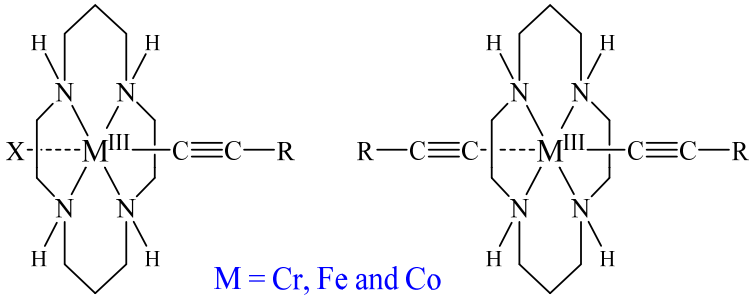
(3) Mahapatro, A. K.; Ying, J.; Ren, T.; Janes, D. B., *Nano Lett* ***2008****, 8,* 2131**.**

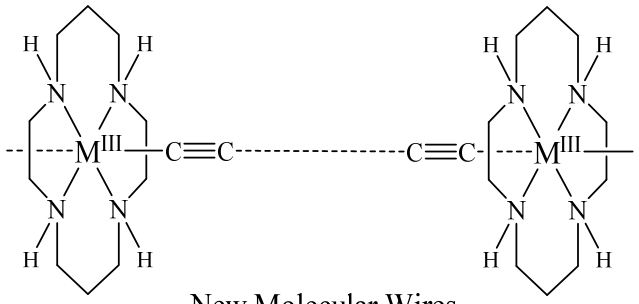
(4) Ying, J.-W.; Liu, I. P.-C.; Xi, B.; Song, Y.; Campana, C.; Zuo, J.-L.; Ren, T., *Angew. Chem. Int. Ed.* ***2010,*** *49,* 954**.**

Area I, Present: Ru to 3d Metals

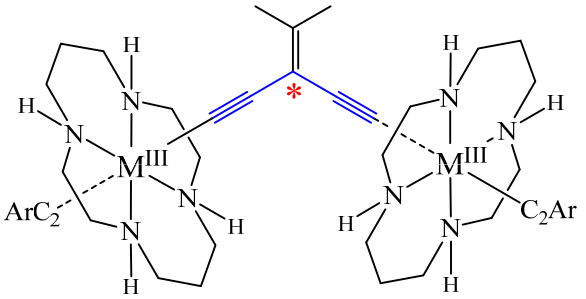


We have had fun with Ruthenium for 20 yrs; but Ru is not one of more abundant metals





New Molecular Wires

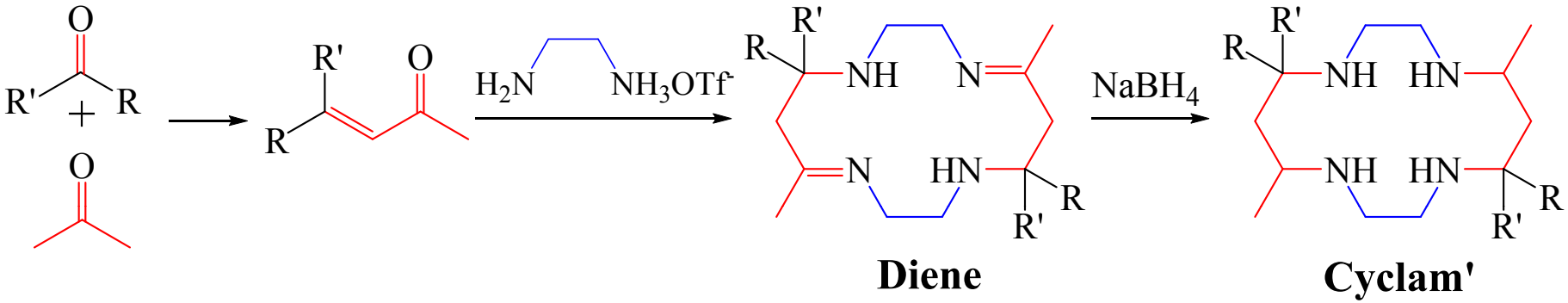


Probing *cross*-conjugation

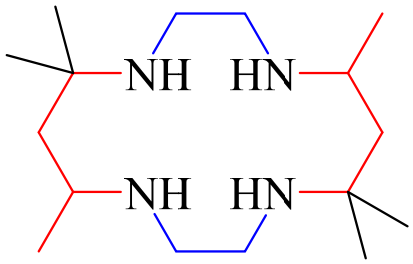
- NSF CHE-1764347: Sustainable Metal Alkynyl Chemistry

Sustainable Ligand Chemistry

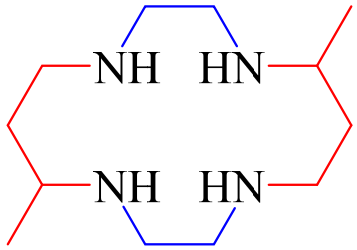
(*C*-substituted cyclam - inexpensive)



Diene **Cyclam'**



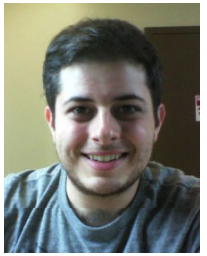
HMC



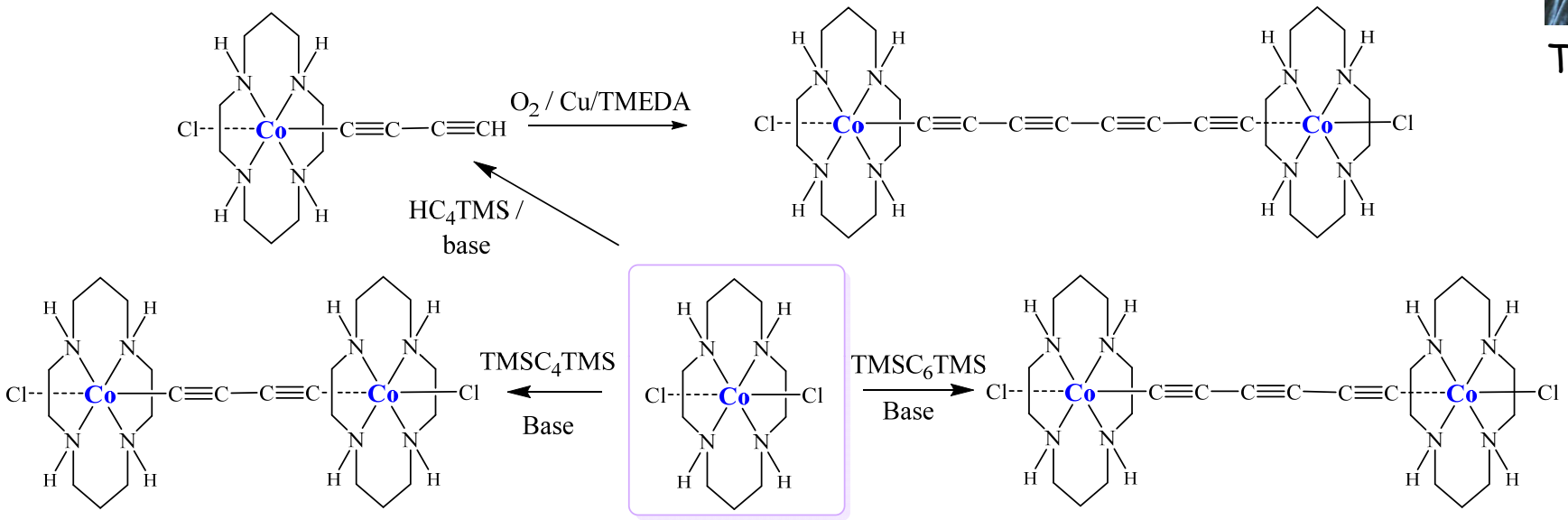
DMC

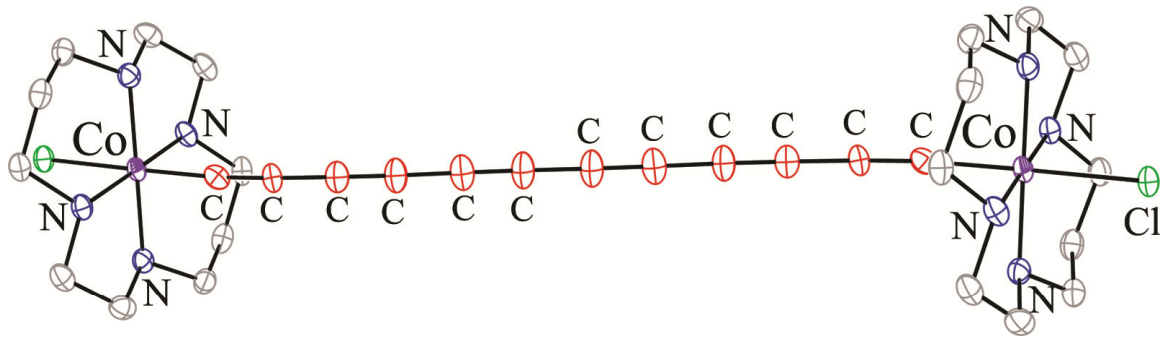
Curtis, *Supramol. Chem.* 2012, *24*, 439-447

Recent examples: $[Co^{III}(cyclam)]_2(\mu\text{-}C_{2n})$



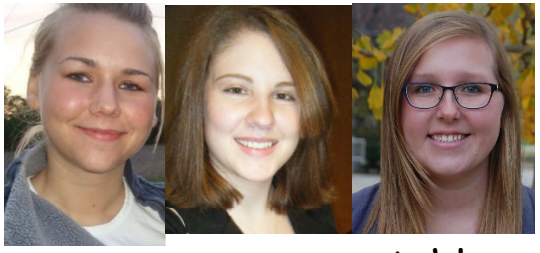
Tim Cook

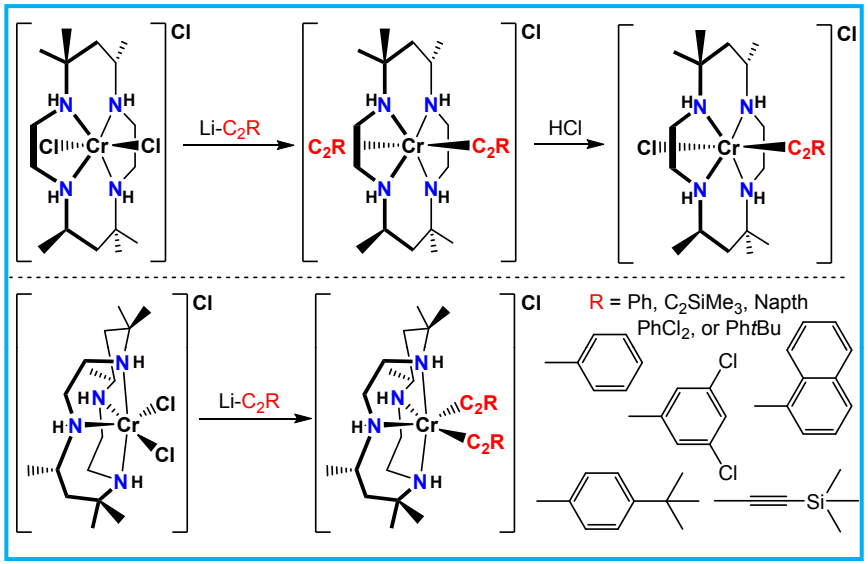


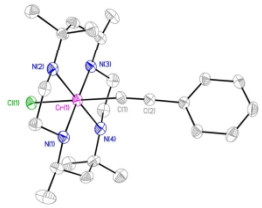


Organometallics **2015**, *34*, 686; **2016**, *35*, 1329

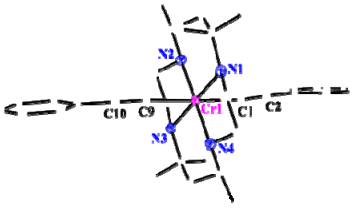
Cr^{III}(HMC) & Cr^{III}(DMC) Complexes



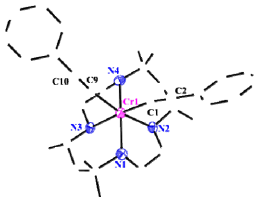




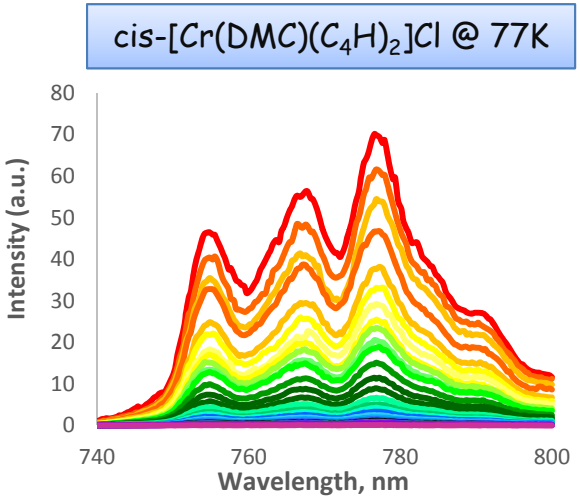
trans-[Cr(HMC)(C_2Ph)Cl]$^+$



trans-[Cr(HMC)(C_2Ph)$_2$]$^+$



cis-[Cr(HMC)(C_2Ph)$_2$]$^+$



- In contrast to cyclam complexes, *cis-/trans*-[Cr(HMC)Cl_2]$^+$ complexes readily convert to the corresponding bis-alkynyls while retaining their configuration
- Cr^{III} bis-alkynyls display vibronic structuring in their absorption spectra and are phosphorescent from the $^2T_{1g}$ excited state
- Bis-alkynyl complexes can undergo acid degradation to form mono-alkynyl complexes – an important intermediate in the synthesis of dissymmetric bis-alkynyls

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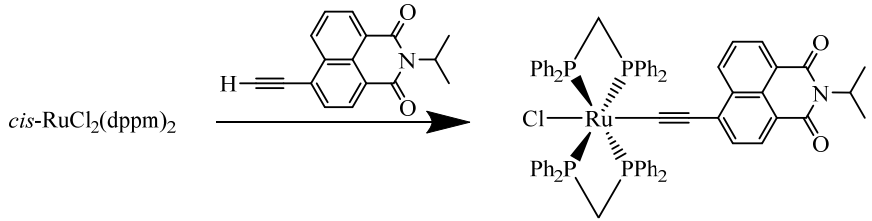
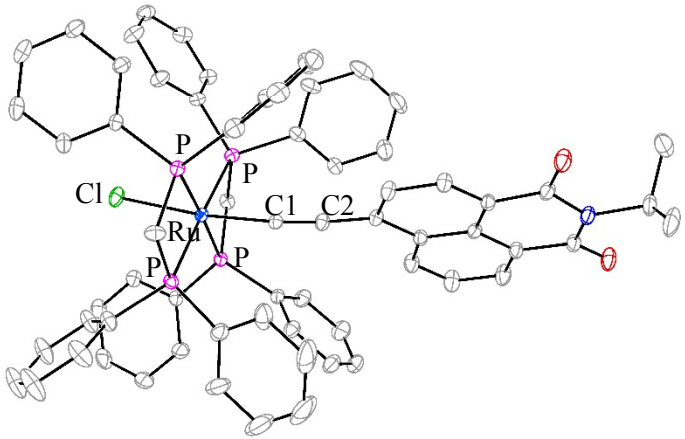
Inorg. Chem. **2016**, *55*, 8736; **2018**, *57*, 2249; *Eur. J. Inorg. Chem.*, **2017**, 4068

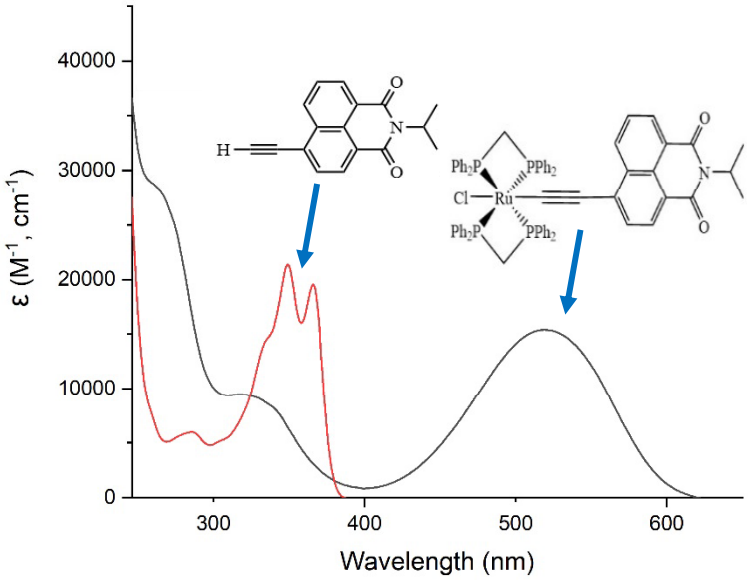
Area I *Return of the Padawan* (Ru)

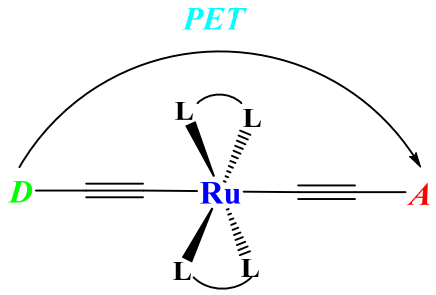
Lyndsy





M: Ru-C1: 1.988 Å; Ru-Cl: 2.465 Å; C1-C2: 1.214 Å



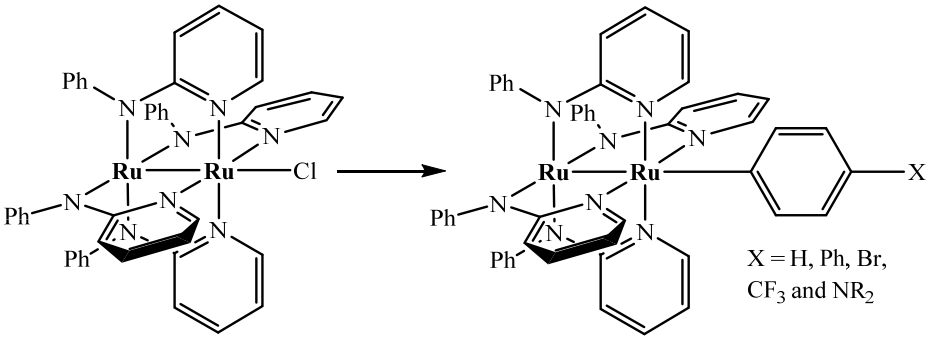


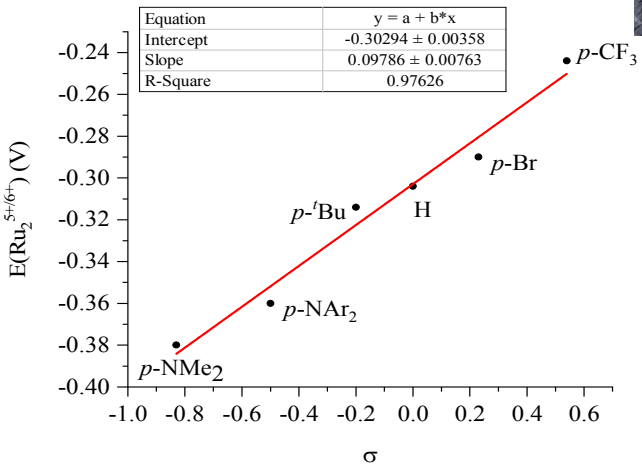
Future: Photo-induced electron transfer dynamics

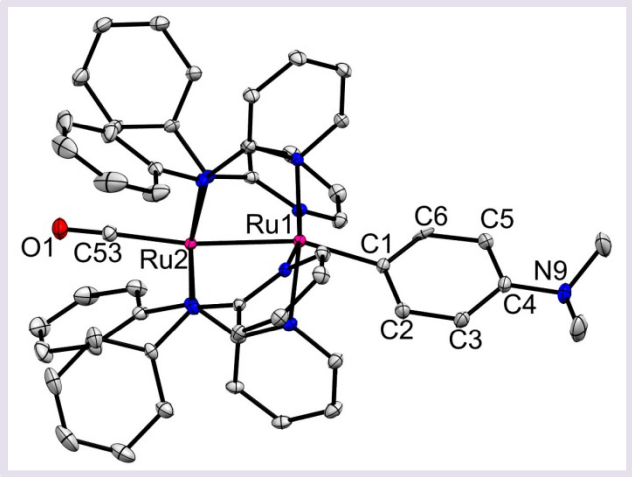
- MLCT dominates Vis spectrum;
- *d-d* band not detected
- *D-B-A* under construction

Unpublished Results

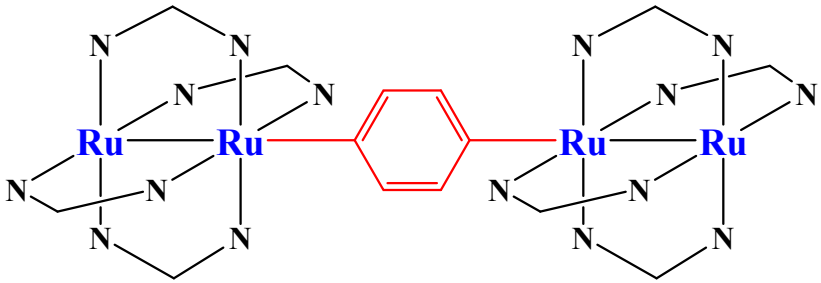
Area I Future – *Return of the Jedi* (Ru_2)







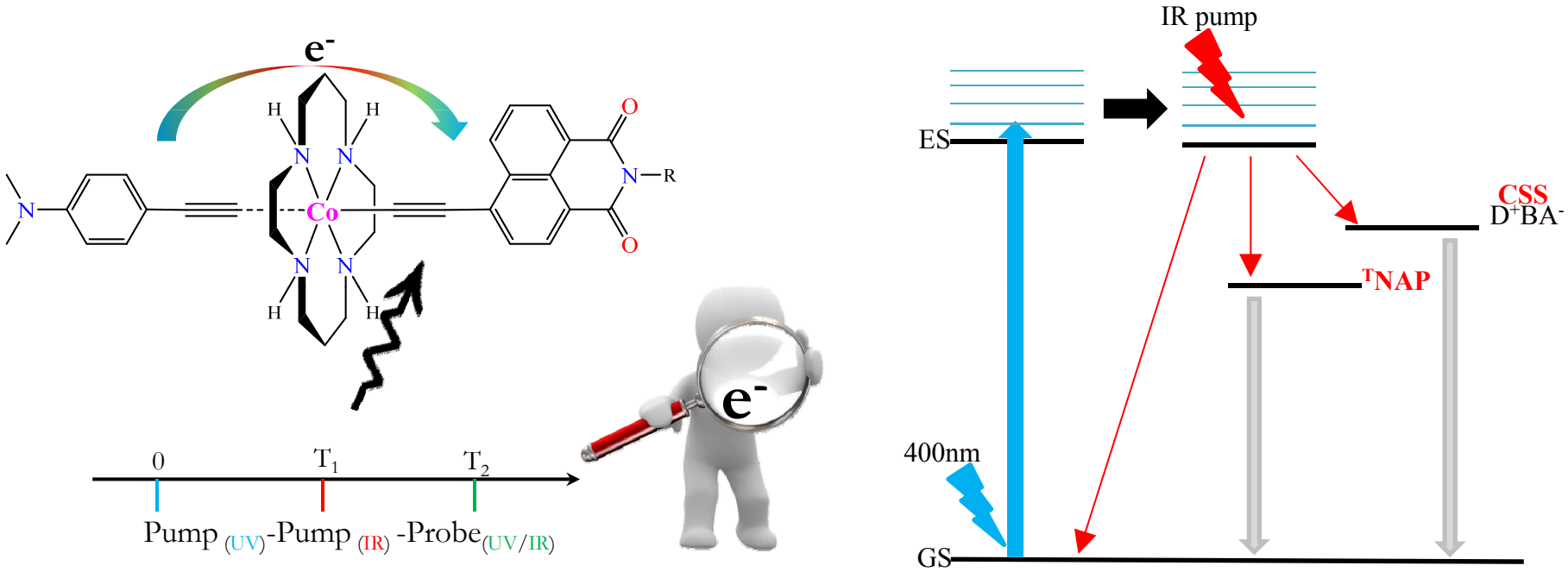
Unique CO complex on Ru2



Challenge: Can we bridge two Ru2 units and explore the electronic coupling mediated by the phenylene?

Inorg. Chem. **2019**, *58*, 2618; **2020**, *59*, 8663; *Orgnometallics*, **2019**, *38*, 3888

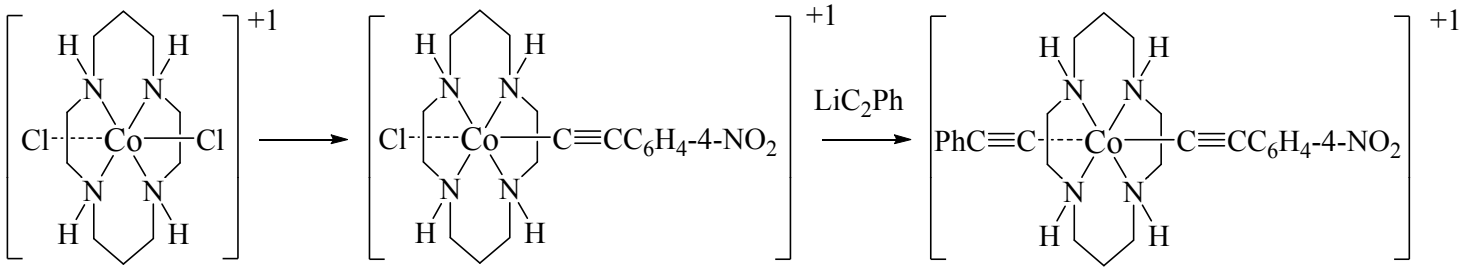
Area I Current – Donor-Bridge-Acceptor (D-B-A) and Photoinduced Electron Transfer



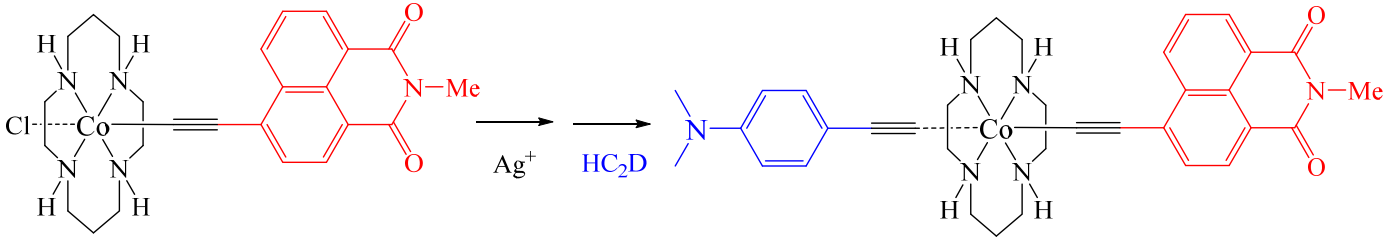
- Perturbation of vibrationally hot excited state (ES) results in dynamic decay to the ground state (GS)
- Likely decay pathway(s) through NAP triplet (^{T}NAP) and charge separated state (CSS)

Area I Donor-Bridge-Acceptor based on Co(Cyclam)

Susie

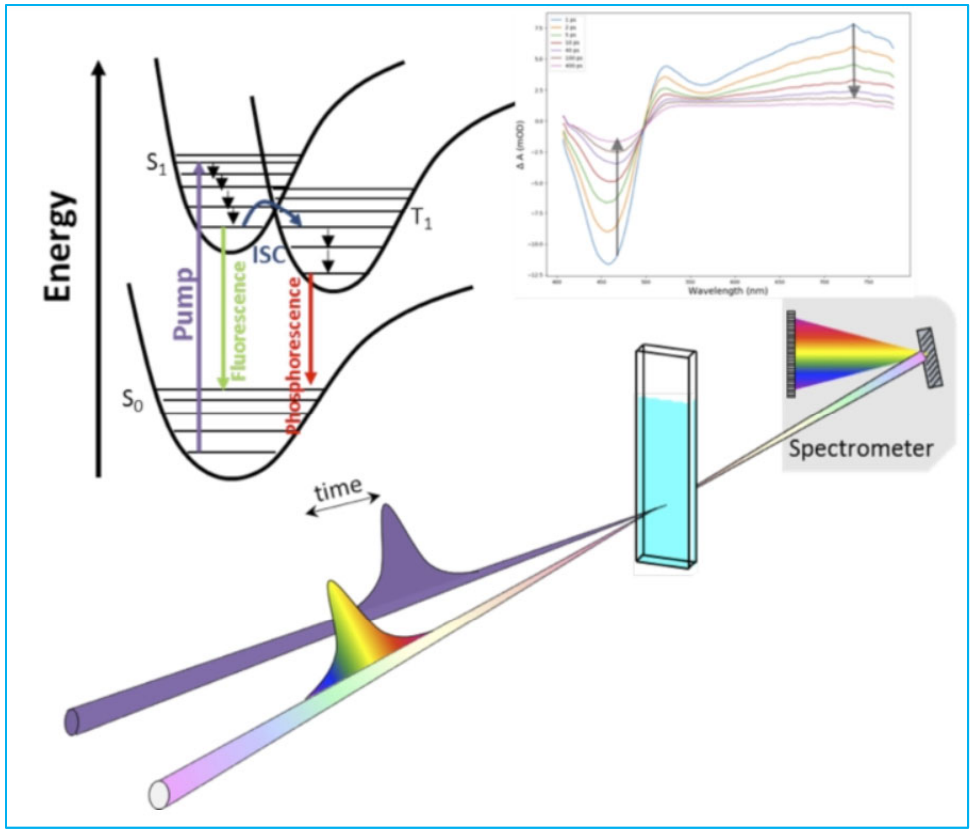


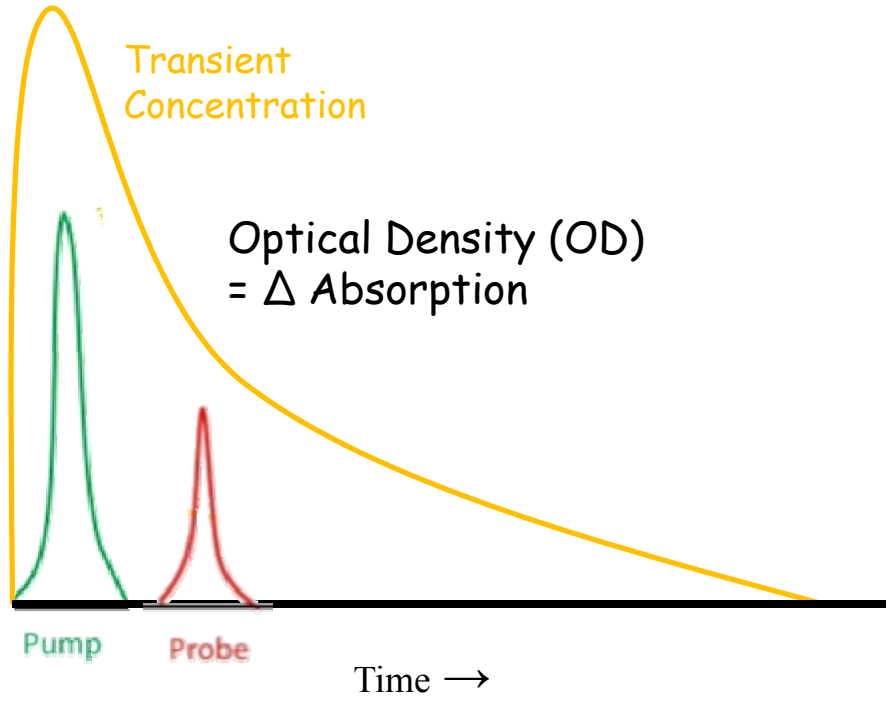
high yield; no by-products



Inorg. Chem. **2019**, *58*, 15487

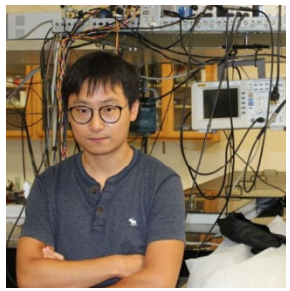
Transient Absorption (TA) Spectroscopy





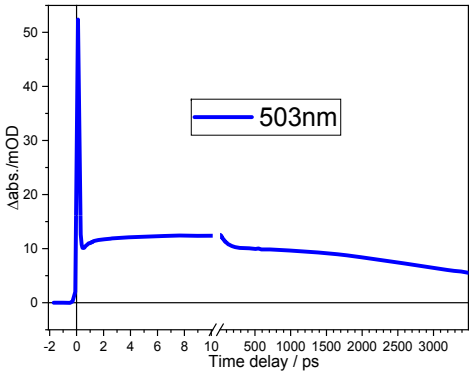
https://www.newport.com/f/transient-absorption-spectrometer

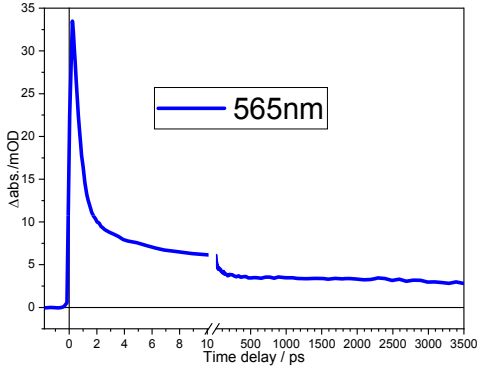
Prof. Igor Rubstov

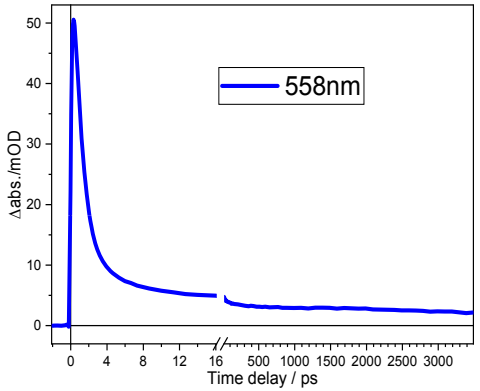


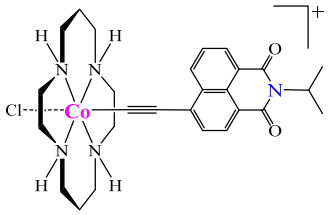
Xiao Li

Transient kinetics: B-A and D-B-A

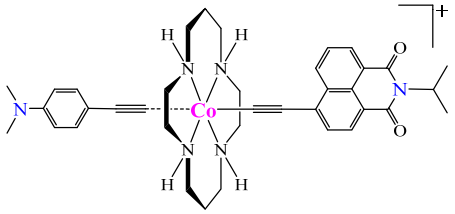




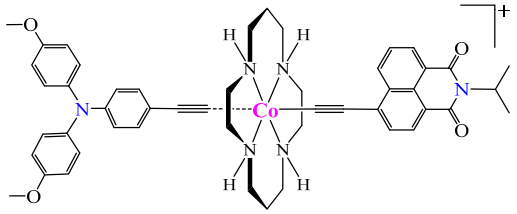




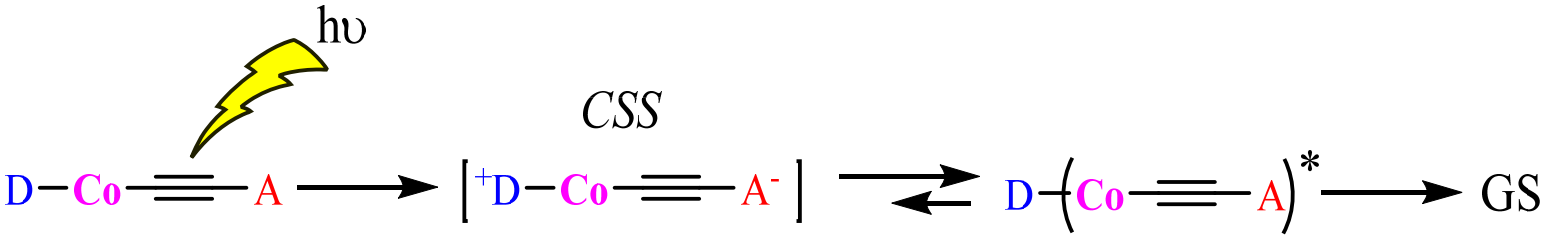
$[1]^+$



$[2a]^+$

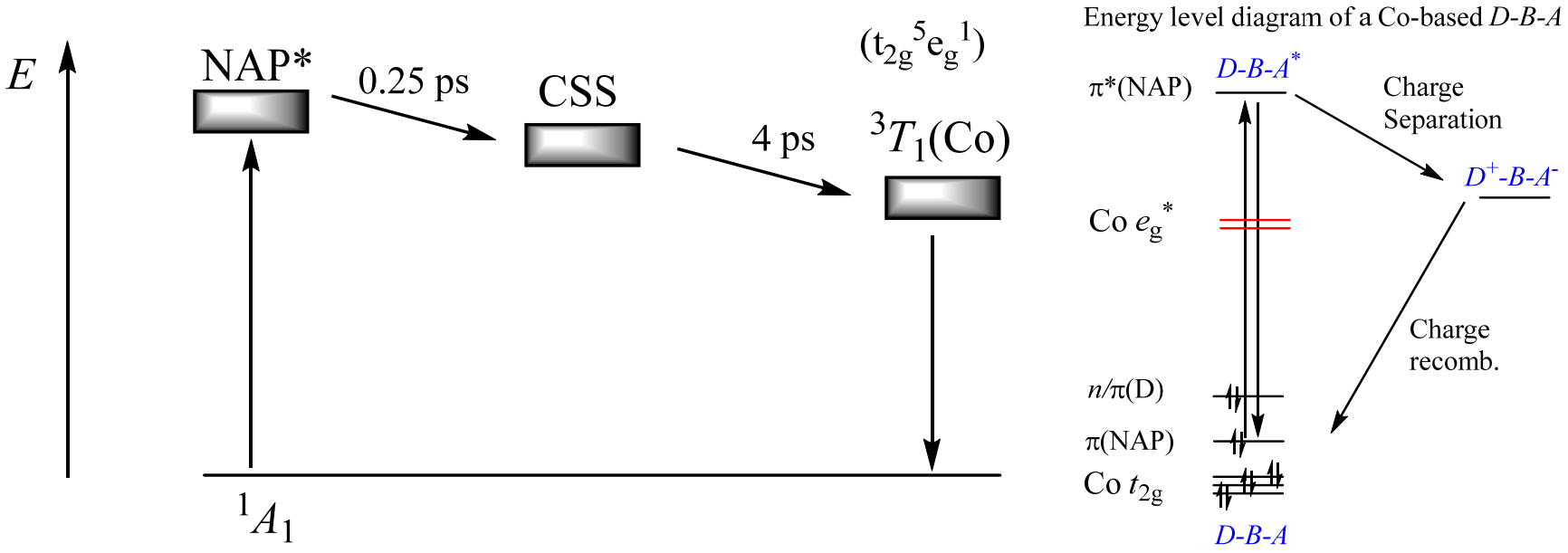


$[2d]^+$



- Short event observed that decays rapidly to a long-lived state, observed in TA
- Long lived state (^{3}Co) lifetime: **1 (5ns) < 2d (7ns) < 2a (10ns)**

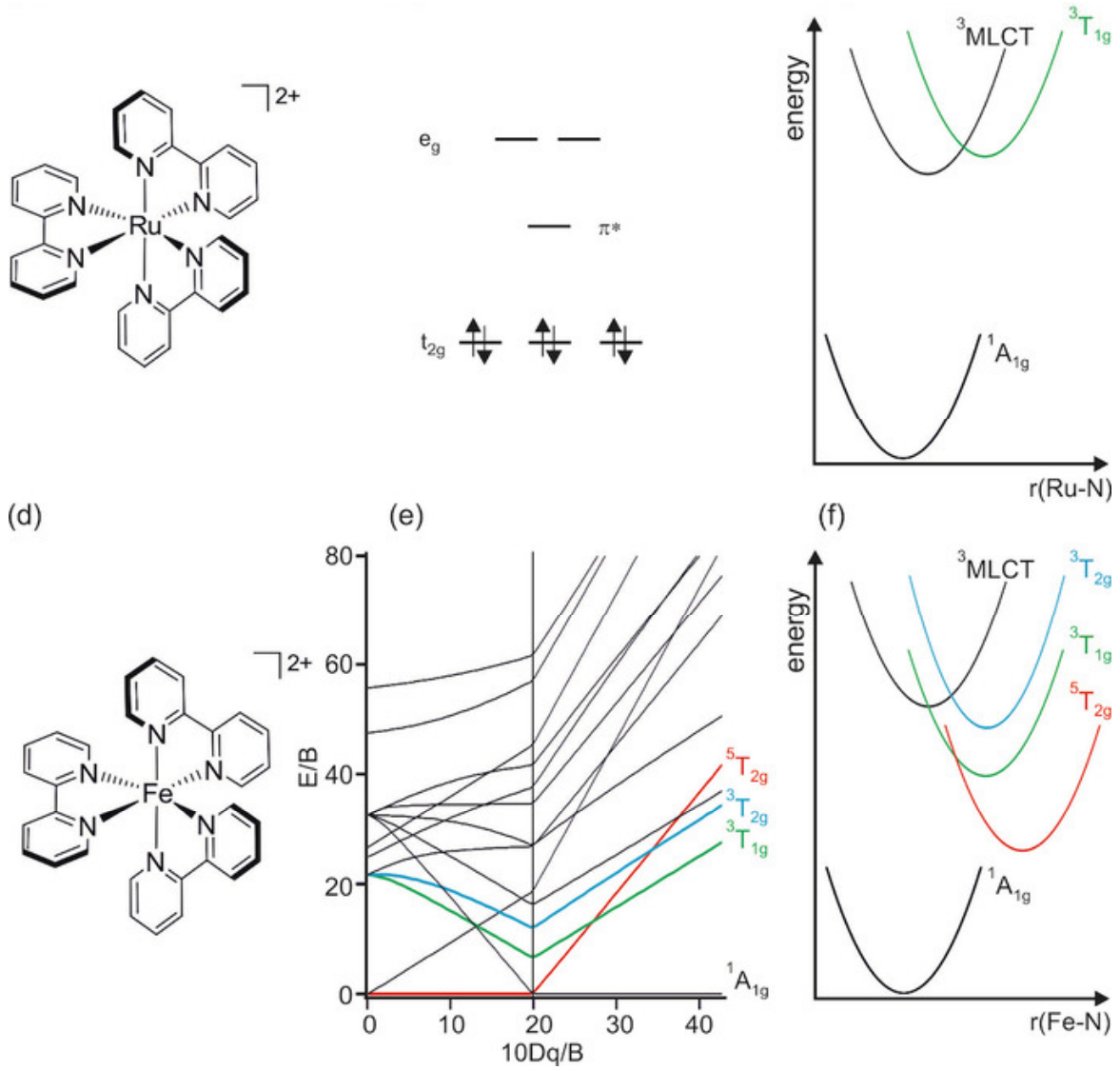
Transient kinetics BIG PICTURE



- Charge separated states are possible with stronger donor
  - Lifetime too short for vibrational pumping
- Long lived state is the low lying LF state at Co (deactivating state)
- Pushing up $^3T_1$ with stronger ligands to favor CSS?
- Metal-free *D-B-A* dyads?

Inorg. Chem. **2019**, *58*, 15487

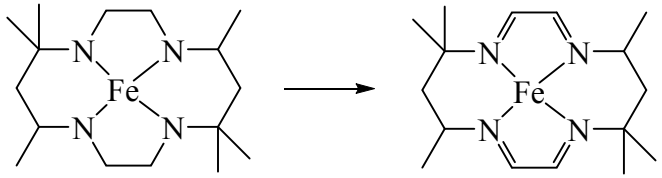
LF State – Public Enemy (of 3*d* Chromophore)



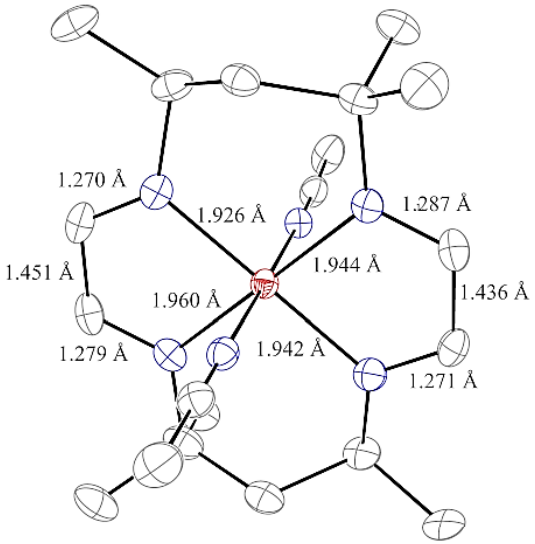
Wenger, *Chem. Eur. J.* **2019**, *25*, 6043-6052

A New Hope: Tetraimine - LF State(s) Lifted

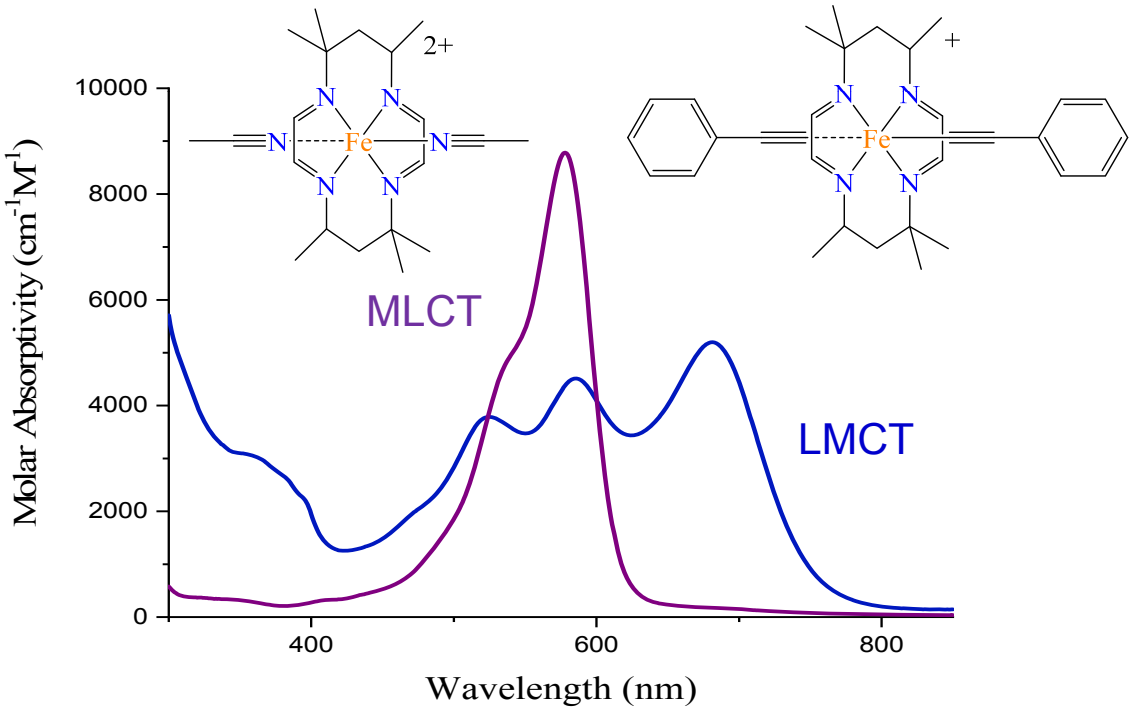

Reese



Fe^{III}(HMC) Fe^{II}(HMTI)



Ave. Fe-N (HMC): 2.11 Å
Ave. Fe-N (HMTI): 1.94 Å

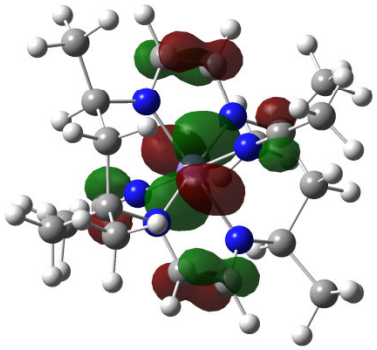


Unpublished Results

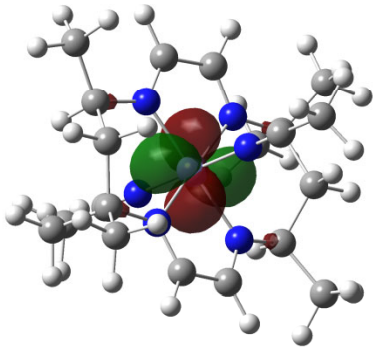
Raised LF State(s) – DFT Proof

Reece

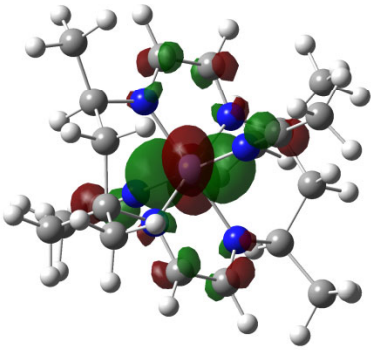
HOMO-2
(d_{xy})

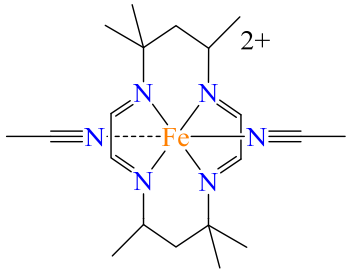


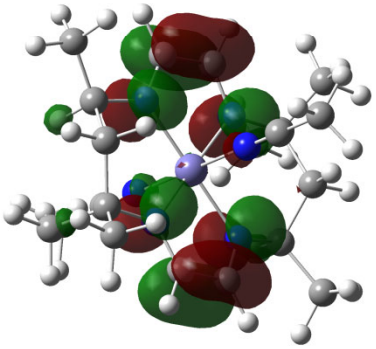
HOMO-1
(d_{xz})



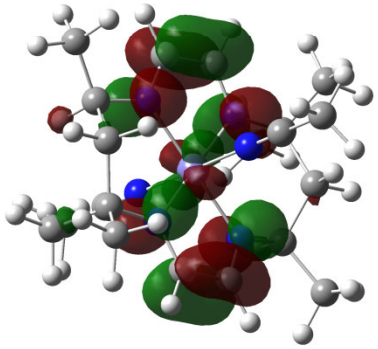
HOMO
(d_{yz})



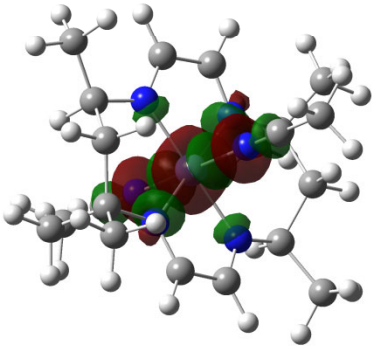




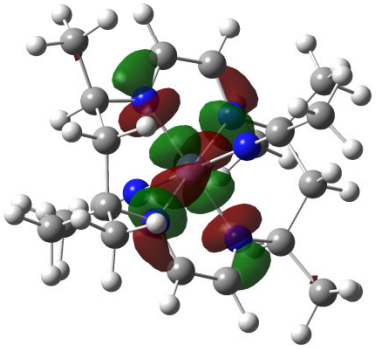
LUMO
(π*(C=N))



LUMO+1
(π*(C=N))



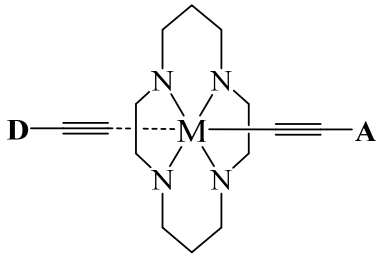
LUMO+2
(d_{z2})



LUMO+3
(d_{x2-y2})

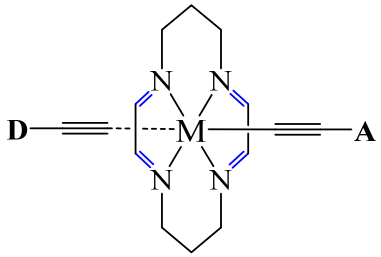
Unpublished Results

Area I Future: 3*d* Complexes of [14]-tetraene-N4



D-B-A dyad based on *cyclam*

NSF CHE-1764347



D-B-A dyad based on [14]-tetraene-N_4

Future NSF project

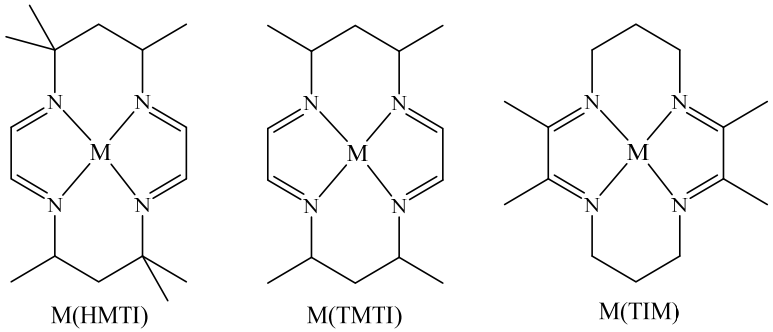


Chart 2. Metal complexes tetra-imino macrocycles; M = $Fe^{II/III}$ and Co^{III}

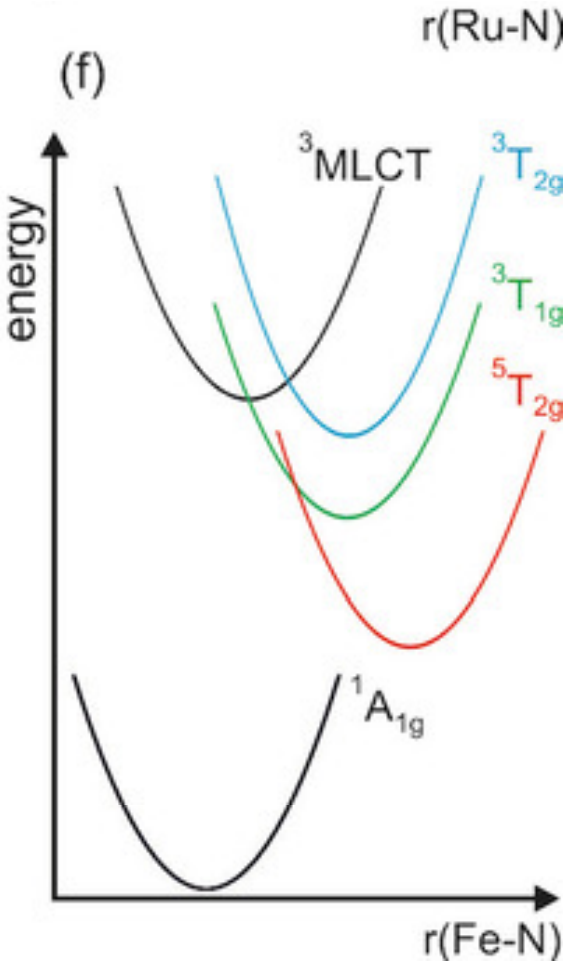
Goals

- Elucidate molecular and electronic structures of novel complexes
- Probing the dynamics of metal-ligand charge transfer (MLCT) and photo-induced electron (PET) states using fs transient spectroscopy and fs XANES spectroscopy
- In depth understanding of excited state electronic structures using CAS-SCF method
- Develop single electron transfer (SET) catalysts based on [14]-tetraene-N4 complexes for selective hydrogenation, CO2 reduction…

Area I Future: Mapping the Excited States

Prof. Josh Vura-Weis
UIUC

Determine the geometries of *the excited states* using the femto-second XANES (X-ray absorption near edge structure) technique.



Prof. Bess Vlaisavljevich
U. South Dakota

Calculate the excited state *potential surfaces* using the complete active space perturbation theory method (CAS PT2)

Area II: CO2 Fixation (NSF CHE-1609151)

- Silica supported catalysts for water oxidation
- **Catalysts for CO_2 reduction and fixations**
- **Catalysis with non-precious metals (Fe, Cu, Co, and Ni)**

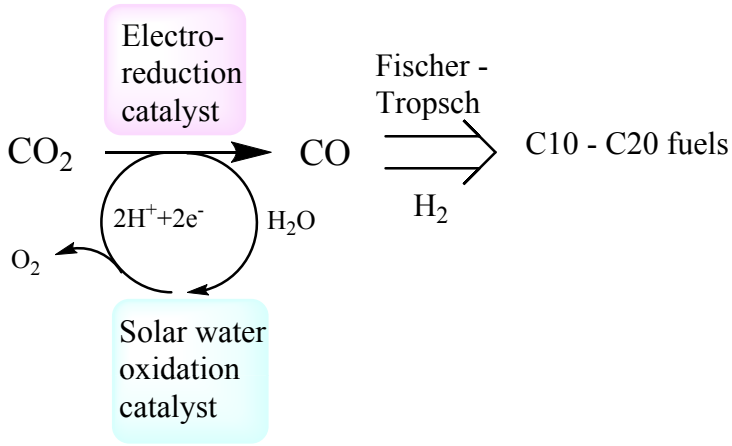
Ashley

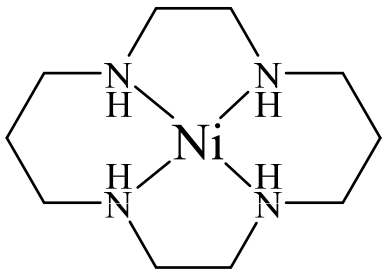
Leo Rodriguez

CO_2 Fixation – A Tera-ton Challenge

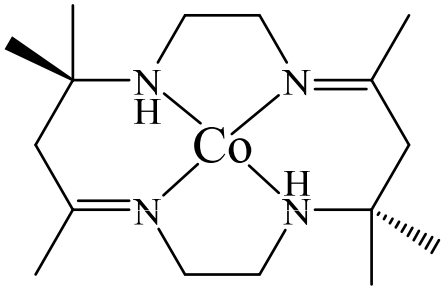
Chart 1

Reaction			E^o/V (vs NHE)
$CO_2 + e^-$	→	CO_2^-	**-1.9**
$CO_2 + 2H^+ + 2e^-$	→	HCO_2H	-0.61
$CO_2 + 2H^+ + 2e^-$	→	$CO + H_2O$	**-0.53**
$CO_2 + 4H^+ + 4e^-$	→	$HCHO + H_2O$	-0.20
$CO_2 + 4H^+ + 4e^-$	→	$C + 2H_2O$	-0.48
$CO_2 + 6H^+ + 6e^-$	→	$CH_3OH + H_2O$	-0.38
$CO_2 + 8H^+ + 6e^-$	→	$CH_4 + H_2O$	-0.24





Ni^{2+}(cyclam)



Co^{2+}(HMD)

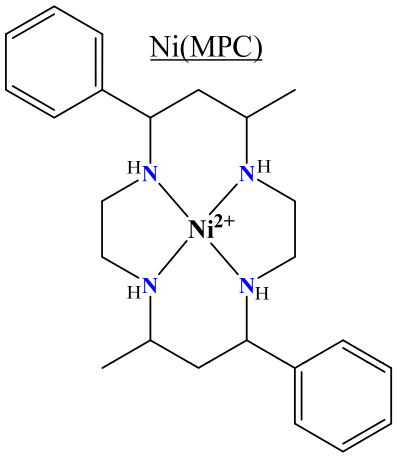
Two of the best electrocatalysts for CO_2 reduction

Improving a Functional Wheel: Cyclam'

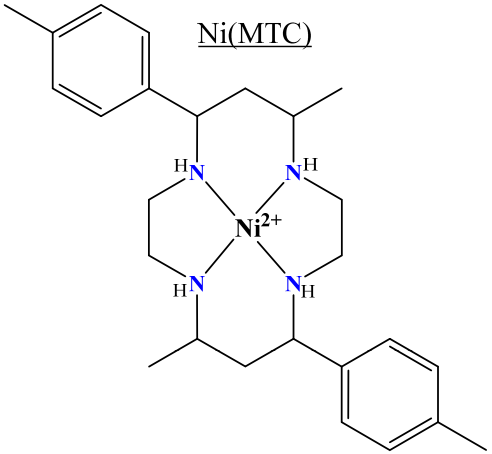

Dr. Cook
Wabash Coll


Dr. Robey
Intel

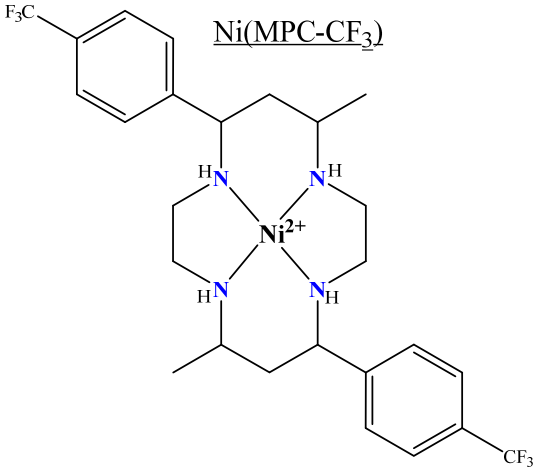
Ni(MPC)



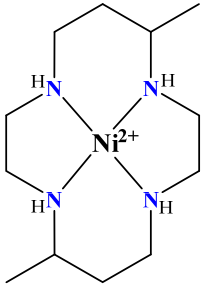
Ni(MTC)

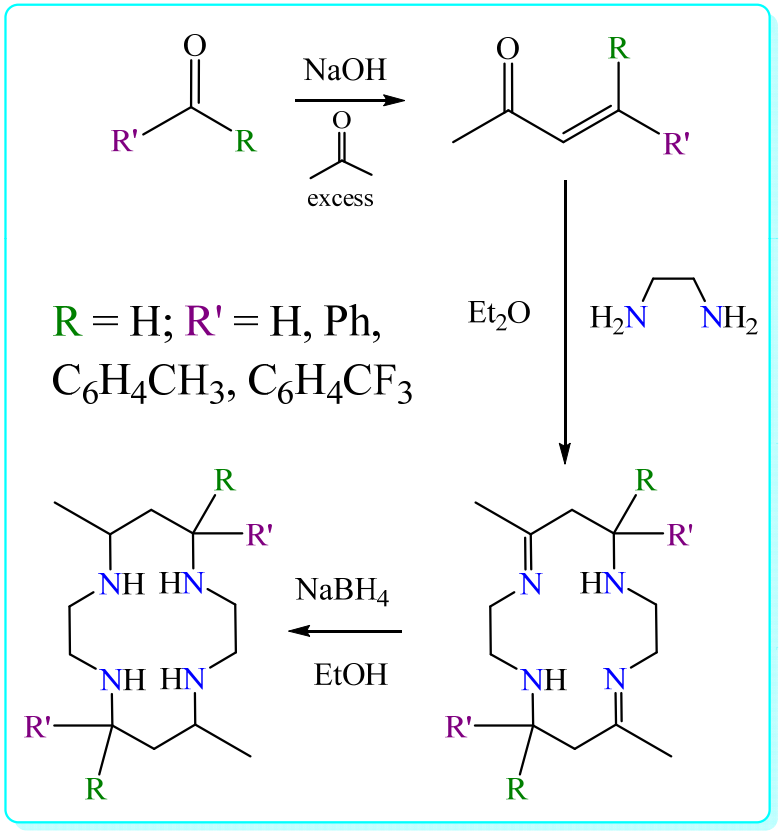


Ni(MPC-CF_3)



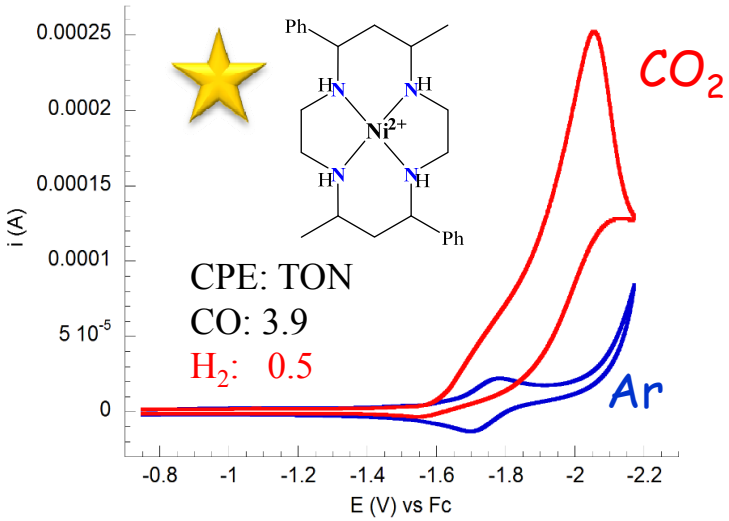
Ni(DMC)

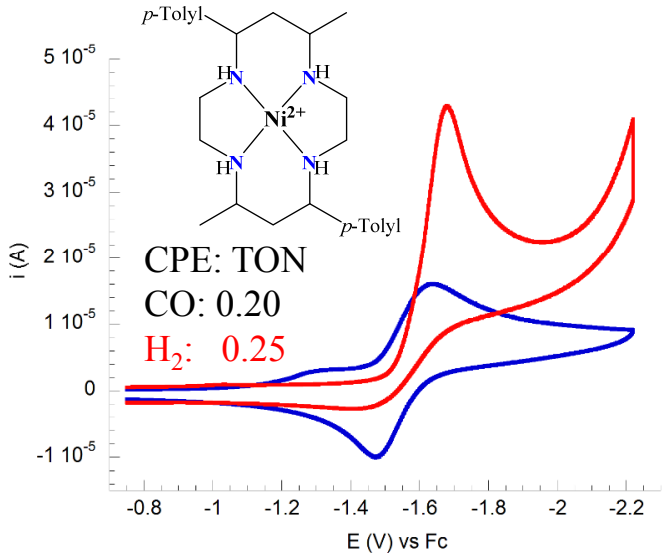




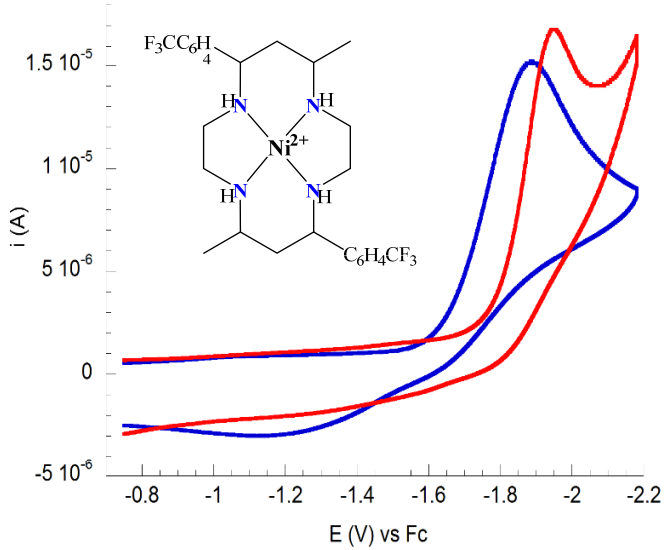
ACS Omega 2017, *2*, 3966-3976

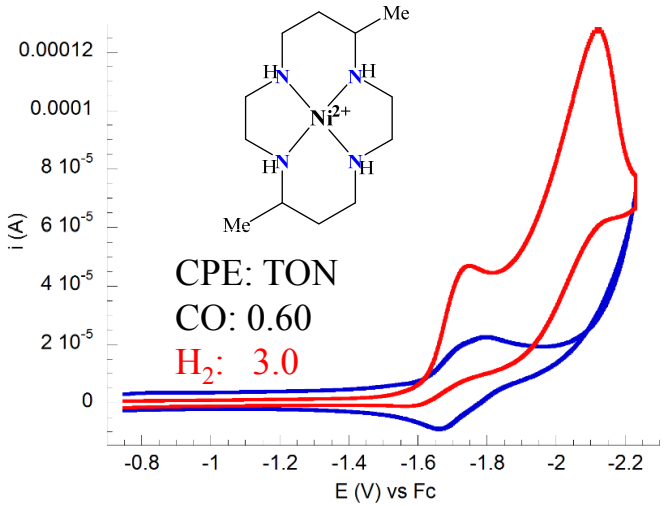
Cyclic Voltammetry & Controlled Potential Electrolysis Studies





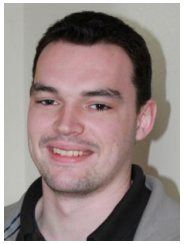
[Ni(cyclam)]Cl_2
CPE: TON
CO: 0.55
H_2: 1.10



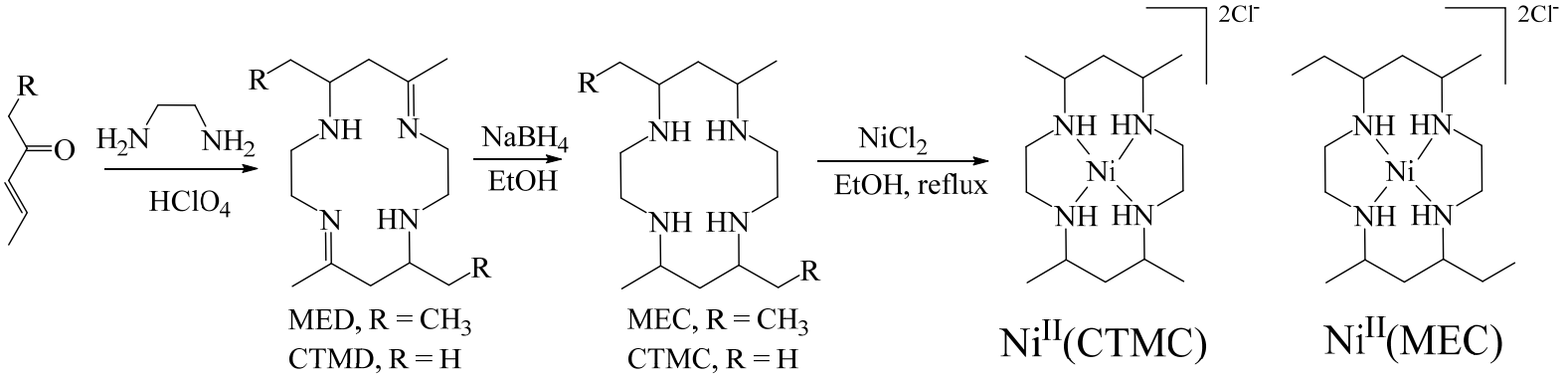


Conditions: MeCN / H_2O (4:1); CV scan rate: 100 mV/s; CPE time: 30 min

Current: Further Improvement of Ni(cyclam')



Brandon

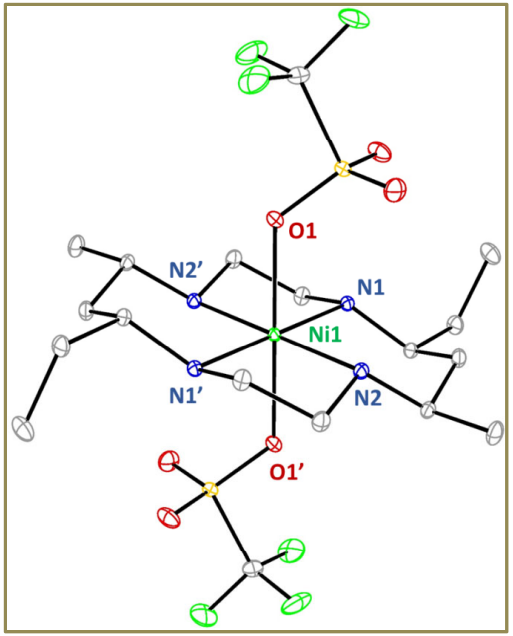


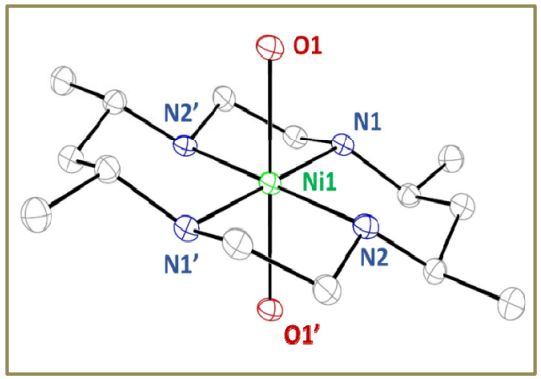
MED, R = CH_3
CTMD, R = H

MEC, R = CH_3
CTMC, R = H

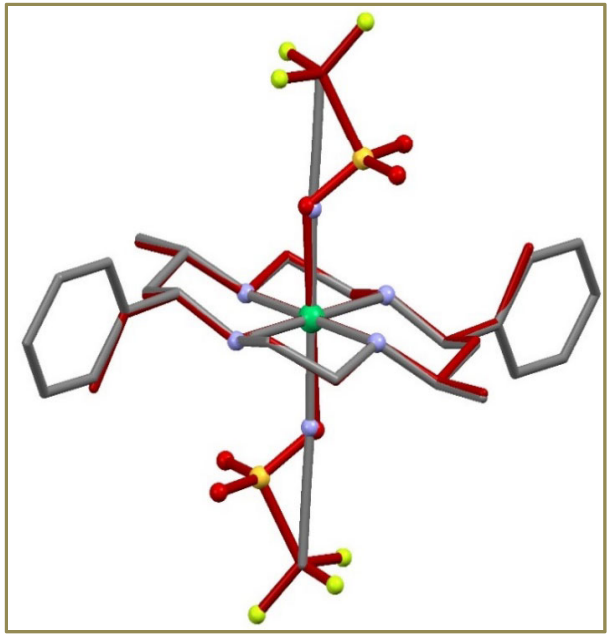
Ni^{II}(CTMC)

Ni^{II}(MEC)



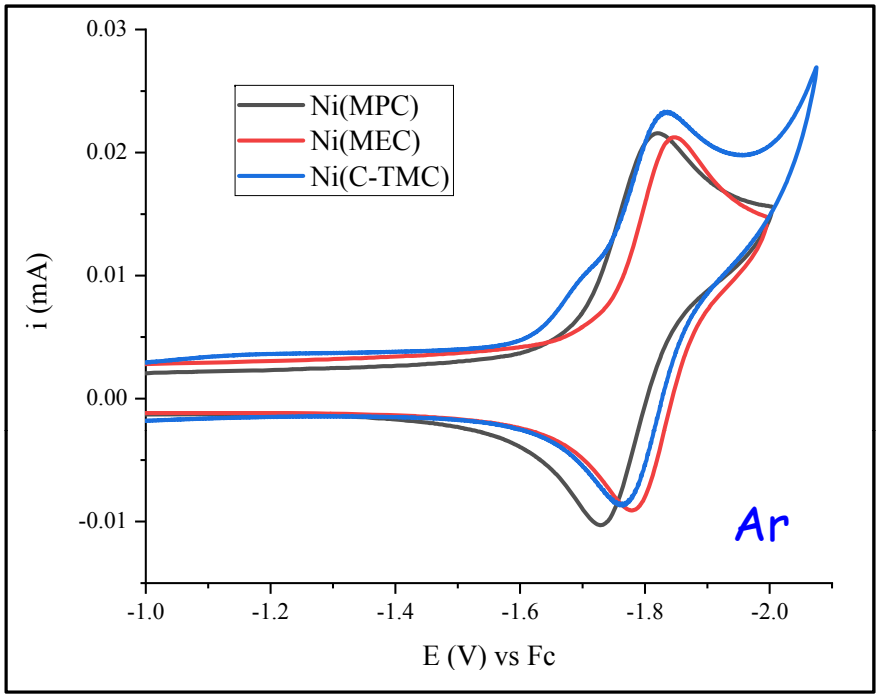


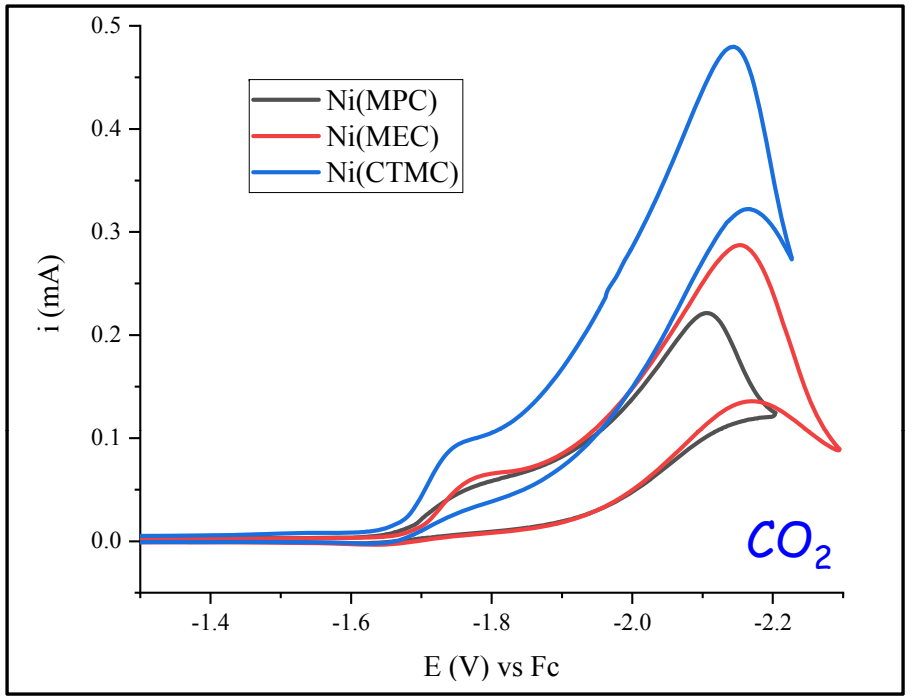
Overlay of Ni(MPC) and Ni(MEC)



Eur. J. Inorg. Chem. 2019, 2065-2070

Performance of Ni(cyclam')





Conditions: MeCN / H_2O (4:1); CV scan rate: 100 mV/s

CPE, -1.72 V, 30 min	TON, CO	TON, H_2	FE, CO (%)	FE, H_2 (%)
$Ni(MEC)^{2+}$	7.3±0.4	2.1±0.9	57±2	16±7
$Ni(CTMC)^{2+}$	7.7±0.3	1.7±0.7	66±1	15±6
$Ni(MPC)^{2+}$	5.5	1.0	52	10
$Ni(cyclam)^{2+}$	2.2	2.4	35	38

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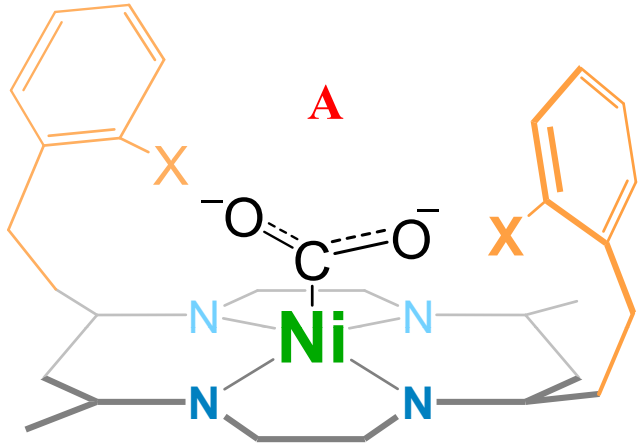
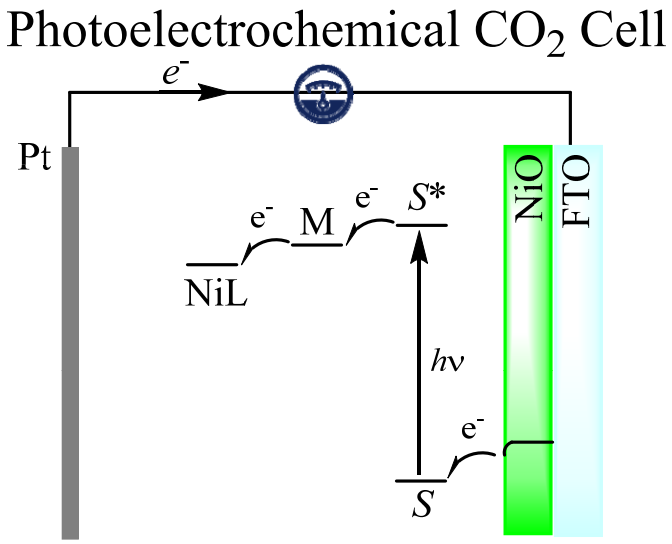
Challenges: Chemical Selectivities & Solar Driven Reduction of CO_2



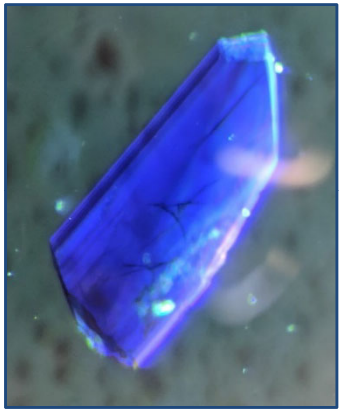


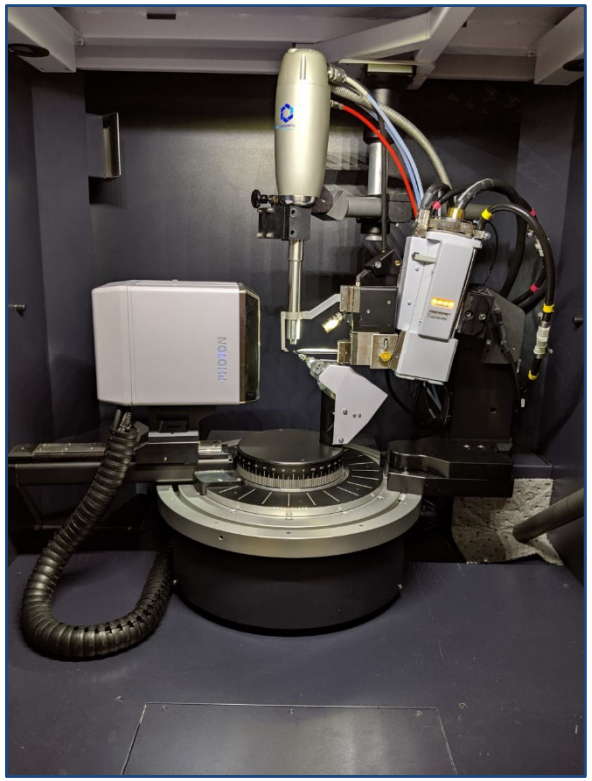
Goals

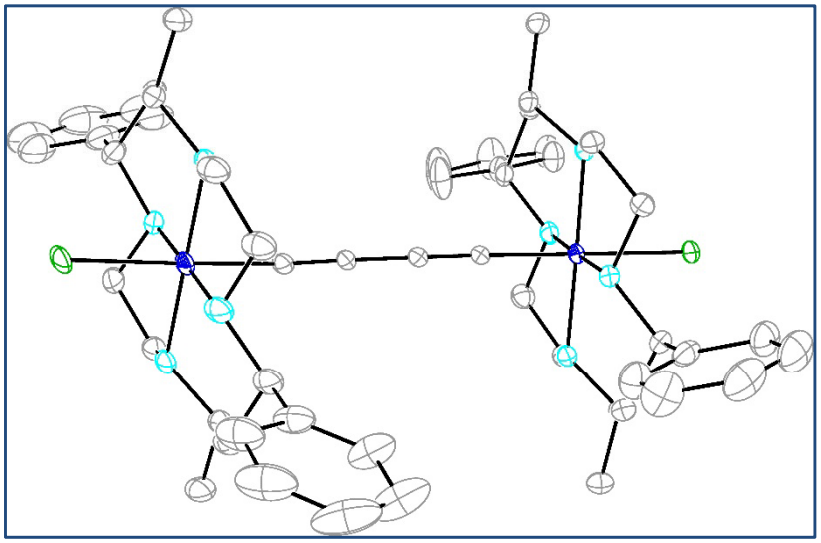
- Using "secondary coordination sphere" to reduce overpotential of CO2 reduction; "X" in **A** can be either a positive charge to stabilize the transition state, or a proton donor to promote proton-coupled electron transfer
- Novel photosentizers (free of precious-metals) are being developed to promote photo-electrochemical reduction of CO2

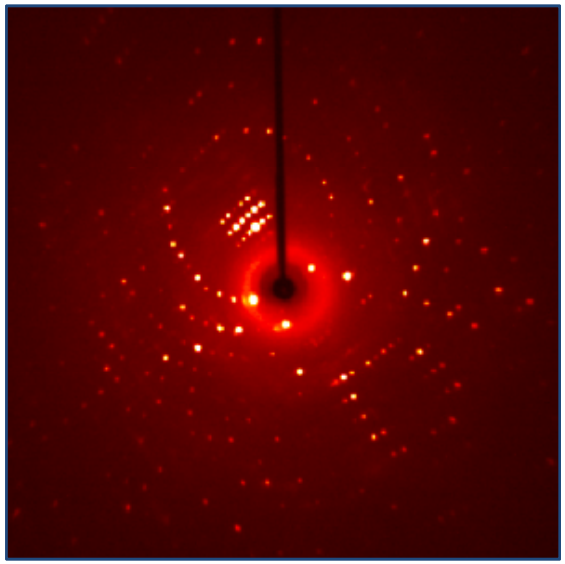
Techniques: X-ray Diffraction

- Structures of small molecules
  - Crystal growth, data collection and structure refinement
- Benefits
  - Low cost
  - Immediate usage
  - Publications
  - Skills transferrable to industry





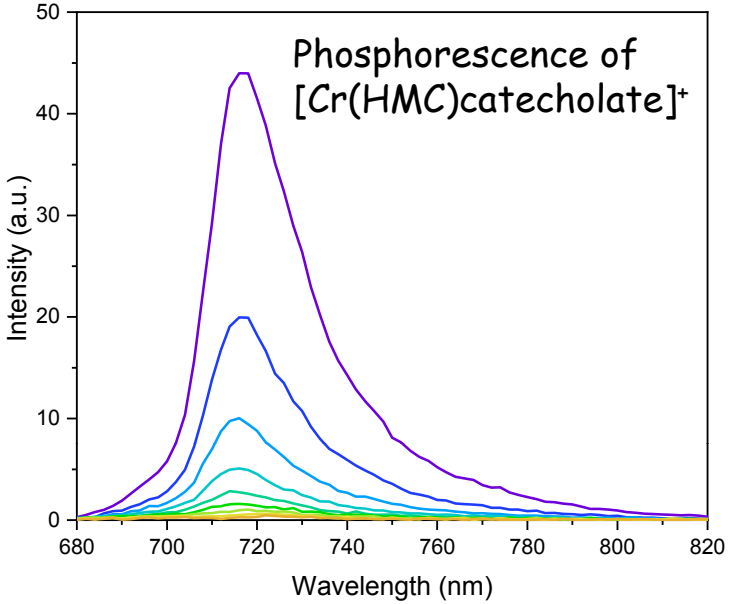


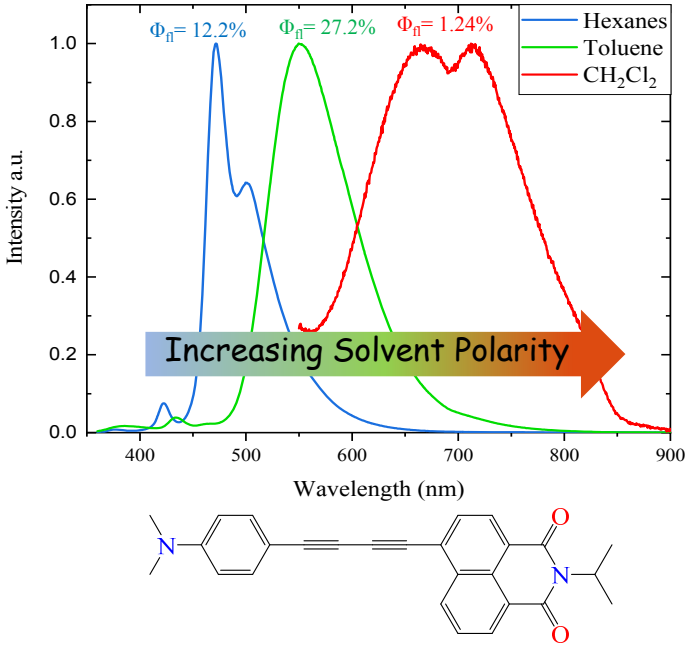


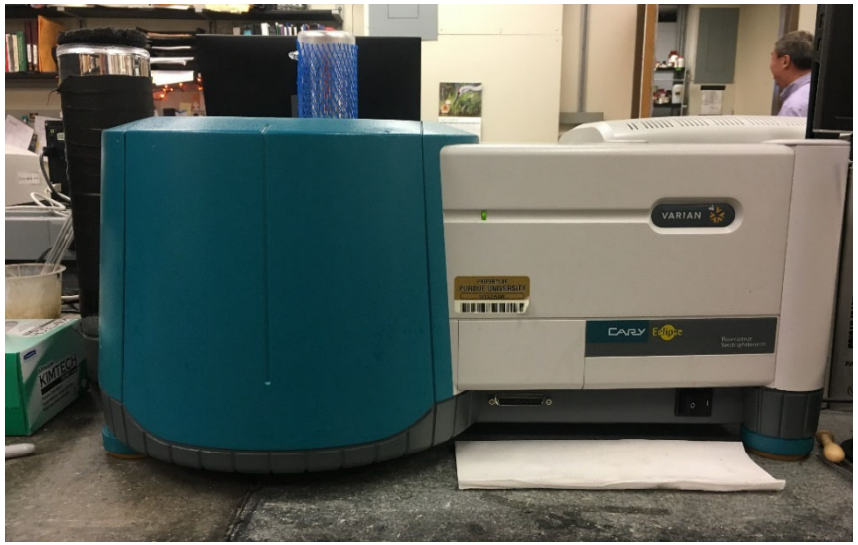
Techniques: Fluorescence and Phosphorescence

- Steady state emission
- Lifetime study (microseconds level)
- Emission quantum yields

Ashley



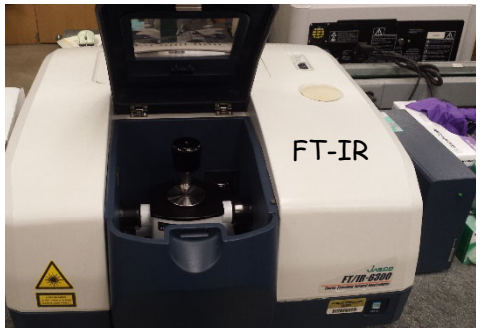




Fluorimeter equipped with Dewar for 77 K measurements

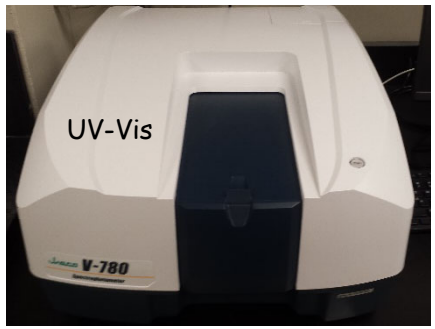
Techniques: UV-vis-NIR and FT-IR Spectro-echem

- Probing electronic spectroscopic features of unstable anionic / cationic species
- Quantifying electronic couplings
- Finger printing IR…



- 4000-600 cm^{-1}
- Multiple ATR Crystals

- 200-2200nm
- Integrating Sphere!



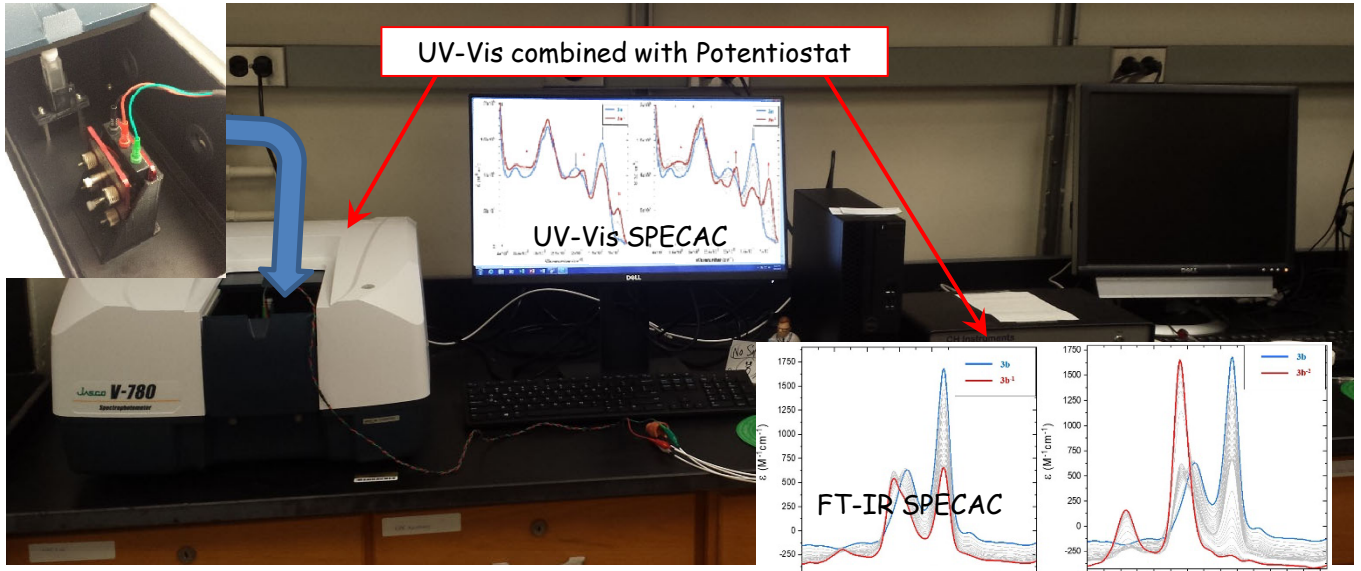
- 200-1600nm
- HIGH SENSITIVITY

Pt aux.

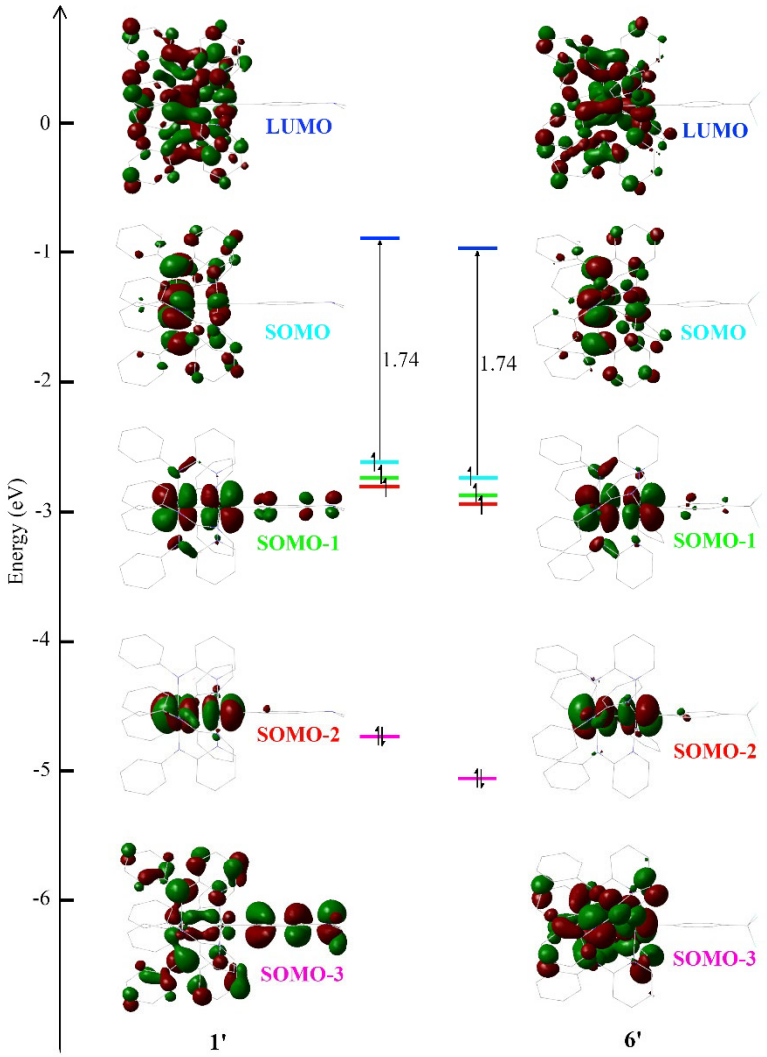
Pt working

Ag ref

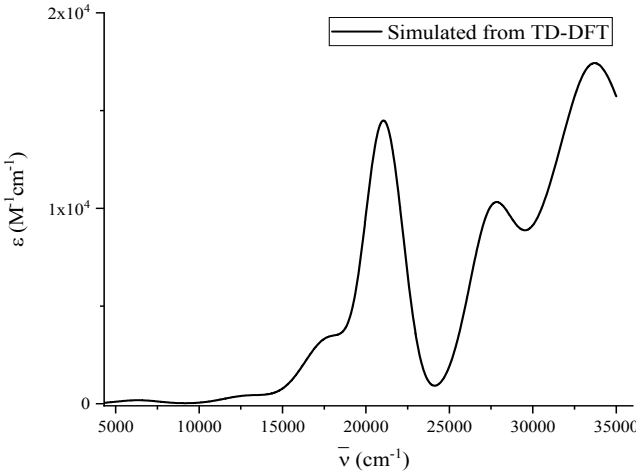
- 0.3 mL of sample!



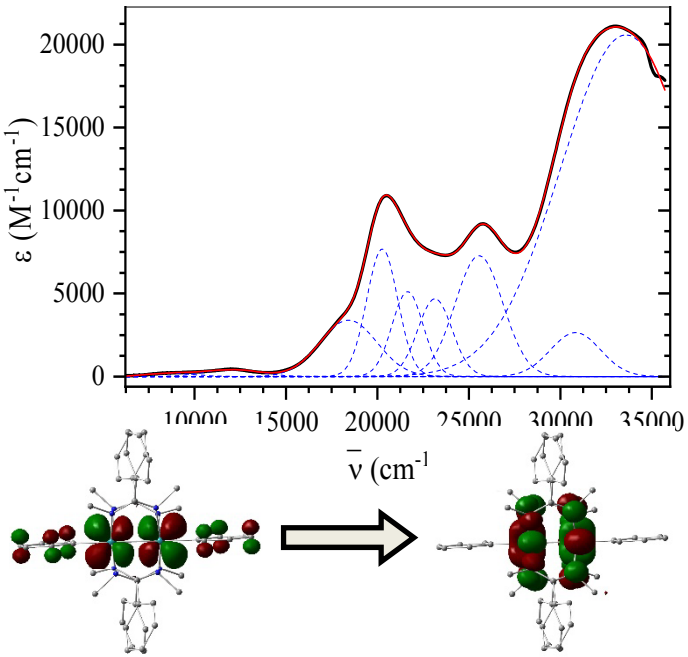
Techniques: DFT and TD-DFT studies



Ligand π-donor strength quantitatively and qualitatively studied by ground-state DFT



Deconvolution of experimental spectrum to extract individual transitions



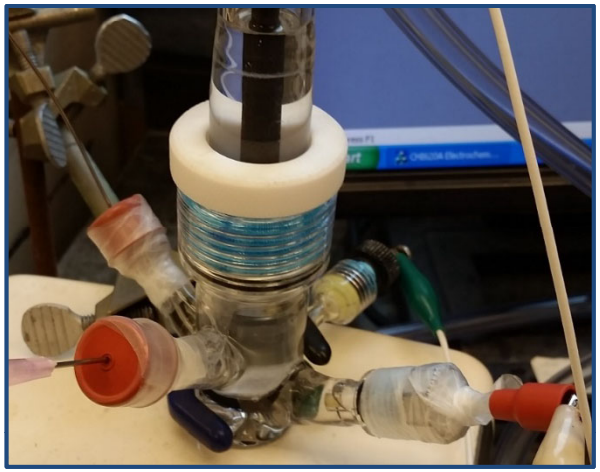
We own two nodes on Purdue's BROWN Cluster

Natural Transition Orbitals depicting "where the electron was and where it ended up"

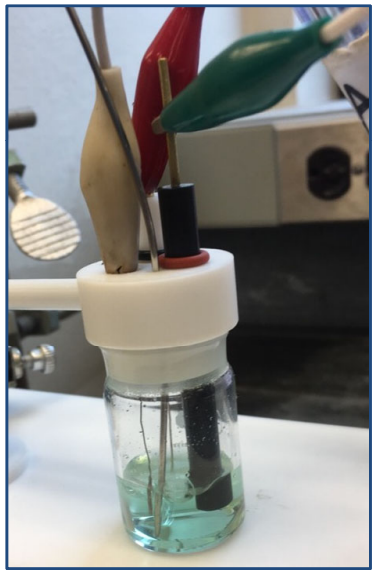
Lyndsy

Techniques: Electro/Photochemistry

Leo



Controlled potential electrolysis
Gas tight cell for product analysis



Cyclic voltammetry for electronic and kinetic properties

Photocatalytic reduction without external bias

In house GC for fast and easy product analysis

Ph.D. Made Easy in Ren's

- 4 – 5 years
- Four ACS publications as the first author
  - *J. Am. Chem. Soc., Angew. Chem., Chem. Sci.*
  - *Organometallics, Inorg. Chem., Dalton Trans., Eur. J. Inorg. Chem., Bioconjugate*
- Two concurrent projects encouraged
- You and your research will be supported

Padawan #1 (your name here)

Padawan #2 (your name here)