Comparison of EUV and electron reactivity for metal oxalate photoresists

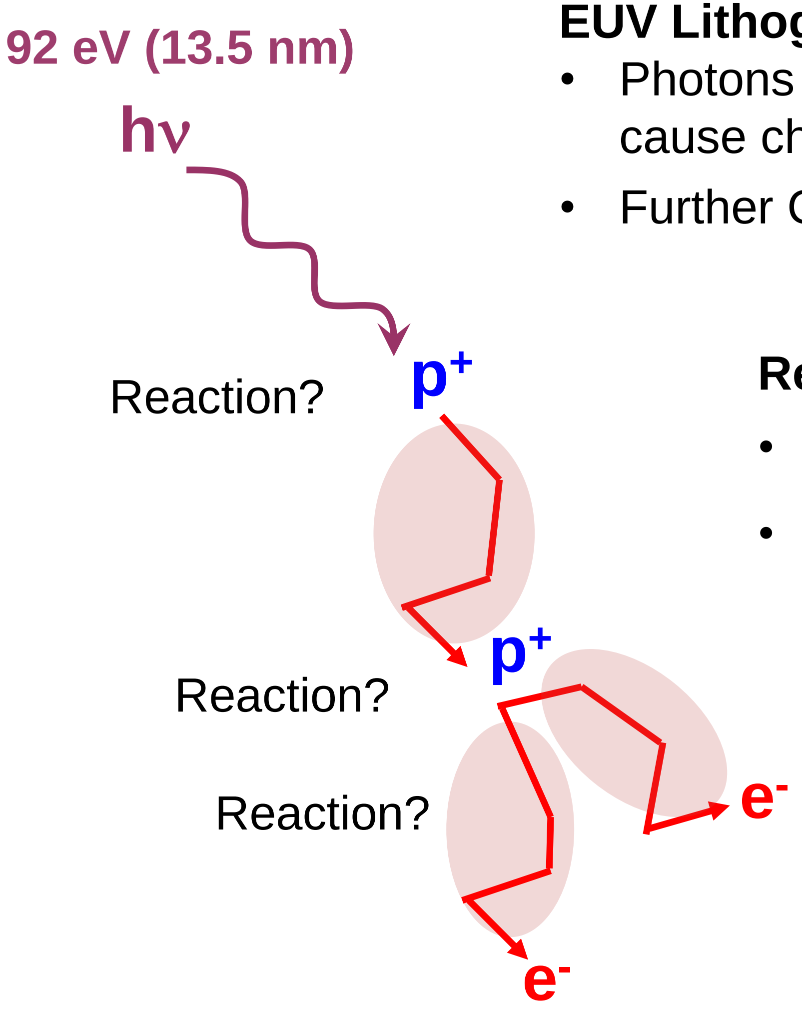
Steven Grzeskowiak,[a] Amrit Narasimhan,[a] Michael Murphy,[a] Jodi Hotalen,[a]
Christian Ackerman,[a] Jake Kaminsky,[a] Lee Napolitano,[b] Daniel A. Freedman,[b]
Robert L. Brainard,[a] and Greg Denbeaux[a]

(a) SUNY Polytechnic Institute – Colleges of Nanoscale Science and Engineering
257 Fuller Rd. Albany, NY, USA 12203
(b) State University of New York at New Paltz, 1 Hawk Drive New Paltz, NY 12561

IEUVI Resist Technical Working Group
February 26th, 2017

Monday 2:20-2:40 pm, **"Reactivity of Metal Oxalate EUV Resists as a Function of the Central Metal,"** Presentation by Steven Grzeskowiak (10146-4)

EUV Lithography



92 eV (13.5 nm)

$h\nu$

Reaction?

p^+

Reaction?

p^+

Reaction?

e^-

e^-

EUV Lithography

- Photons liberate electrons in the resist and possibly cause chemistry to occur in the process
- Further Chemistry due to electron-resist interactions

Resist chemistry can be improved by:

- Increasing the number of photons absorbed
- Efficient reactivity of secondary electrons

References

[1] T. Kozawa and S. Tagawa, *Jpn. J. Appl.Phys.*, **49 (3)** (2010) 030001.

[2] A. Narasimhan, S. Grzeskowiak, et al., *Proc. SPIE*, **9779** (2016) 97790F.

[3] J. Torok, et al., *J. Photopolym. Sci. and Technol.*, **26 (5)** (2013) 625–634.

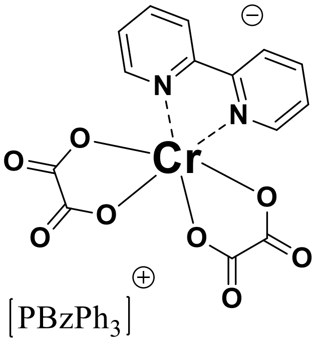
[4] P. de Schepper, et al., *Proc. SPIE*, **9425** (2015) 942507.

[5] T. H. Fedynyshyn, et al., *Proc. SPIE*, **5039** (2003) 310.

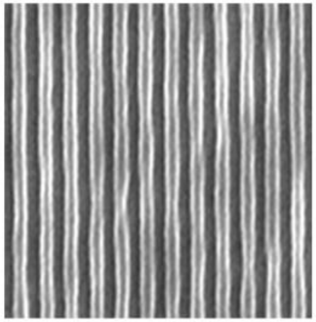
Number of Electrons?

2-4 e^-/photon[1-5]

Comparison of Metal Centers Previous Work

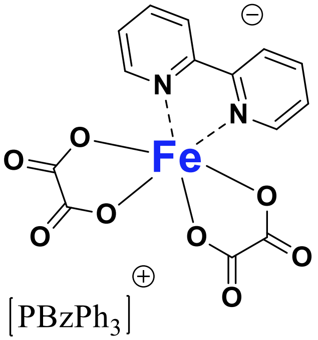


NP4: Cr

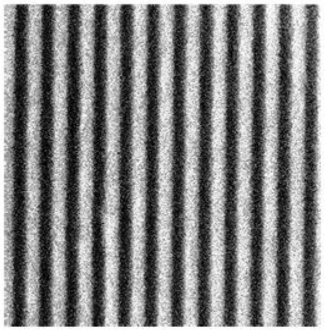


$E_{size} = 70$ mJ/cm^2

- Number of d electrons = 3
- Oxidation State = (III)
- *Calculated EUV abs. = 5.8 µm^{-1}

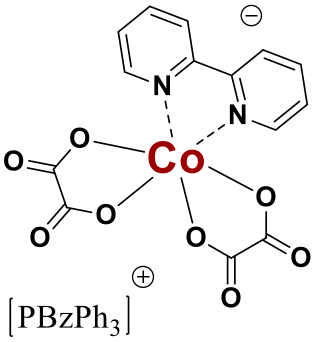


NP3: Fe

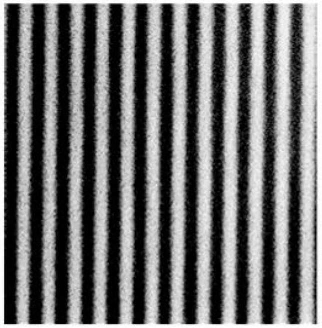


$E_{size} = 48$ mJ/cm^2

- Number of d electrons = 5
- Oxidation State = (III)
- *Calculated EUV abs. = 6.0 µm^{-1}



NP1: Co



$E_{size} = 27$ mJ/cm^2

- Number of d electrons = 6
- Oxidation State = (III)
- *Calculated EUV abs. = 6.1 µm^{-1}

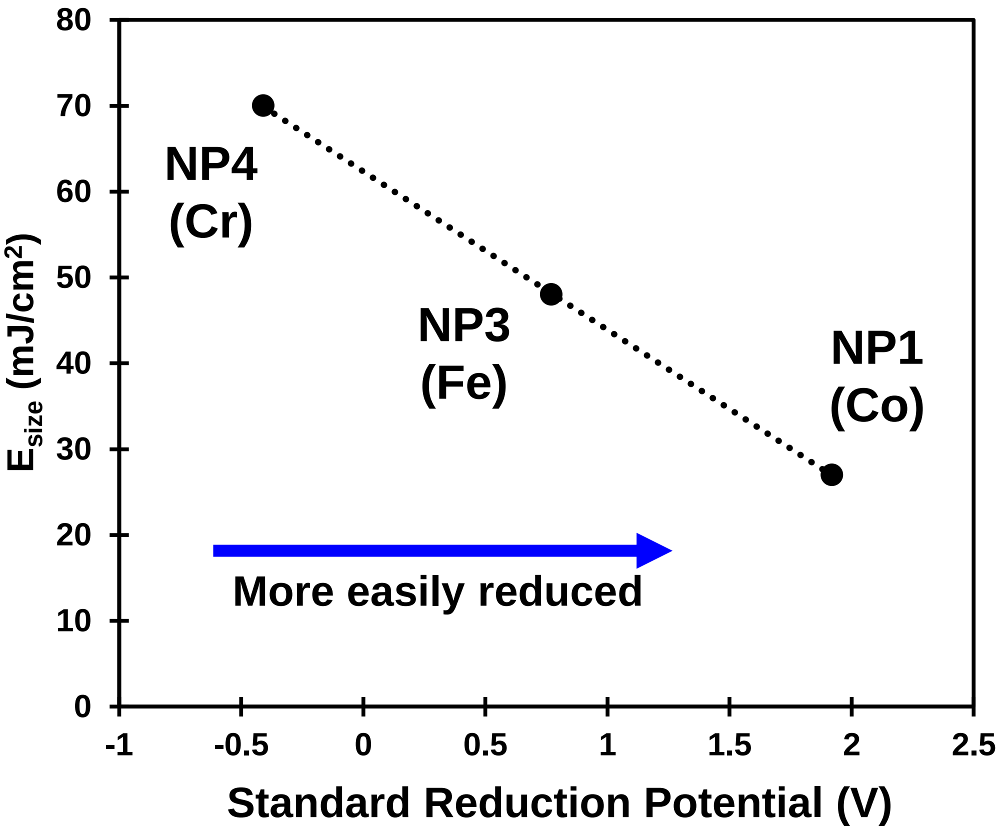
Improved Sensitivity

35 nm h/p lines

*Calculated values are based on CXRO absorption using an assumed film density of 1.5 g/cm^3

[7] M. Marnell, et al., “***A Molecular Inorganic Approach to EUV Photoresists***”, *presented at SPIE advanced lithography conference*, (February 2014), San Jose, CA.

E_{size} *vs.* Metal Center Redox Potential



Literature Values[8-12]

Metal Reduction from (III to II)	**Standard Redox Potential (V)**
$Co^{3+} + e^- \rightleftarrows Co^{2+}$	+1.92
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.77
$Cr^{3+} + e^- \rightleftarrows Cr^{2+}$	-0.41

[8] D. R. Lide (Editor-in-Chief), "***CRC Handbook of Chemistry and Physics, 83rd edition***," *CRC Press,* (2002-2003).

[9] Nobuyuki Tanaka, and Michio Nanjo, "***The Thermal Decomposition of Metal Oxalato Complexes***." *Bull. Chem. Soc. Jpn.* **40 (2)** (1967) 330-333.

[10] A. J. Bard, R. Parsons, and J. Joseph, "***Standard potentials in aqueous solution***," *CRC Press* **6**, (1985).

[11] G. Milazzo and S. Caroli, "***Tables of Standard Electrode Potentials***," *Analytica Chimica Acta* **105** (1979) 459.

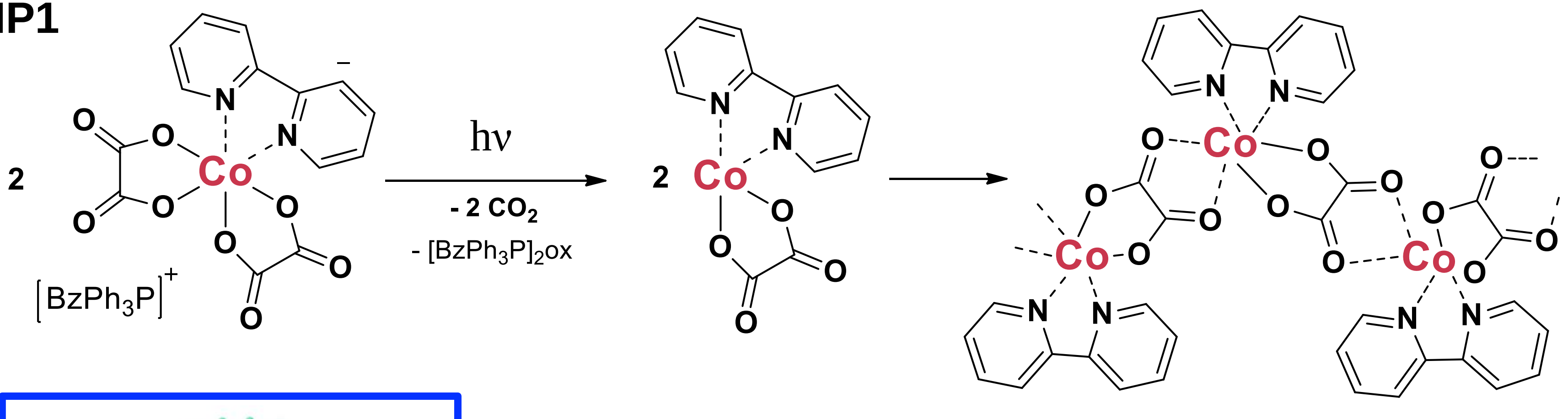
[12] D. C. Harris, "***Quantitative chemical analysis***, ***8th edition***," *Macmillan* (2010).

- There appears to be a correlation between the reducibility of the metal and E_{size}.
- **Hypothesis:** There may be a correlation between reducibility of the metal and CO_2 outgassing based upon the photo-mechanism.

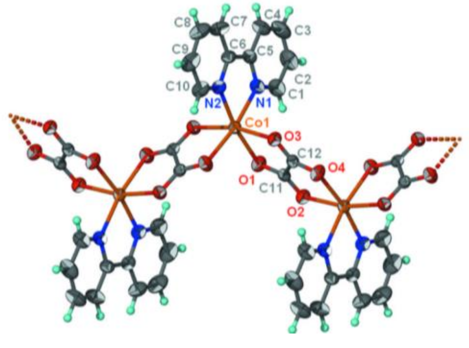
Molecular Organometallic Resists for EUV (MORE): Cobalt Compound (NP1)

Current understanding of photo-mechanism:

NP1



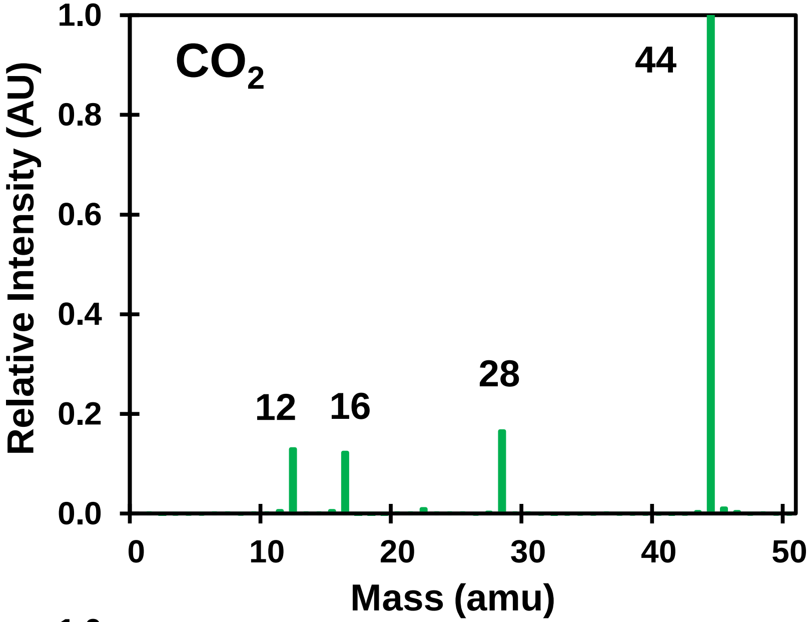
Co(II)(bpy)(ox)

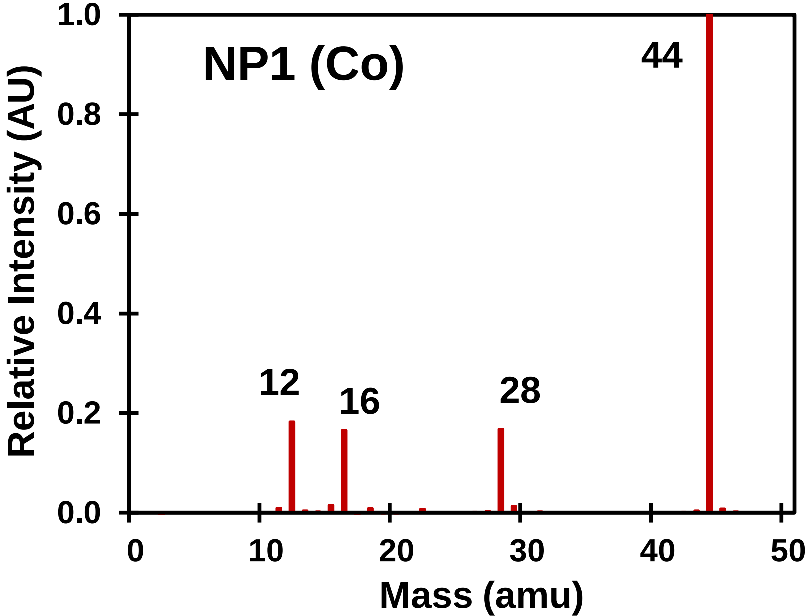


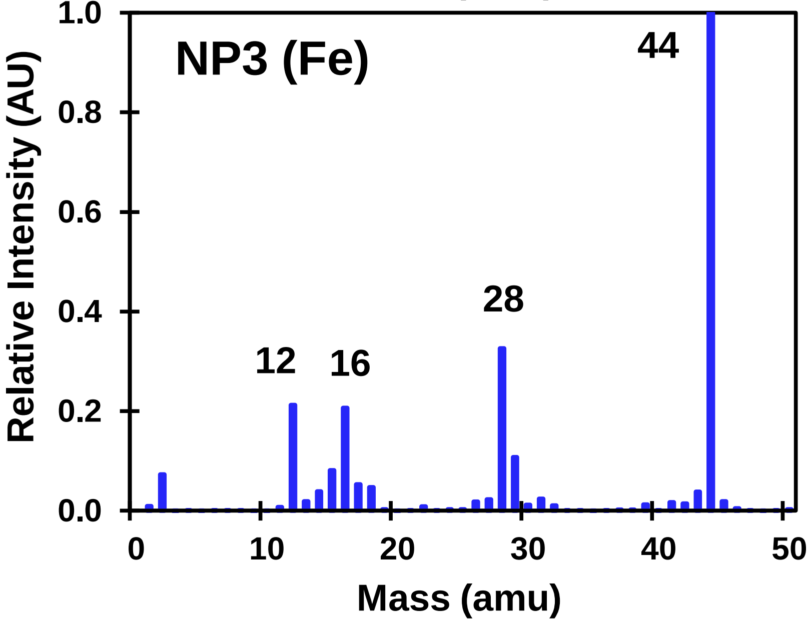
Acta Crystallographica, Section E: Structure Reports Online **65 (10)** (2009).

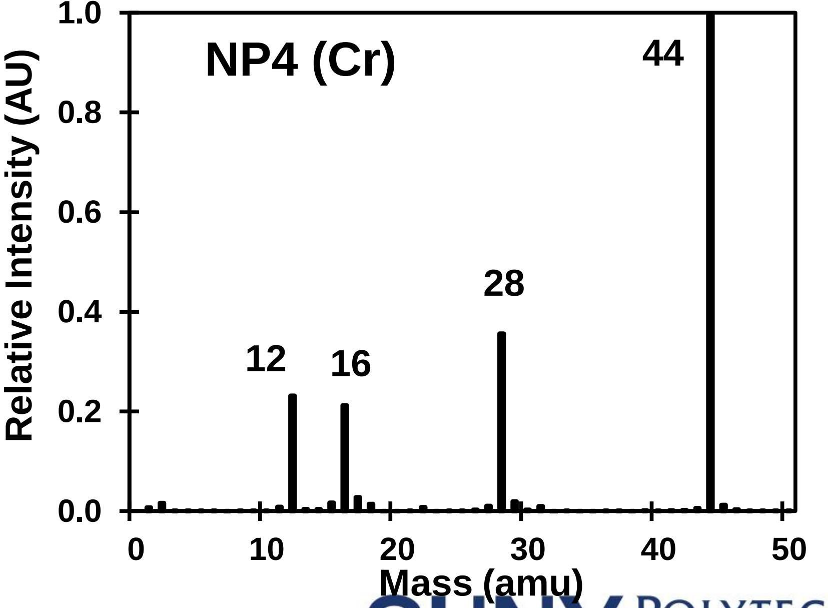
- Upon Exposure to EUV light or electrons CO_2 is generated and outgassed from the resist.
- The photoproduct, Co(II)(bpy)(ox), is a coordination polymer that polymerizes through bridging oxalate ligands.
- This bridging occurs when one of the oxalate ligands is eliminated as CO_2

Outgassing Spectra (electrons)

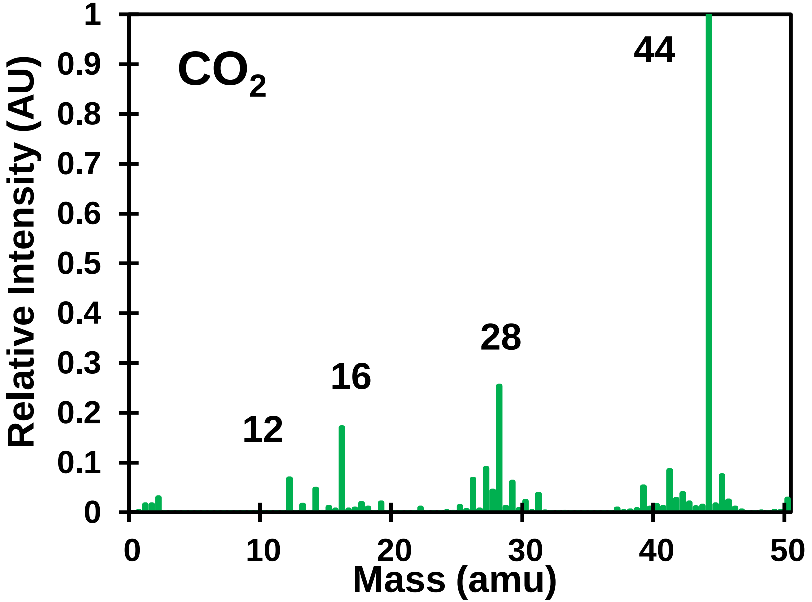


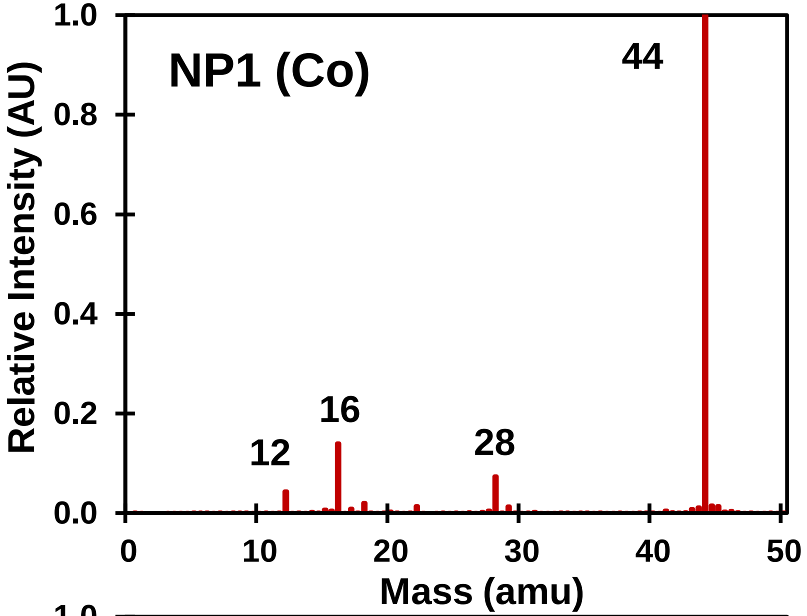


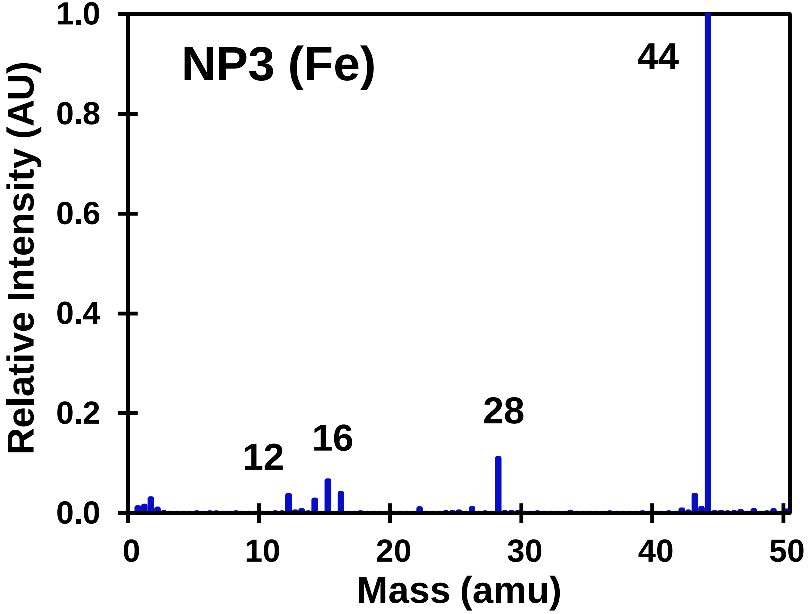


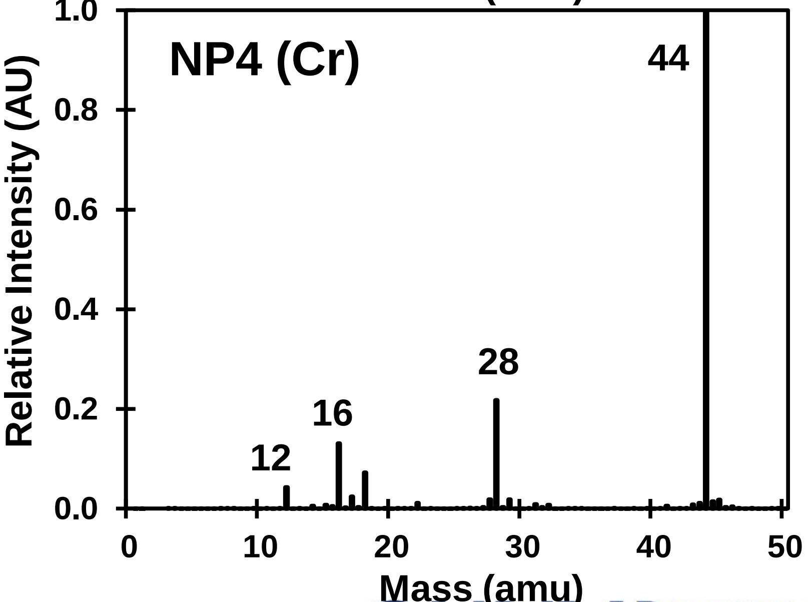


Outgassing Spectra (EUV)

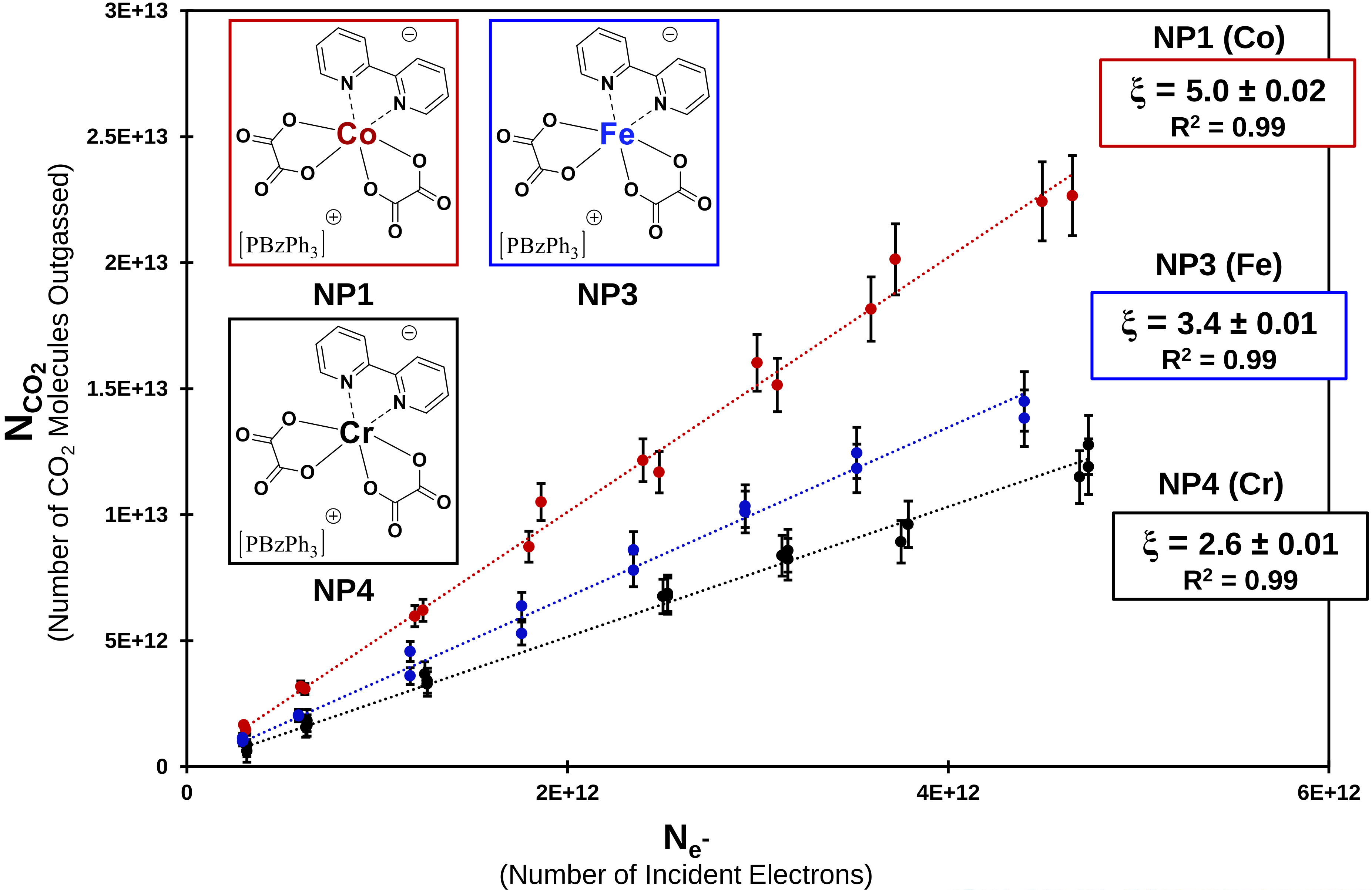




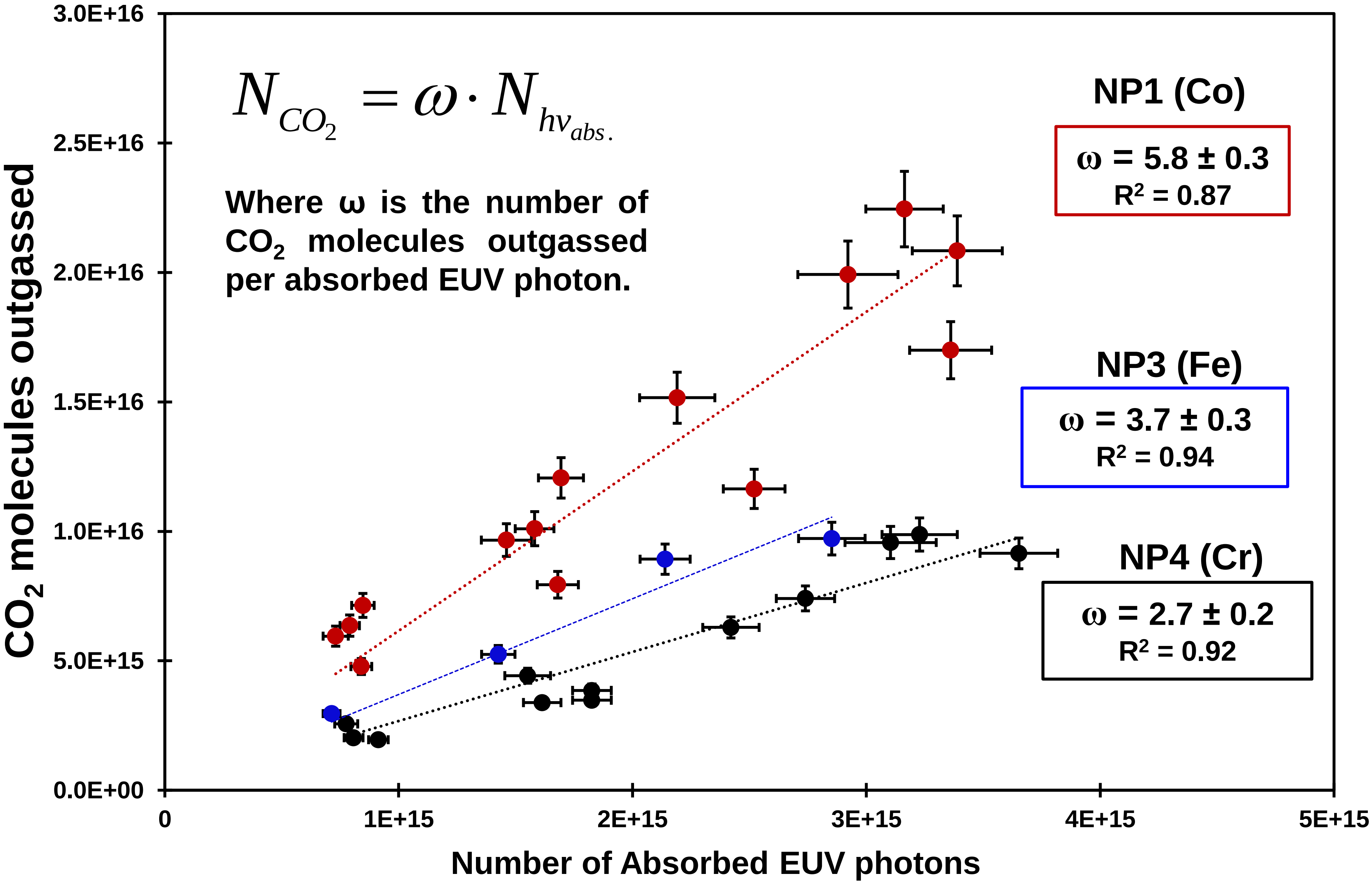




CO_2 Liberated per Incident Electron: 80 eV



CO_2 Liberated per Absorbed EUV Photon



$$N_{CO_2} = \omega \cdot N_{h\nu_{abs.}}$$

Where ω is the number of CO_2 molecules outgassed per absorbed EUV photon.

NP1 (Co)

ω = 5.8 ± 0.3
R^2 = 0.87

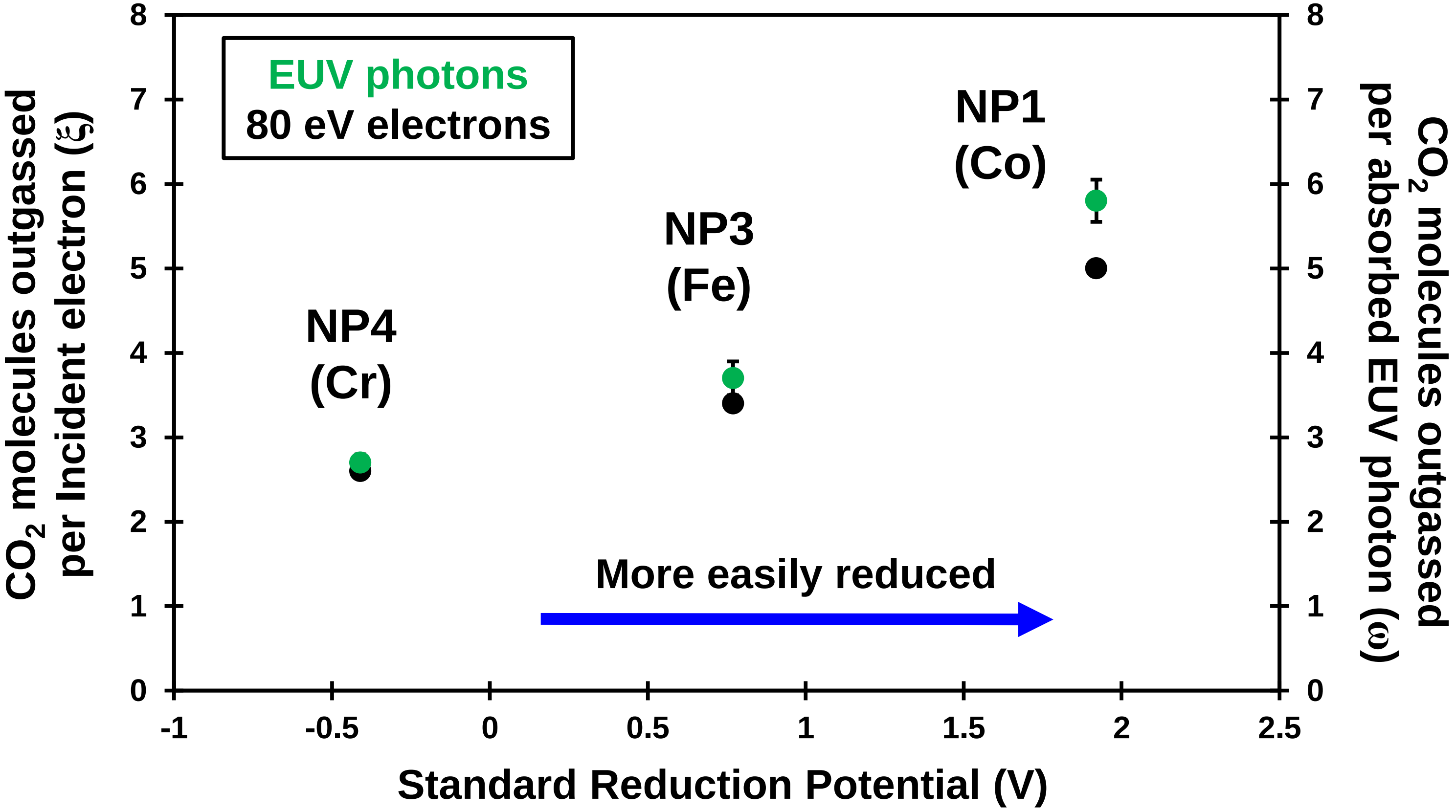
NP3 (Fe)

ω = 3.7 ± 0.3
R^2 = 0.94

NP4 (Cr)

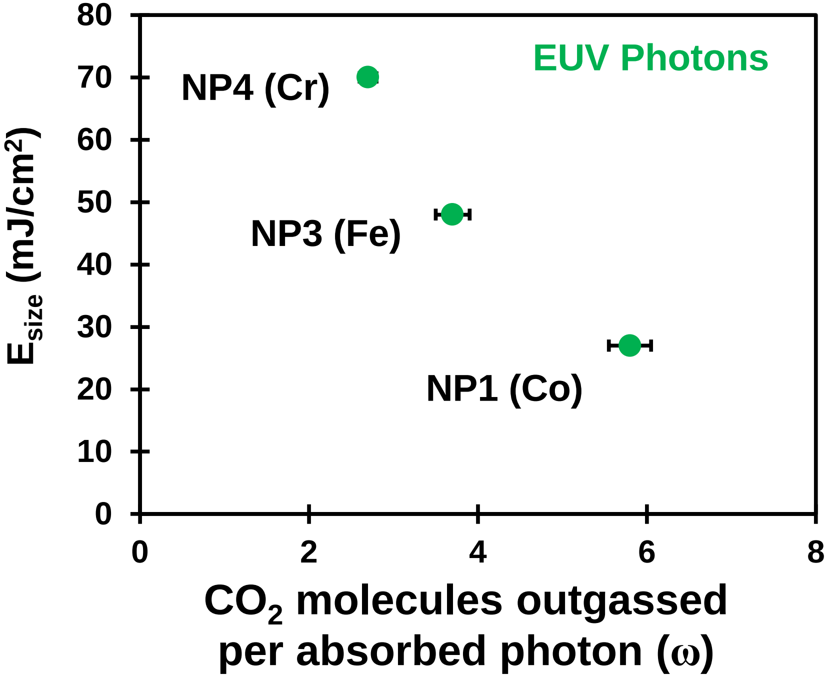
ω = 2.7 ± 0.2
R^2 = 0.92

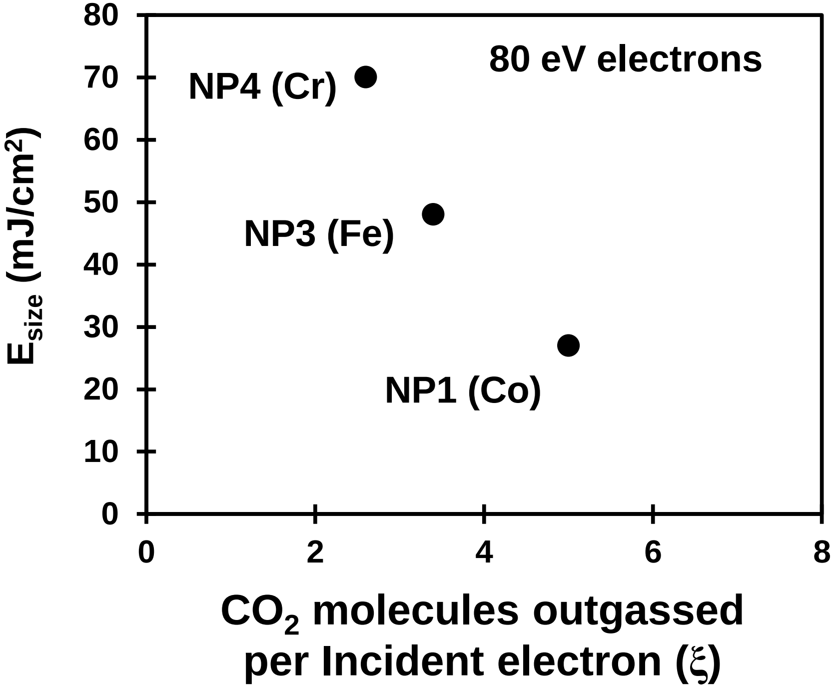
CO_2 Outgassing *vs. Metal Reducibility*



- More easily reduced molecule outgasses more CO_2.
- This could explain the change in E_{size} when varying the central metal.

Conclusions





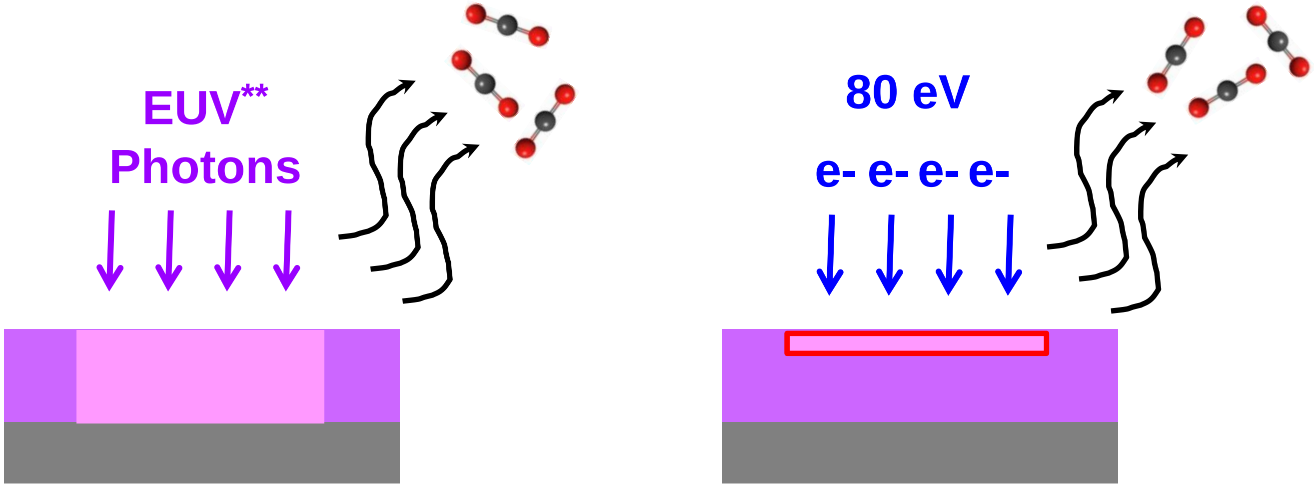
- Between the three photoresists, a small change in EUV absorption does not account for the large change in E_{size}.
- Based upon our understanding of the photo-mechanism increased CO_2 outgassing should improve sensitivity.
- The rate of CO_2 outgassing seems to be correlated to the reducibility of the central metal.

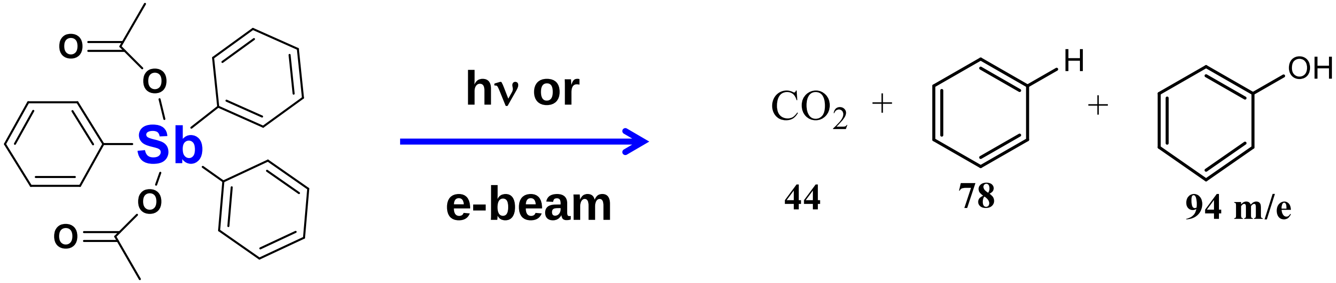
Monday 2:00-2:20 pm**,**

“EUV exposure mechanisms of antimony resists,**”**

Presentation by Michael Murphy (10143-3)

III. Mechanistic Studies of Antimony Resists



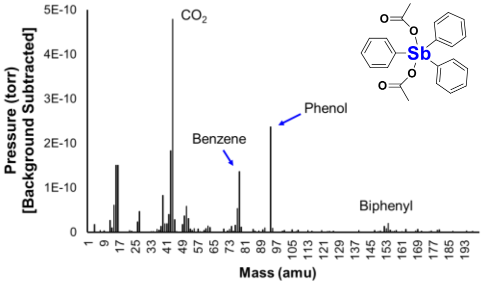


We Exposed Antimony Resists using EUV and E-beam (80 eV) Following Reactions using Mass Spectroscopy.*

*S. Grzeskowiak et al.; J.Vac. Sci.Tech. B 33, 06FH01 (2015).

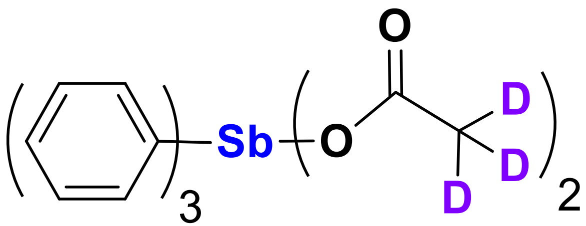
**EUV generated by Xenon plasma source

III. Mechanistic Studies of Antimony Resists



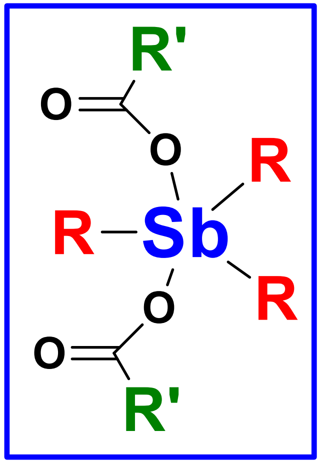
Study #1:

- Reaction monitoring via outgassed products



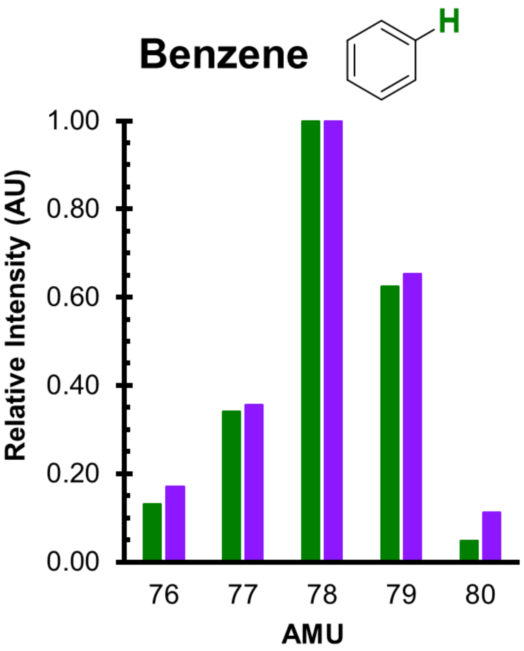
Study #2:

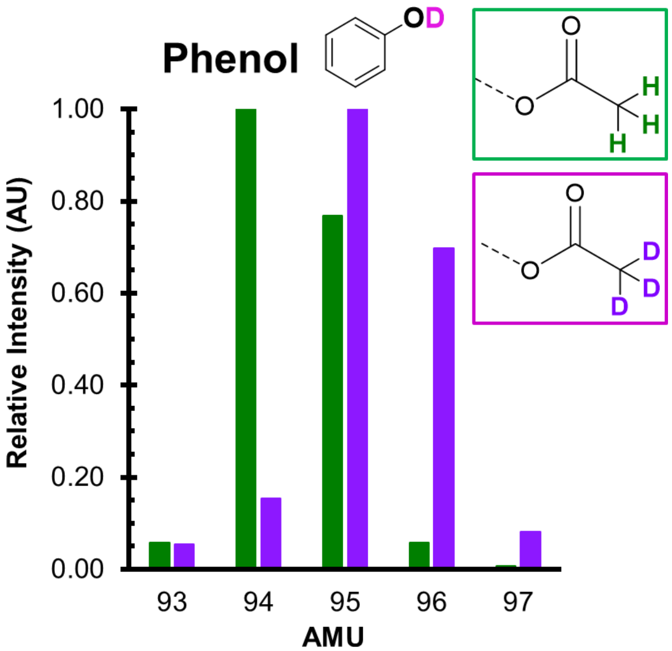
- Deuterium labeling, site of Hydrogen Abstraction



Each complex abstracts a specific proton with 95% isotopic purity:

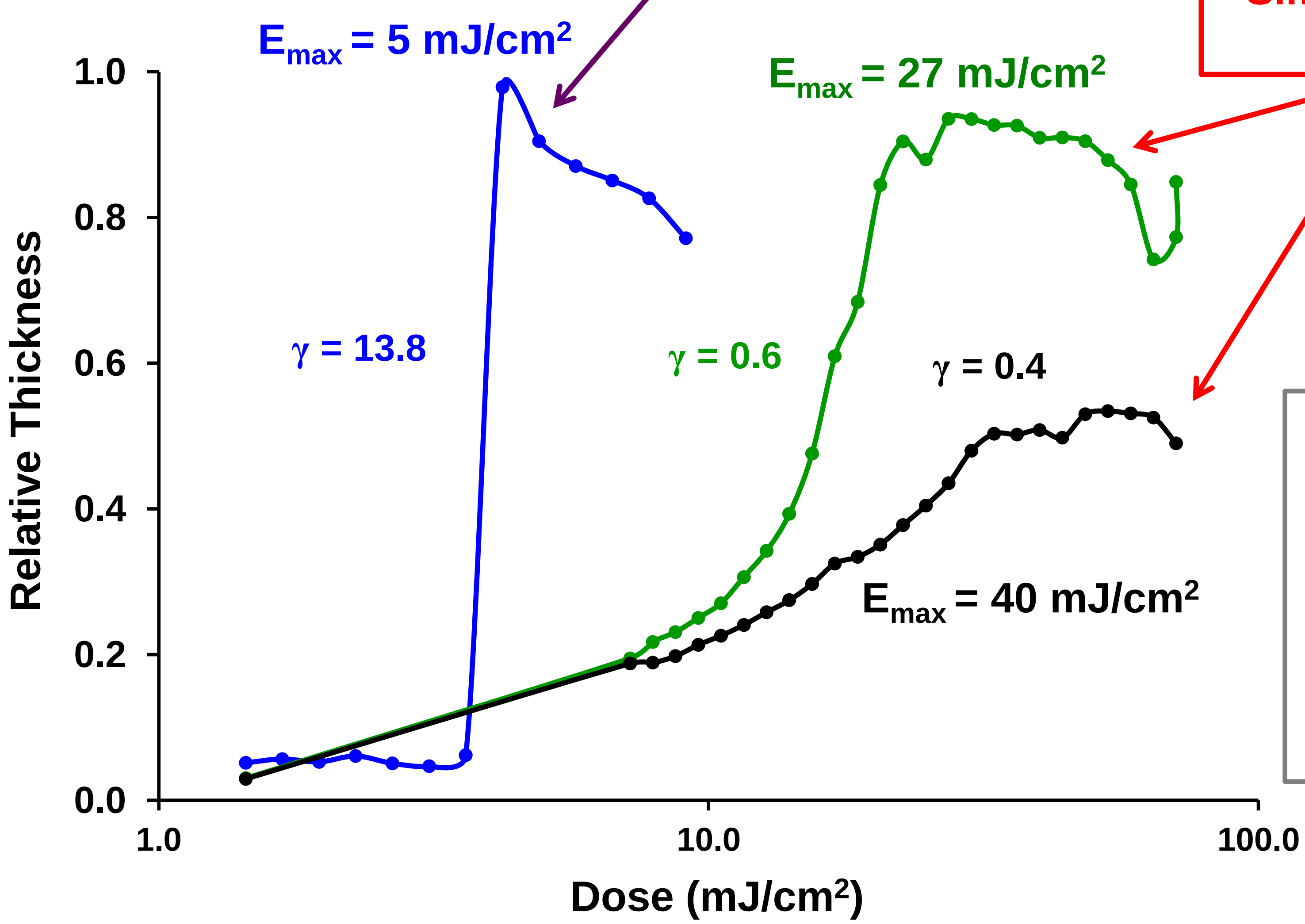
- **Benzene from phenyl ligand**
- **Phenol from acetate ligand**





Monday 3:20-3:40 pm**,**
“Advanced development techniques for metal-based EUV resists,”
Presentation by Jodi Hotalen (10143-5)

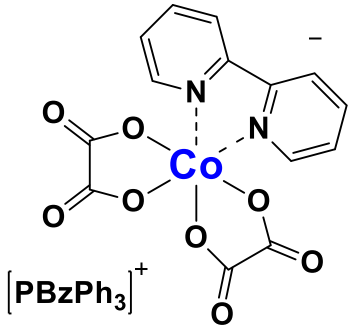
Optimizing Development of Metal-Based Resist



Reactive Developer

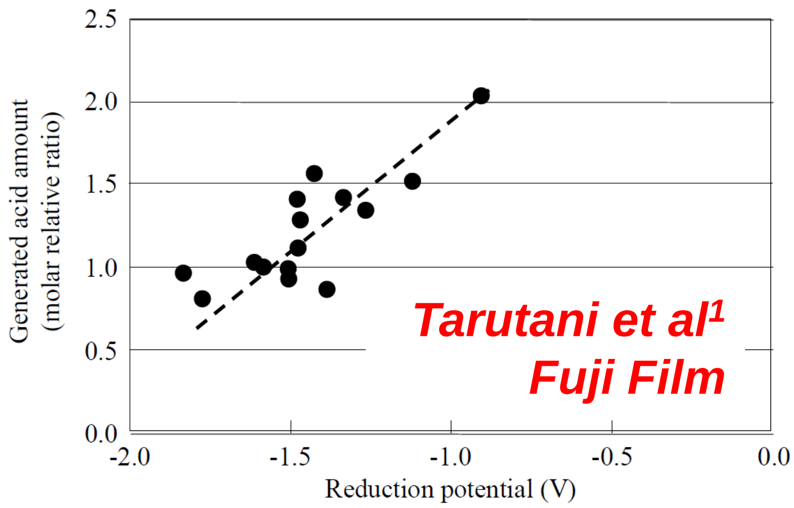
Simple Organic Solvents

Resist: NP1



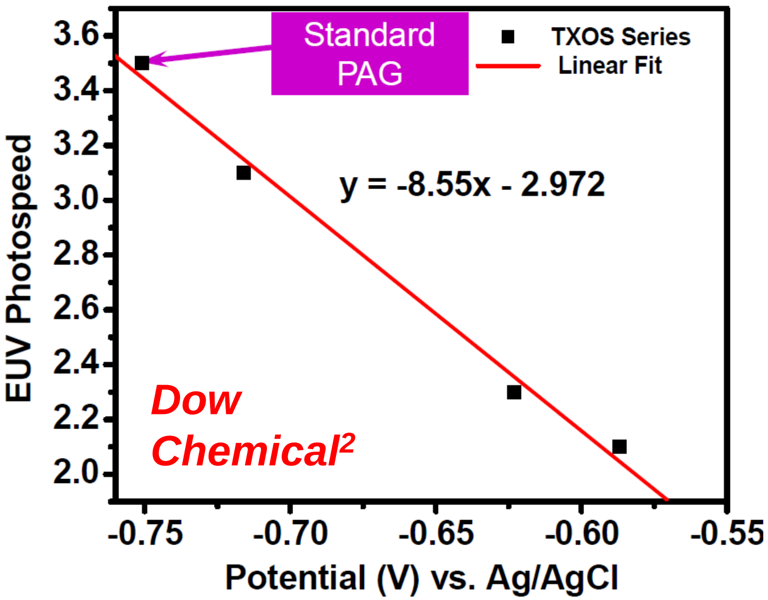
Wednesday 10:40-11:00 am, **“Mechanisms of EUV exposure: electrons, holes, and molecular interactions**,” Presentation by Amrit Narasimhan (10143-28)

IV. PAG Reduction Potentials

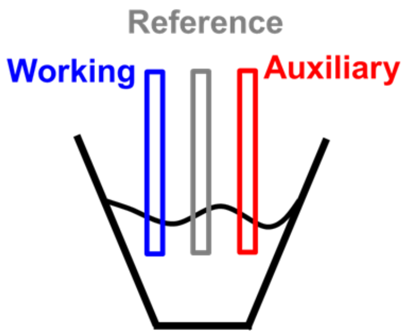


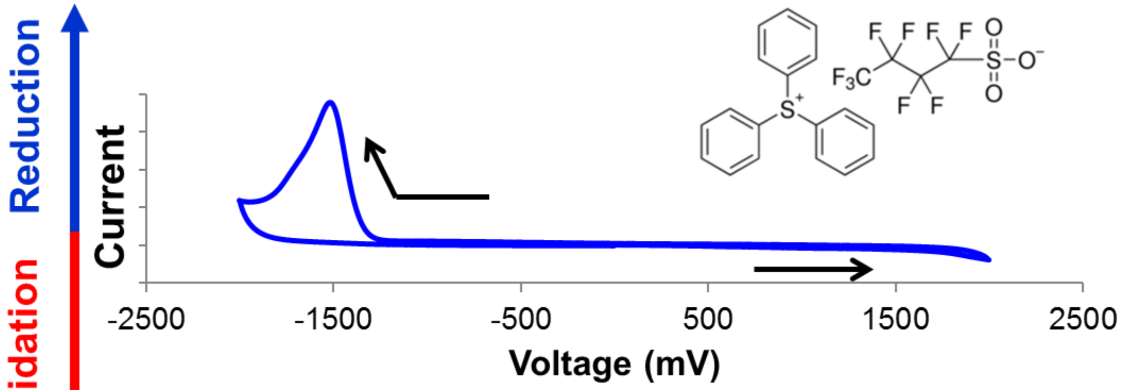
Tarutani et al[1]
Fuji Film

Fig. 4. Relation between reduction potential and acid generation yield.



Dow Chemical[2]





Reduction: A molecule gains an electron
Oxidation: A molecule loses an electron

(1) *Tarutani et al. Photopol 2010*
(2) *Thackeray et al. SPIE 2013*

SUNY POLYTECHNIC INSTITUTE

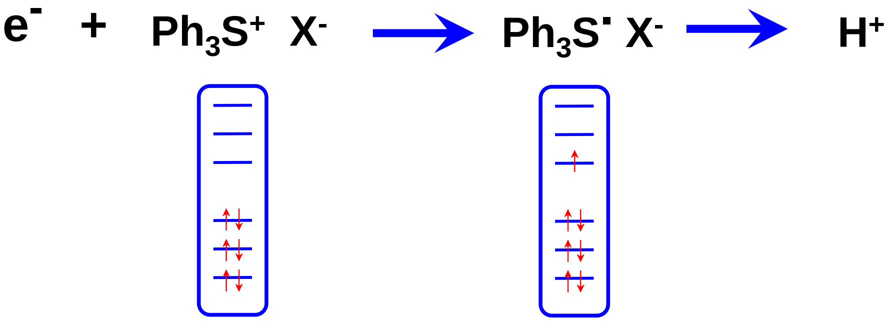
IV. Does PAG + e$^-$ → H$^+$?

Electron Trapping

Electron Trapped by PAG:

e$^-$ + PAG → H$^+$

(ΔE = 2-3 eV)

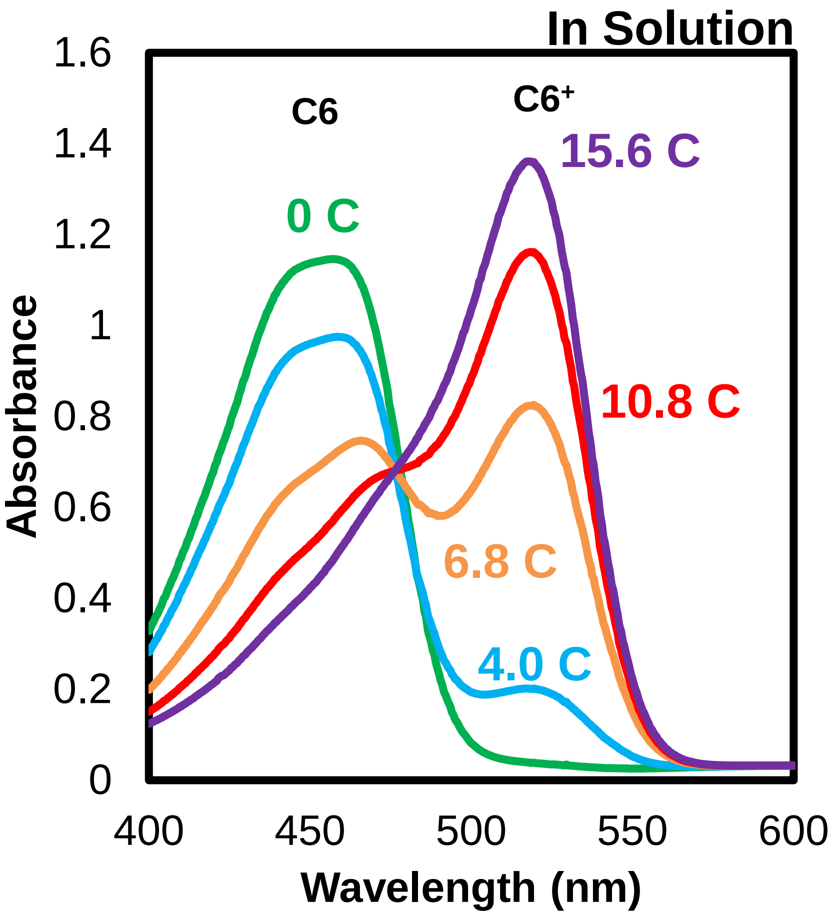


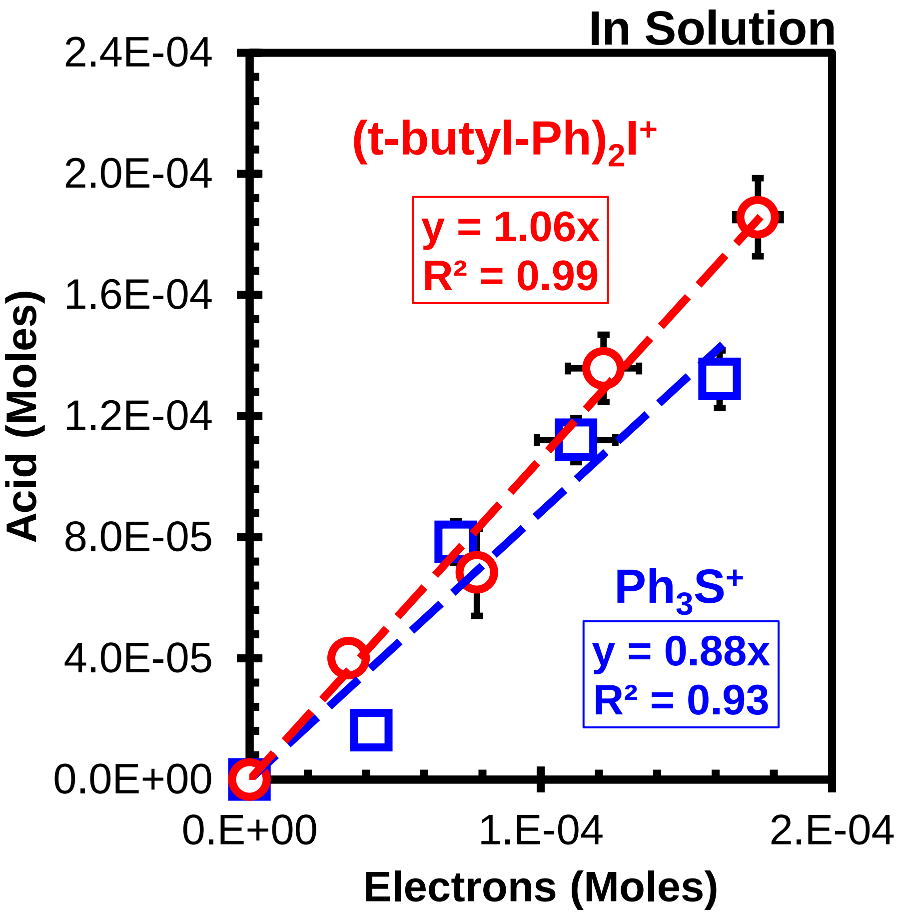
$$e^{-} + Ph_3S^{+}\ X^{-} \longrightarrow Ph_3S^{\cdot}\ X^{-} \longrightarrow H^{+}$$

Bulk Electrolysis with Acid-sensitive dye "indicator":

- Maintain reduction potential
- Extract aliquots and add to Coumarin 6 indicator solution
- Use standard curve to convert absorbance to [H$^+$]

IV. Does PAG + e^- → H^+? Yes!





Bulk electrolysis of PAGs (in Acetonitrile) produces acid