Protasiewicz "Dr. P." Research Group

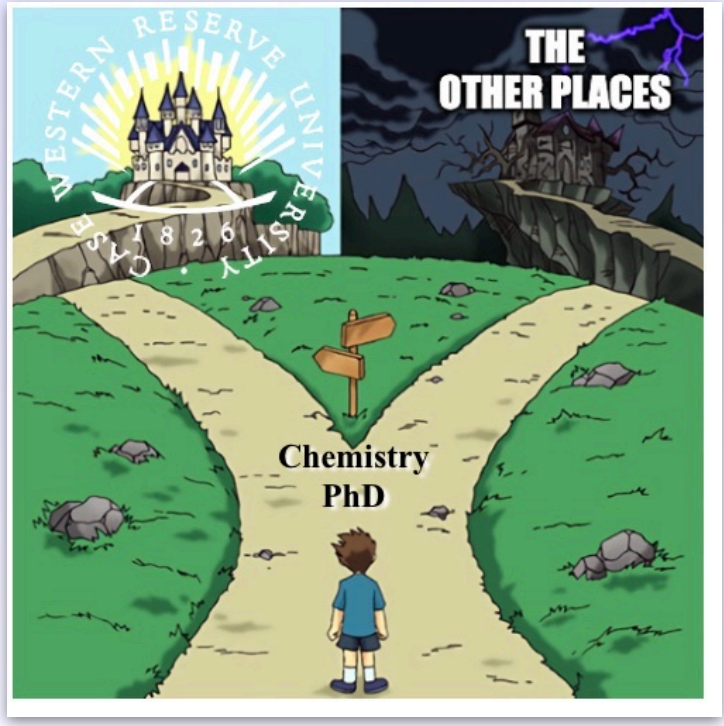
Inorganic & Main Group Chemistry

Current projects

1. Conjugated Inorganic Materials/Photophysics
2. Lithium Ion Battery Electrolytes

Crosscutting Themes:

Synthesis, Inorganic, Main Group, Materials, Photophysics, Catalysis, Energy Storage & Conversion

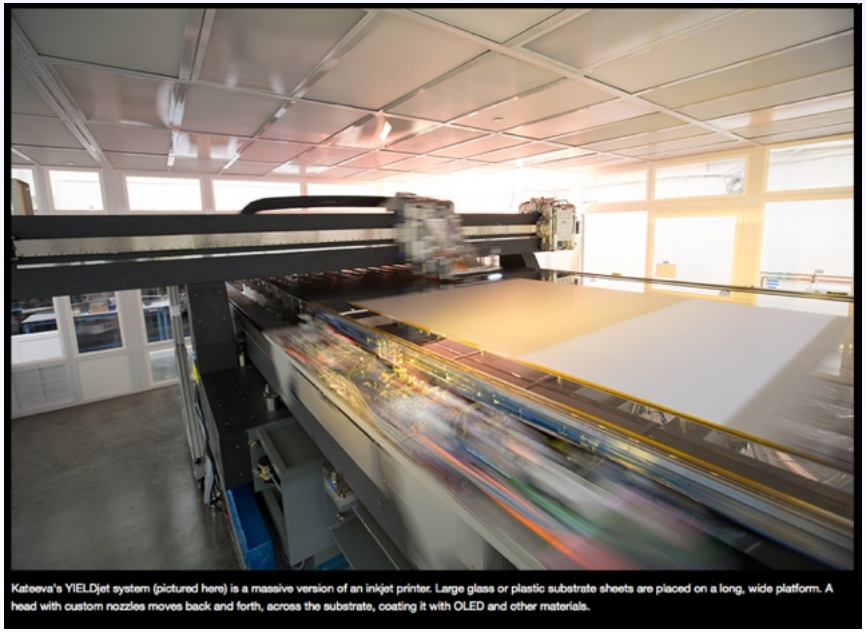



Sept 2018 Collision Bend Brewery


Sept 2022 Cleveland Museum of Art

Area 1. Connections of our Basic Science to Technology:
Flexible, Portable, Printable Display Devices + Solar Voltaic Devices

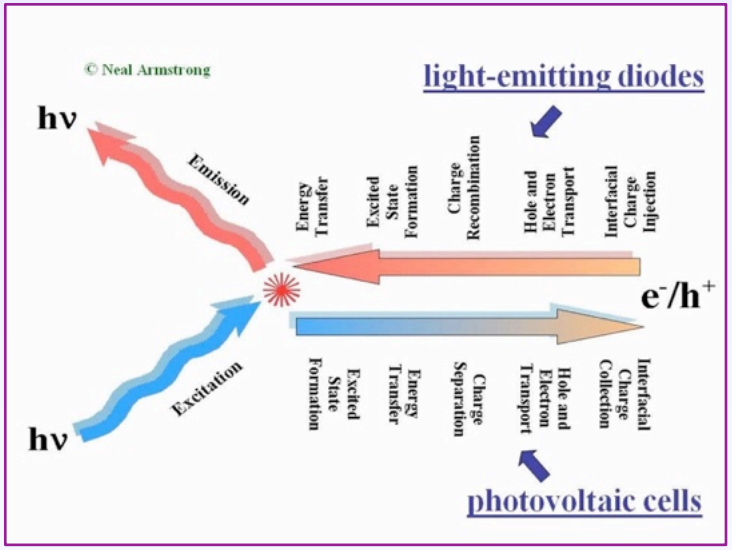




Kateeva's YIELDjet system (pictured here) is a massive version of an inkjet printer. Large glass or plastic substrate sheets are placed on a long, wide platform. A head with custom nozzles moves back and forth, across the substrate, coating it with OLED and other materials.

http://newsoffice.mit.edu/2015/mass-produced-inkjet-printed-oled-displays-0212

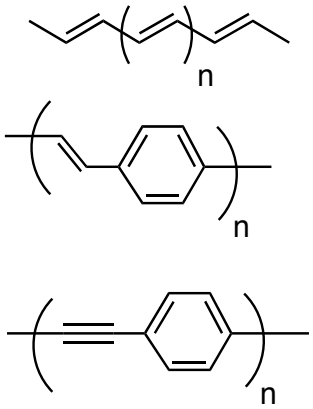
Underlying Physical Chemistry



http://photonicswiki.org/images/9/9a/Led-opvcompared.JPG

Area 1. OLEDs, PVs, & π-Conjugated Materials

Underlying Organic Chemistry



PA

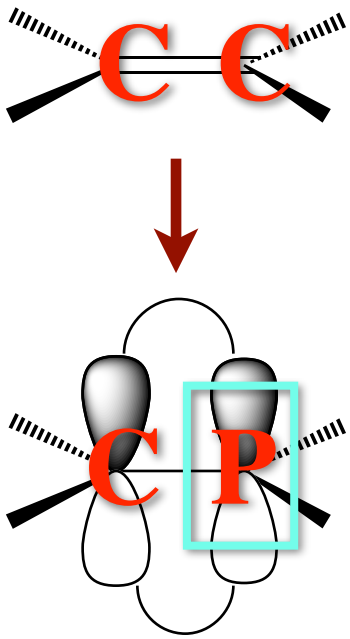
PPV

PPE

- *Conducting Polymers*
- *Molecular Electronics*
- *Redox Systems*
- *Optical Properties*
- *Light Emitting Diodes*
- *Field Effect Transistors*
- *Photovolatics*
- *Non-linear Optics*
- *Display Devices*

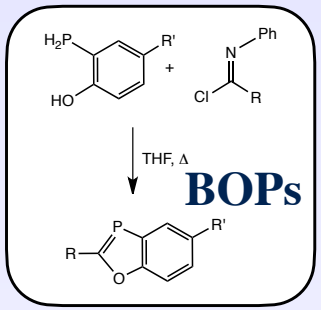
Heeger, A. J. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2591.
MacDiarmid, A. G. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2582.
Shirakawa, H. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2574.

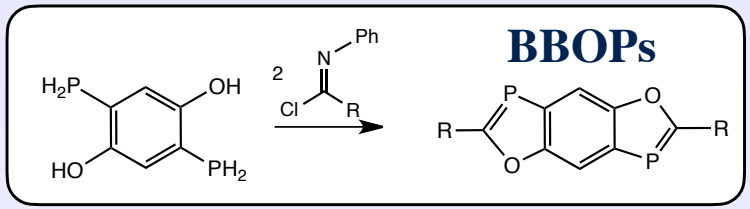
Recruiting Other Elements from Periodic Table

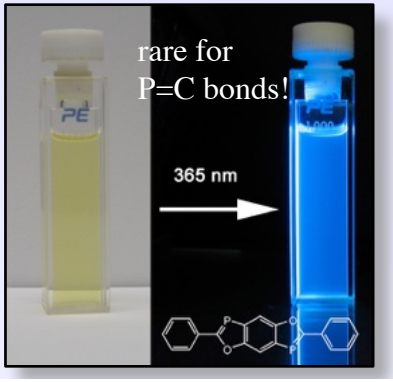


- sigma + pi bond
- non-polar bonds
- sp^2 hybridized atoms
  w/120° bond angles about atom

Area 1. Molecules & Materials: *1,3-Benzoxaphospholes & 1,3-Benzobisoxaphospholes*

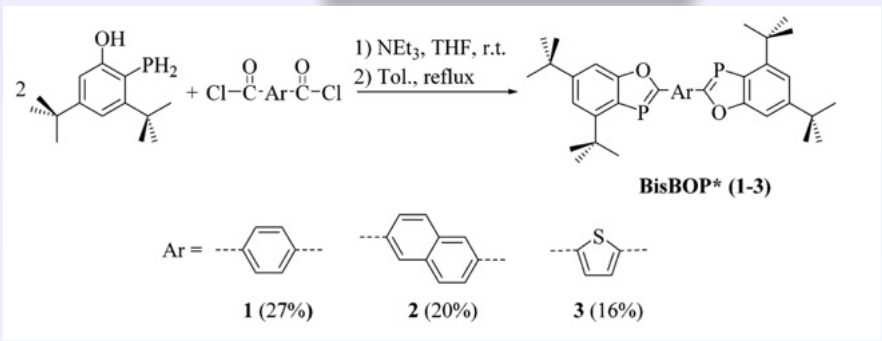




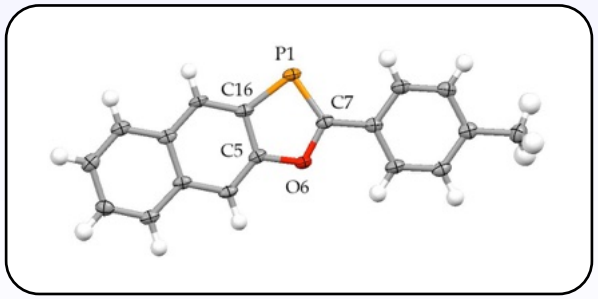


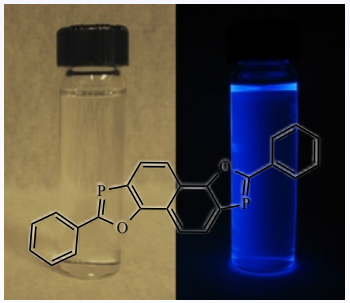
Φ_f
4-69%
(R =Aryl >Alkyl)

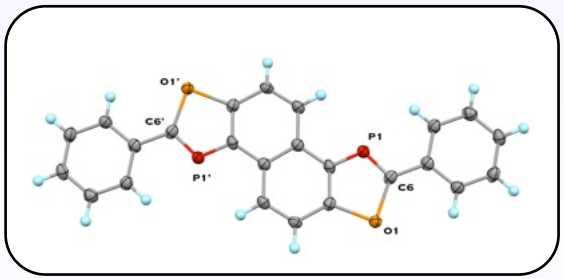








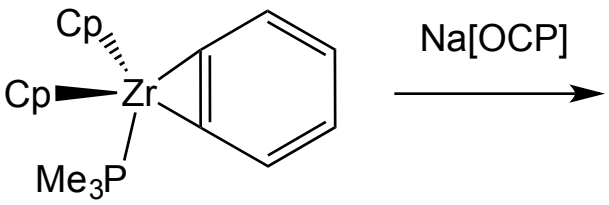




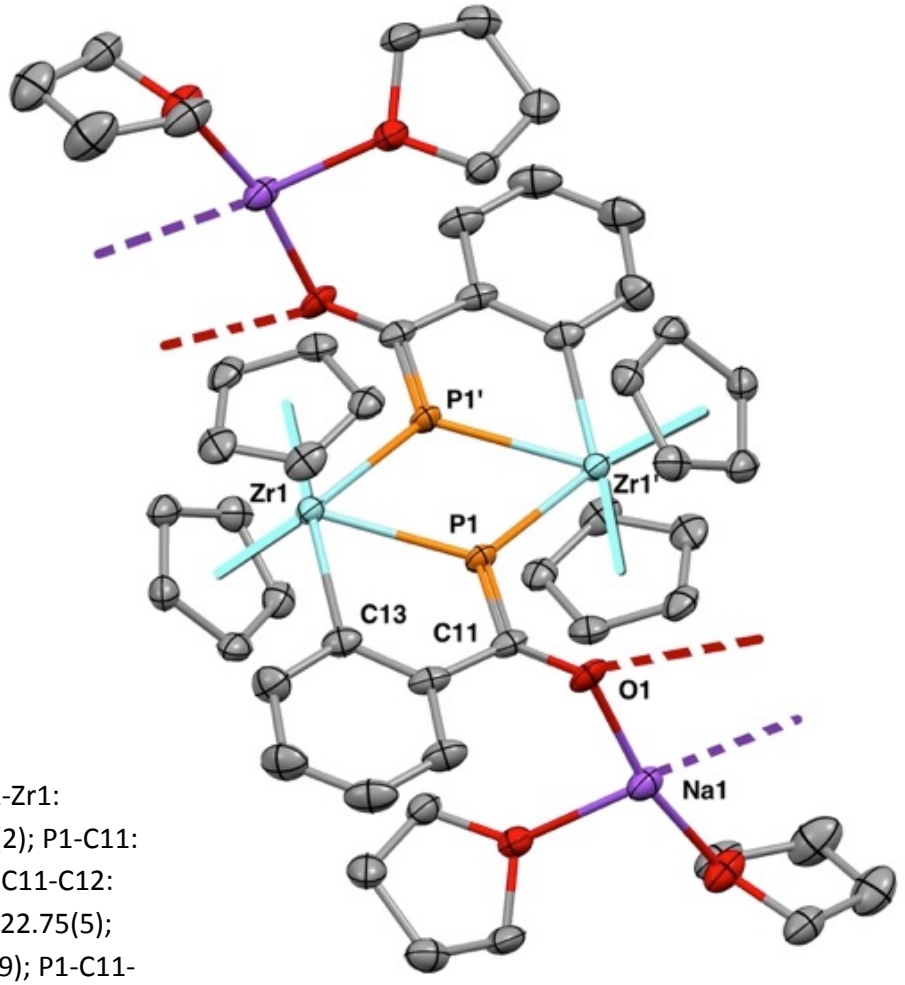
- Washington, M.P.; Gudimetla, V. B.; Laughlin, F. L.; Deligonal, N.; He, S., Payton, J. L.; Simpson, M. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 4566.
- Laughlin, F. L.; Rheingold, A. L.; Deligonul, N.; Laughlin, B. J.; Smith, R. C.; Higham, L. J.; Protasiewicz, J. D. *Dalton Trans.* **2012**, 12016.
- Laughlin, F.L., N. Deligonul, A.L. Rheingold, J.A. Golen, B.J. Laughlin, R.C. Smith, and J.D. Protasiewicz *Organometallics* **2013** *32*, 7116.
- Wu, S., A.L. Rheingold, and J.D. Protasiewicz *Chem. Commun.*, **2014**. *50*, 11036.

National Science Foundation
WHERE DISCOVERIES BEGIN

Area 1. Organometallic Chemistry: New Routes to *1,3-Benzoxaphospholes*



Na[OCP]

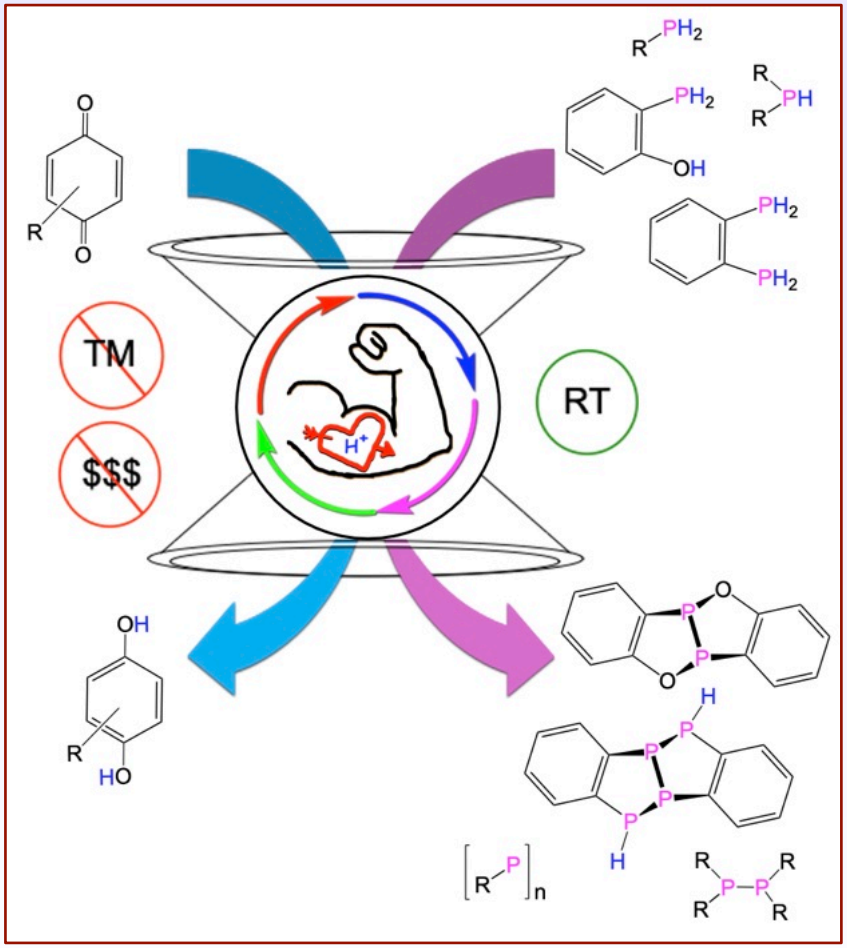


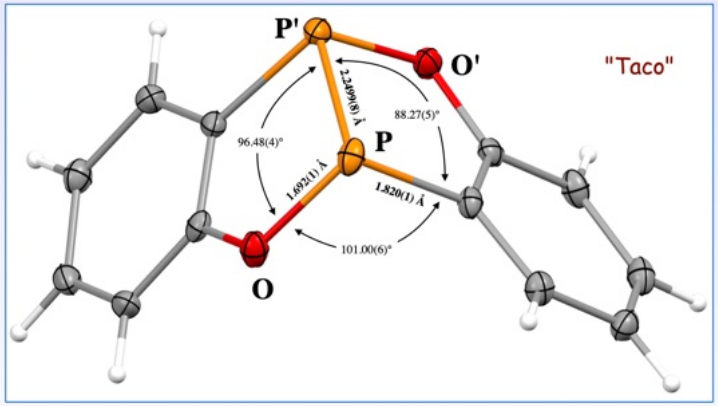
Selected bond distances [Å] and angles [°]: P1-Zr1: 2.6151(14); P1-Zr1': 2.7010(14); P1-P1': 2.548(2); P1-C11: 1.743(5); Zr1-C13: 2.406(5); O1-C11: 1.276(6); C11-C12: 1.488(8); P1-Zr1-C13: 71.04(14); Zr1-P1-Zr1': 122.75(5); Zr1-P1-C11: 109.37(19); Zr1'-P1-C11: 127.22(19); P1-C11-O1: 125.6(4).

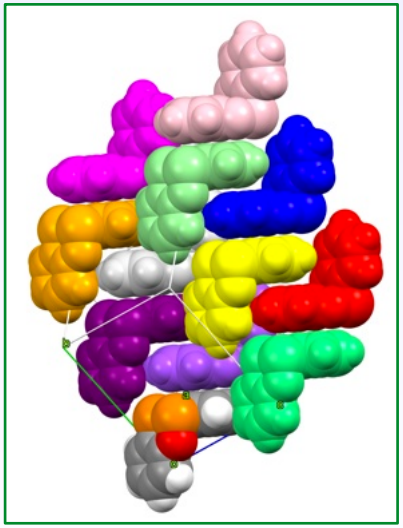
Kieser, J. M.; Gilliard R. J. Jr.; Rheingold, A. L.; Grützmacher, H.; Protasiewicz, J. D. "Insertion of Sodium Phosphaethynolate, Na[OCP], into a Zirconium-Benzyne Complex". *Chem. Commun.*, **2017**, *53*, 5110-511

National Science Foundation
WHERE DISCOVERIES BEGIN

Area 1. Catalysis Chemistry: New Routes to *Dehydrocoupling Reactions*







Ekstrom, Zakary T.; Stone, Alexander M.; Li, Guobi; Hassoun, Hannah D.; Kornokovich, Anthony D.; Delgado Rosario, Emalyn; Espinosa Ferao, Arturo; Zeller, Matthias; Rheingold, Arnold L.; Protasiewicz, John D.

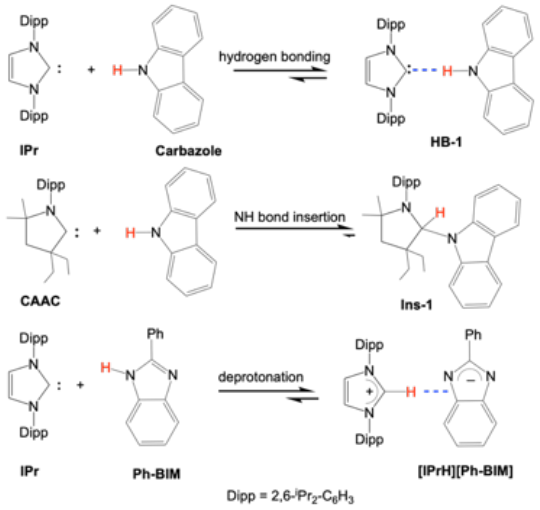
"Acid-Catalyzed Dehydrocoupling of Phosphines",
Inorg. Chem. **2026**, *65*, 10571–10580. https://doi.org/10.1021/acs.inorgchem.6c00218

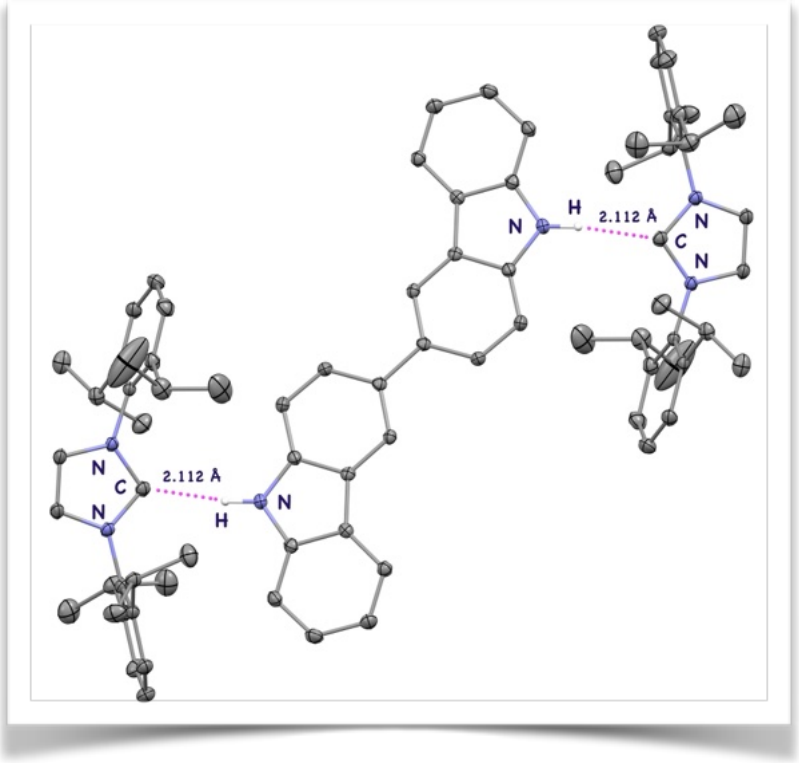
National Science Foundation
WHERE DISCOVERIES BEGIN

Area 1. Supramolecular & Non-Covalent Chemistry

- **Conjugated Materials featuring E=C and E=E bonds**
- **Novel Luminescent compounds and Systems**
- **Sensors based on Stable Carbenes**

National Science Foundation
WHERE DISCOVERIES BEGIN

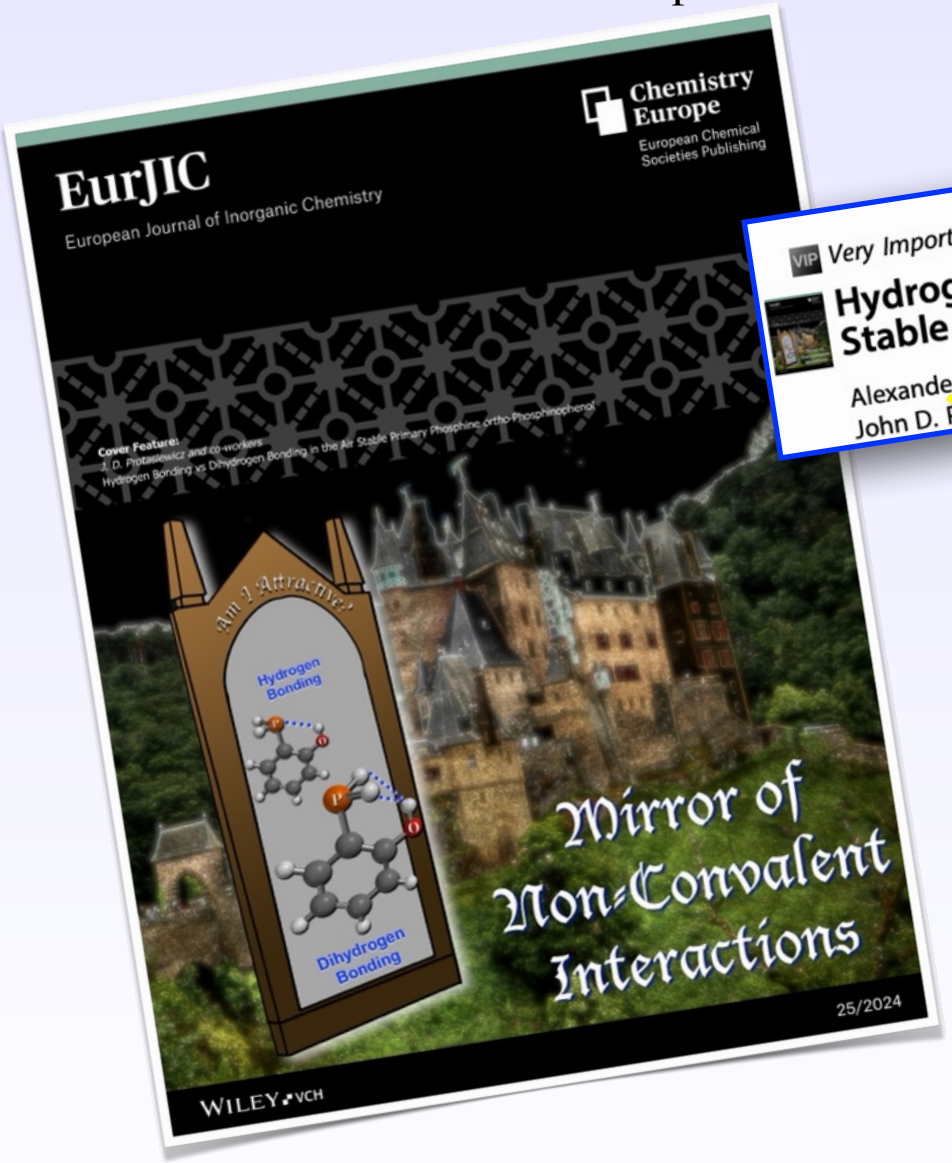




J. Kieser, Z. Kinney, S. Evariste, J. Gaffen, A. M. Harrison, A. Rheingold, J. D. Protasiewicz *JACS*, ***2019***, *141*, 12055-12063
Z. Kinney, A. Rheingold, J. D. Protasiewicz *RSC Advances*, **2020**, *10*, 42164 - 42171

National Science Foundation
WHERE DISCOVERIES BEGIN

Area 1. Supramolecular & Non-Covalent Chemistry



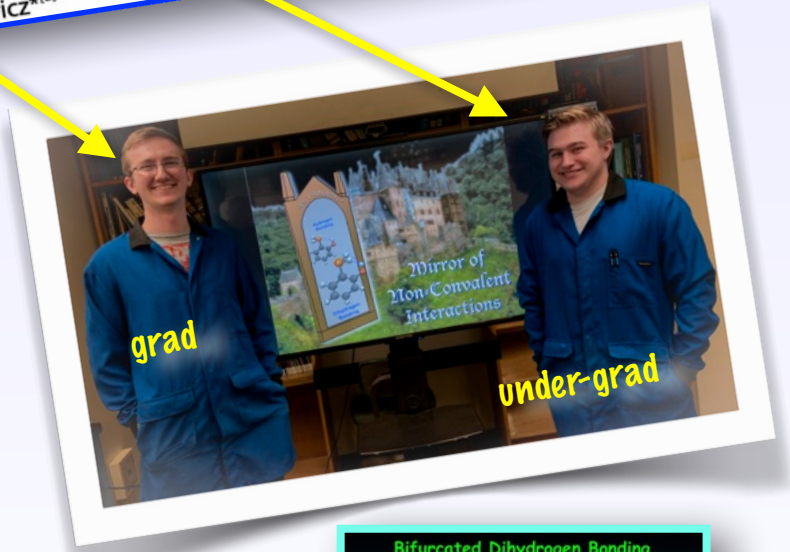
Selected as VIP and for Cover Art 2024

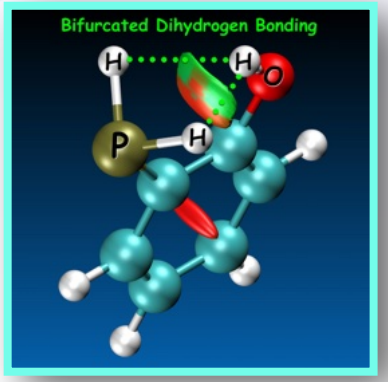
www.eurjic.org

VIP Very Important Paper

Hydrogen Bonding vs Dihydrogen Bonding in the Air Stable Primary Phosphine *ortho*-Phosphinophenol

Alexander M. Stone,[a] Andrew R. Golden,[a] Shan M. Daniel,[a] Arnold L. Rheingold,[b] and John D. Protasiewicz*[a]



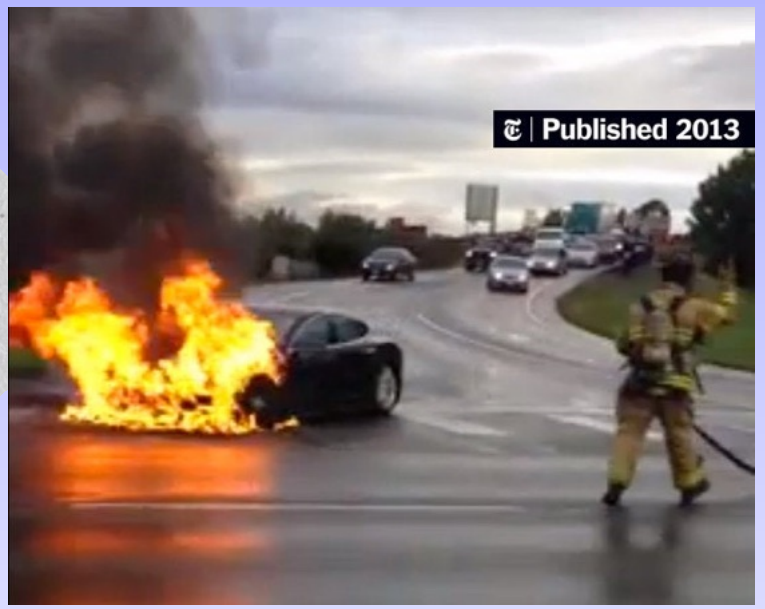


National Science Foundation
WHERE DISCOVERIES BEGIN

2.Fear of Batteries





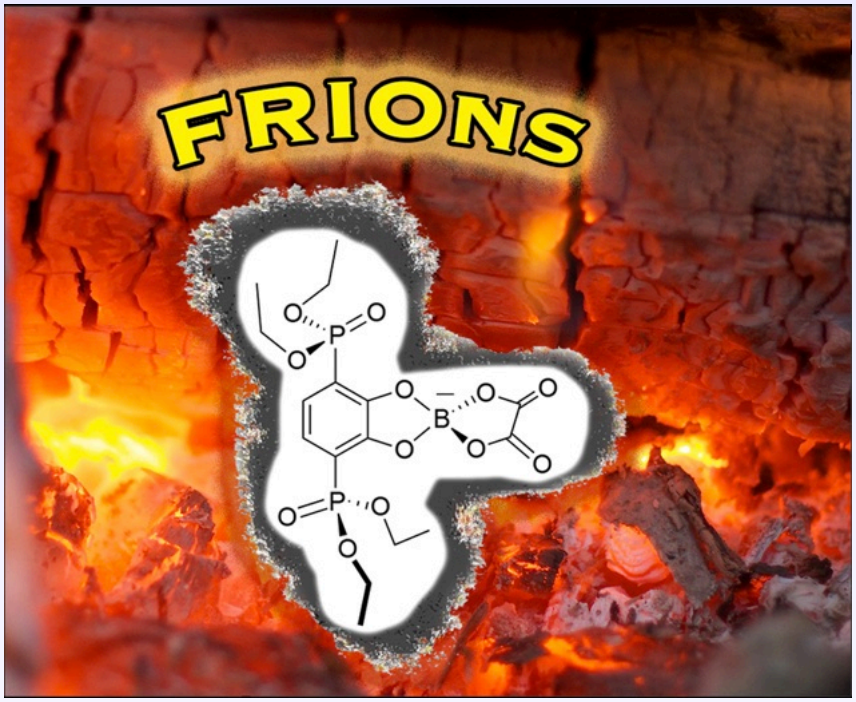


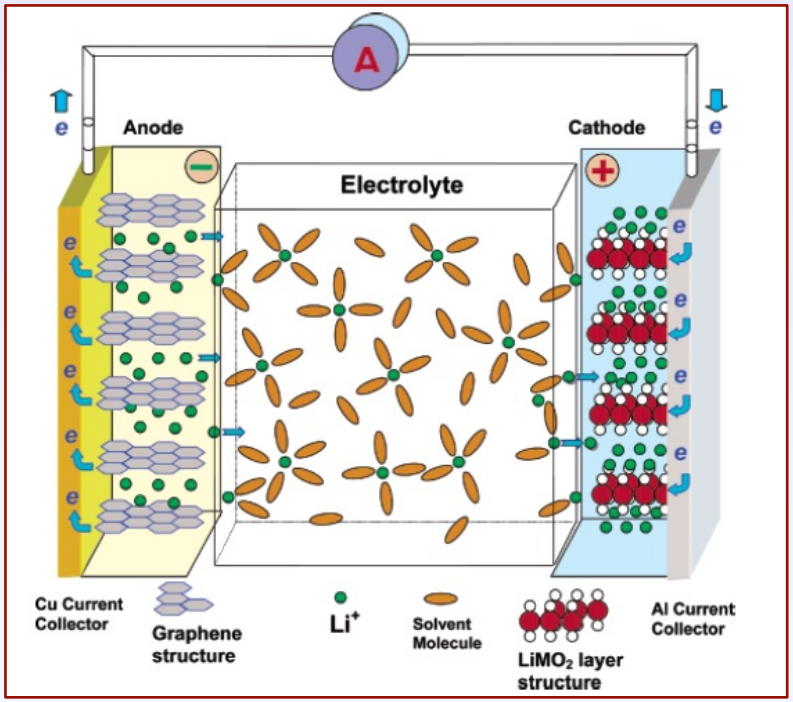


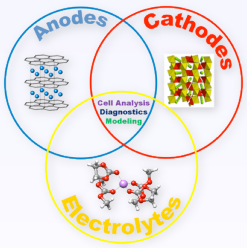


UL Research Institutes

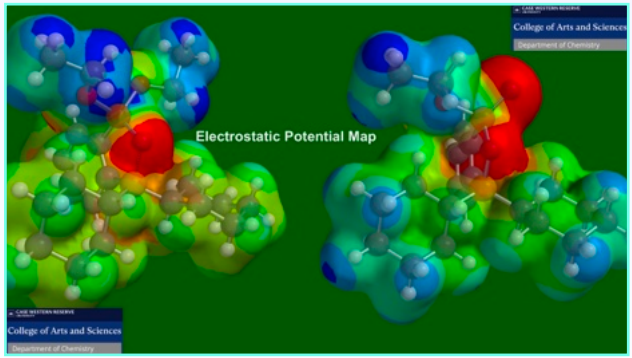
Area 2. FRIONs: Flame Retardant Ions for safer lithium ion batteries







Research Institutes®



Shaffer, A. R.; Deligonul, N.; Scherson, D. A.; Protasiewicz, J. D., "A Hybrid Lithium Oxalate-Phosphinate Salt" *Inorg. Chem.* **2010**, *49*, 10756-10758.

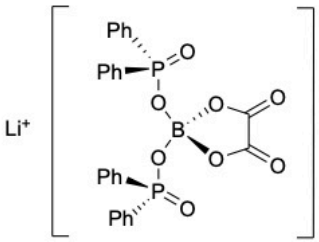
Rectenwald, M. F.; Gaffen, J. R.; Rheingold, A. L..; Morgan. A, B.; Protasiewicz, J. D. "Phosphoryl-Rich Flame Retardant Ions (FRIONs): Towards Safer Lithium Ion batteries" *Angew. Chem. Int. Ed.* **2014**, *53*, 4173-4176

Delgado Rosario, E., Rectenwald, M.F., Gaffen, J.R., Rheingold A. L. and Protasiewicz, J. D. *Dalt. Trans.*, **2021**, *50*, 6667–6672.

Area 2. FRIONs: Flame Retardant Ions for safer lithium ion batteries

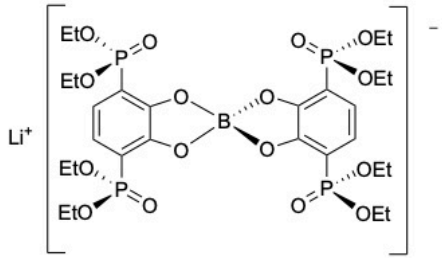
Previous work on FRIONs

1st Generation FRIONs



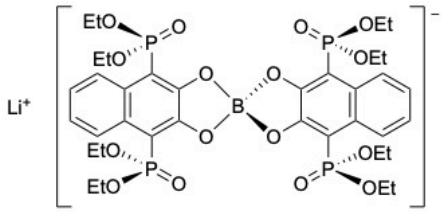
FRION 1

2nd Generation FRIONs



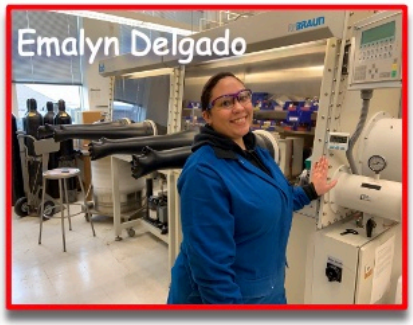
Li[B(DPC)$_2$]

3rd Generation FRIONs



Li[B(DPN)$_2$]

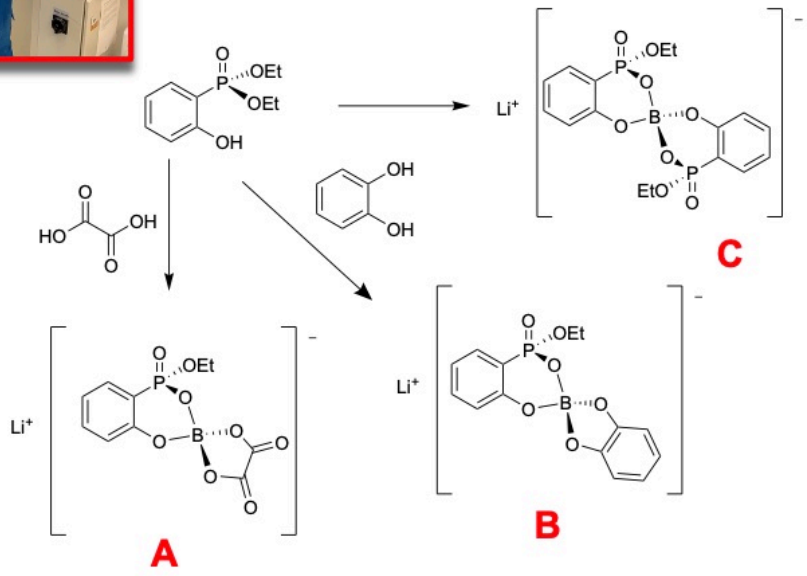
New Target Precursors and FRIONs

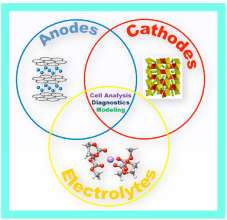




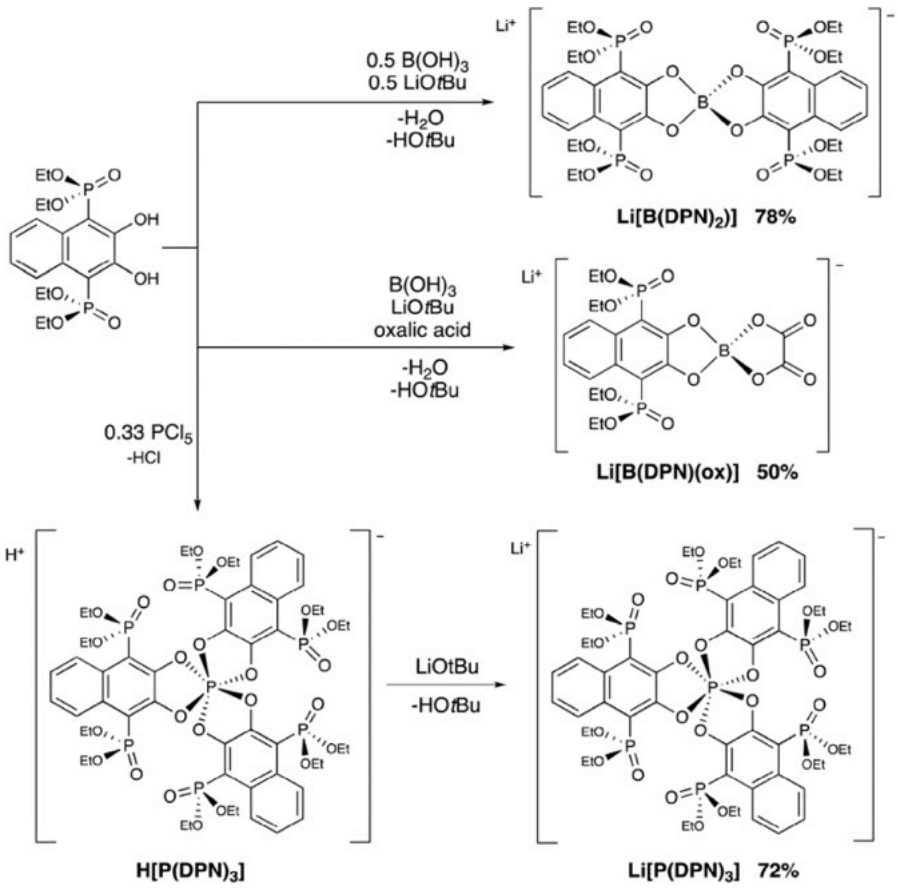
new precursor

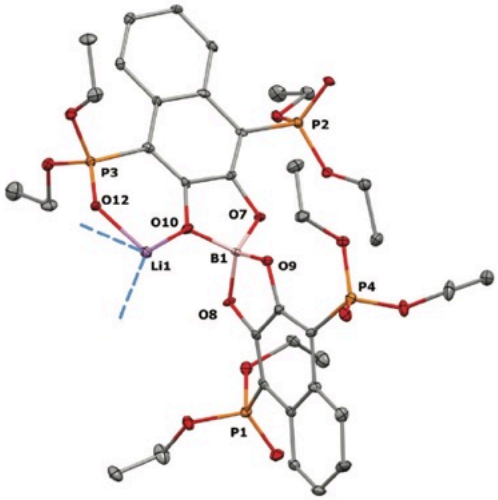
New FRIONs A-C



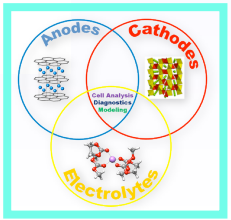


Area 2. FRIONs: Flame Retardant Ions for safer lithium ion batteries

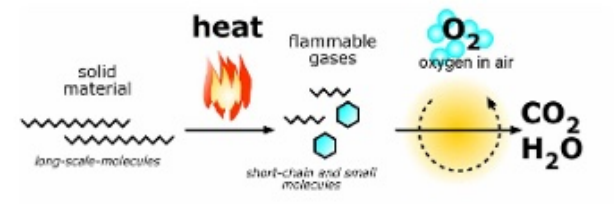


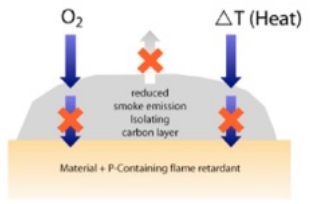


Delgado Rosario, E.; Rectenwald, M. F.; Gaffen, J. R.; Rheingold, A. L.; Protasiewicz, J. D. "Organophosphorus Decorated Lithium Borate and Phosphate Salts with Extended π-Conjugated Backbone", *Dalton Trans.* **2021**, *50*, 6667-7762.



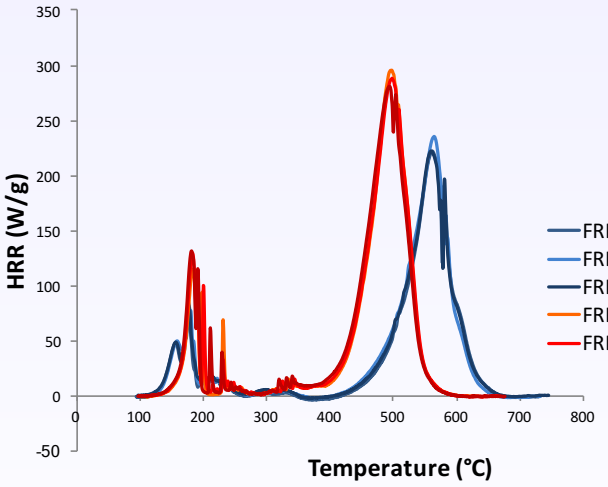
Area 2. FRIONs: Flame Retardant Ions for safer lithium ion batteries

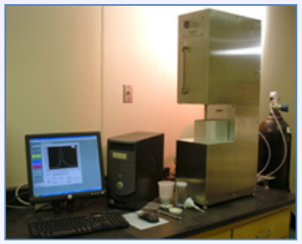




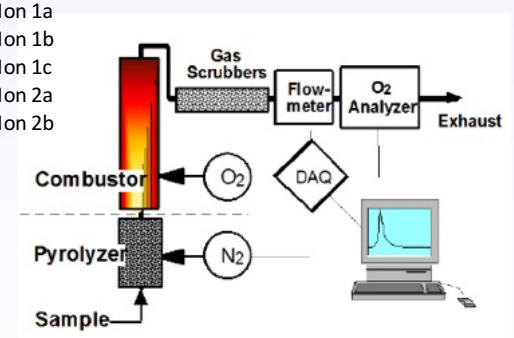
Flammability Testing

Pyrolysis Combustion Flow Calorimetry

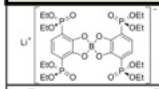
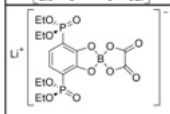
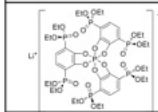
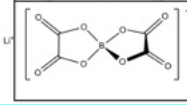


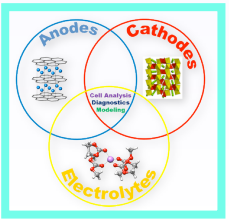


FRIon 1 Ar = Ph
FRIon 2 Ar = 2-MePh



Heat Release Rate (HRR) Data

Sample	Avg. Char Yield (wt%)	Avg. Total Heat Release (kJ/g)
	42.20 (0.43)	12.2 (0.3)
	49.6 (0.05)	8.7 (0.1)
	40.24 (0.69)	10.4 (0.1)
	19.0 (5.2)	3.0 (0.1)



Data collected by Dr. Alexander Morgan at **University of Dayton**, Dayton, OH

Skills, Techniques, Methods, etc

- ☑ Dryboxes and Vacuum Lines
- ☑ Synthesis
- ☑ Multinuclear and VT NMR
- ☑ IR, Raman, UV-vis Spectroscopy
- ☑ X-ray Crystallography
- ☑ Molecular Modeling
- ☑ Electrochemistry
- ☑ Collaborate w/Macro Dept.

P hotoluminecense

P -functional materials

P ROTASIEWICZ RESEARCH GROUP

P -energy storage



Work Hard



Rock on!



Play Hard

UL Research Institutes

National Science Foundation
WHERE DISCOVERIES BEGIN