SAND2017-11009PE

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INTERNATIONAL BIOLOGICAL and CHEMICAL THREAT REDUCTION

NON-TRADITIONAL CHEMISTRY RESEARCH: FROM ORGANIC ELECTRONICS TO COOPERATIVE THREAT REDUCTION – WITH A STOP IN EXPLOSIVES ON THE WAY

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October 10, 2017

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A Three Part Series…

- Part I: Graduate School
  - Interdisciplinary Research
  - The Design, Synthesis, and Use of Phosphonic Acids for the Surface Modification of Metal Oxides
- Part II: Explosives
  - Focused Research
  - Another Level of Rigor
  - Opportunities to Support Non-Scientists
- Part III: Cooperative Threat Reduction
  - Non-laboratory Research
  - Opportunity to Support Other Nations

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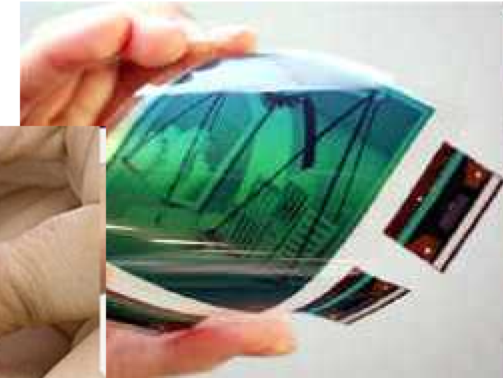
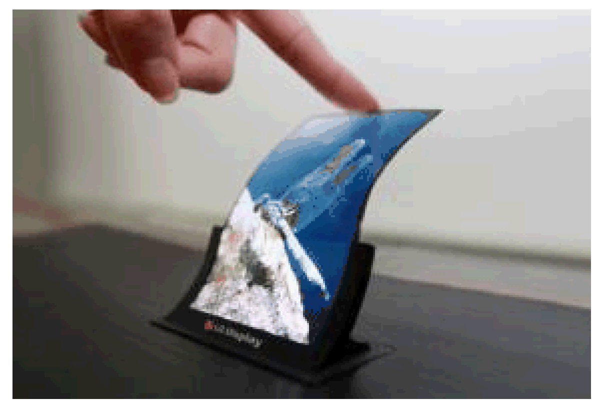
Part I





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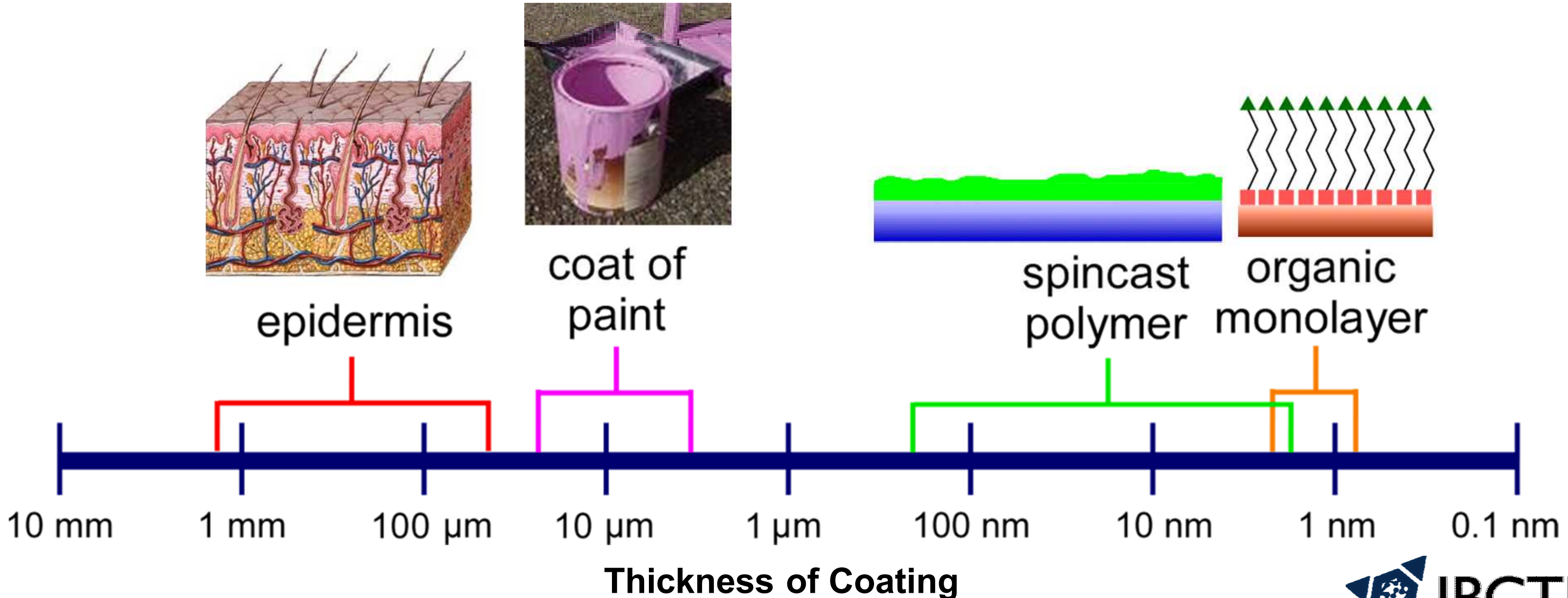
Importance of Surfaces

- Surfaces govern many physical properties of materials
  - Surfaces often play a key role in how materials will interact with each other
- Chemical, physical, electronic, and mechanical properties can all be tuned
- The ability to tune the surface, but maintain a material’s bulk properties, is the foundation of many advanced materials
- One way to modify the surface of a material is to apply a coating of another material.



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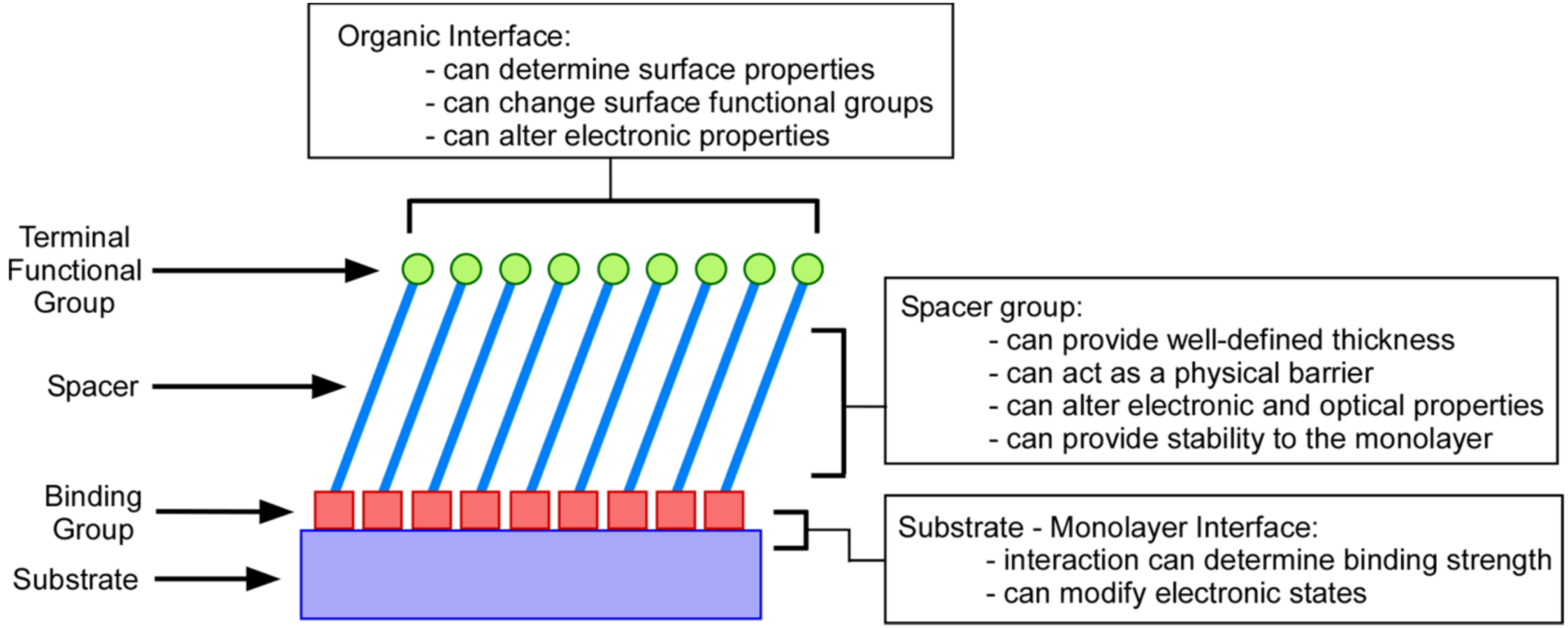
What Can Monolayers Do?



Science of monolayers can be divided into three main parts:

Design and synthesis of ligands

Characterization of monolayers on surfaces

Study of the properties and applications

Love *et al*., *Chem. Rev.* **2005**, *105*, 1103

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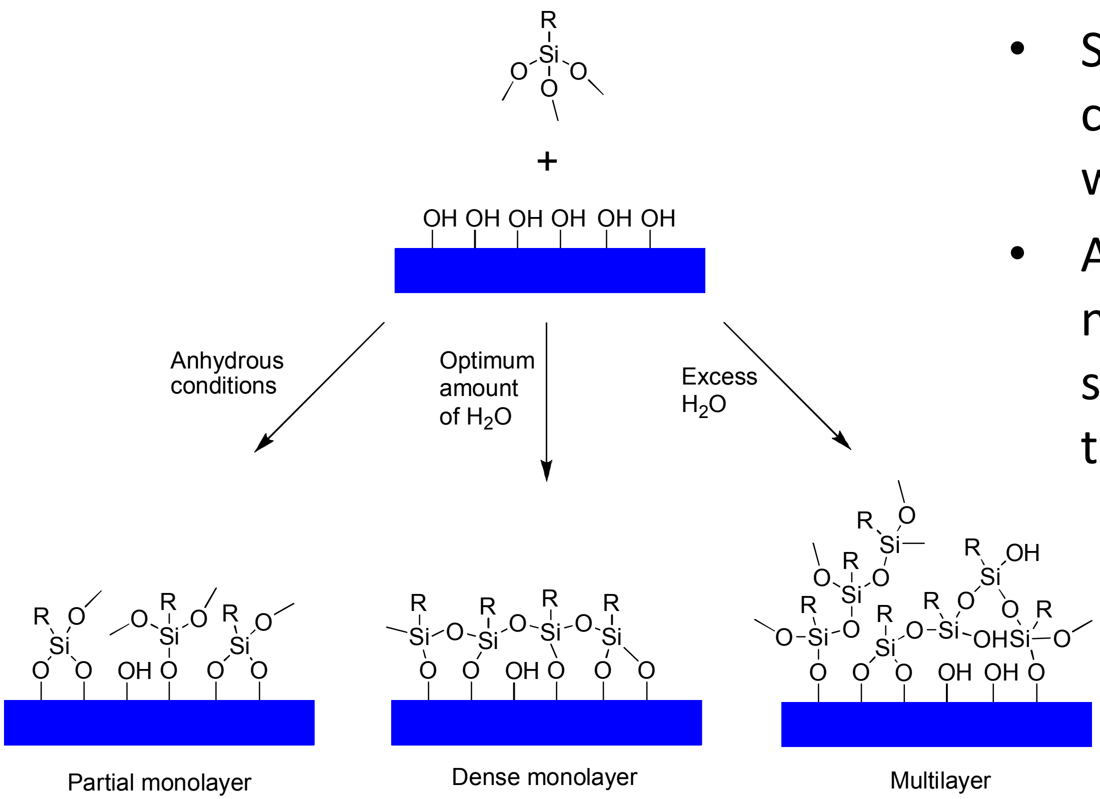
Why Phosphonic Acids?

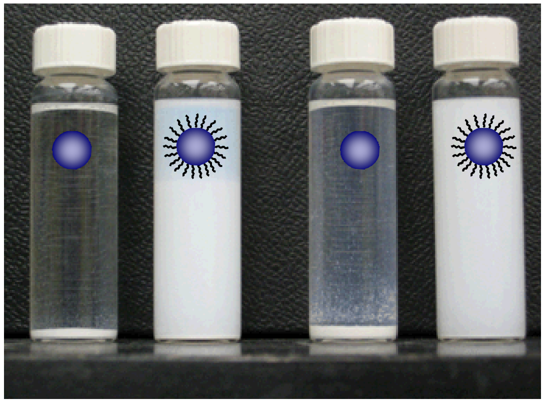
- Can bind to an oxide surface with up to 3 bonds.
- Do not self-condense easily, resulting in less multilayer formation
- Are often crystalline solids and stable in ambient environments, i.e. no special storage necessary



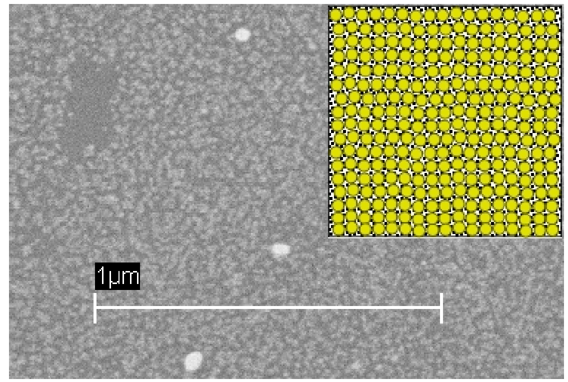
- Surface modification can be completed in the presence of water
- Are effective at reducing the number of OH groups on the surface that can act as charge traps in applications

A Range of Applications

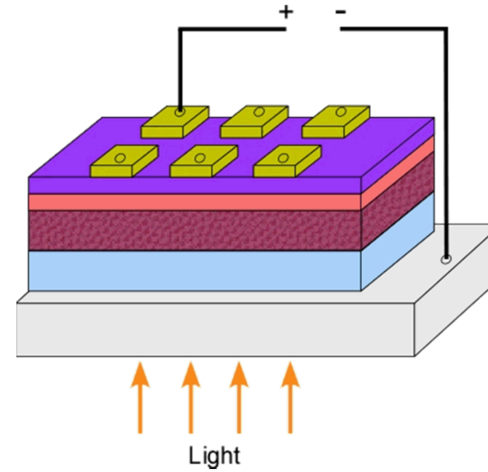
$BaTiO_3$ TiO_2



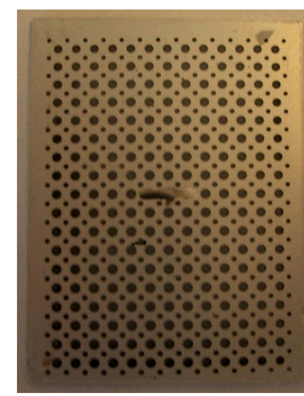
Changing Dispersibility



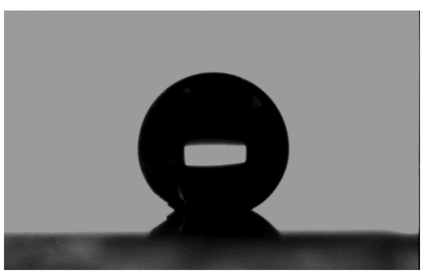
Gold-nanoparticle Templating



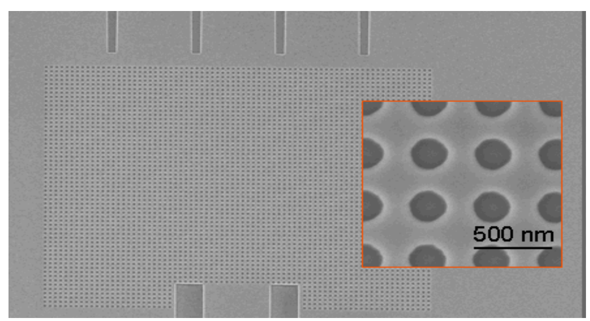
OPVs and OLEDs



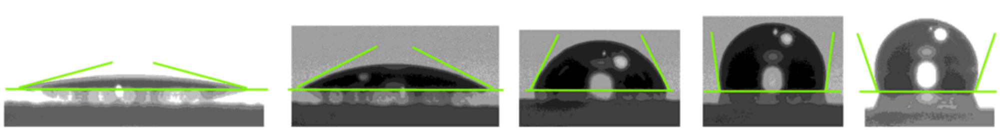
Capacitors



Changing Surface Energy



Planar Photonic Crystals



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General Synthetic Scheme

X = Cl, Br, I

- An S_N2 reaction that works for primary and secondary aliphatic halides (benzyl halides work especially well)
- Does not work for aryl or tertiary aliphatic halides – arylphosphonates can be synthesized *via* other methods
- Synthesis and purification is usually trivial
- Resulting phosphonate is very stable
- Phosphonic acids can usually be recrystallized and/or washed with organic solvents
- Yields are often high

Michaelis, *et al.*, *Chem. Ber.* **1898**, *31*, 1048

Arbuzov, *J. Russ. Phys. Chem.* **1906**, *38*, 687

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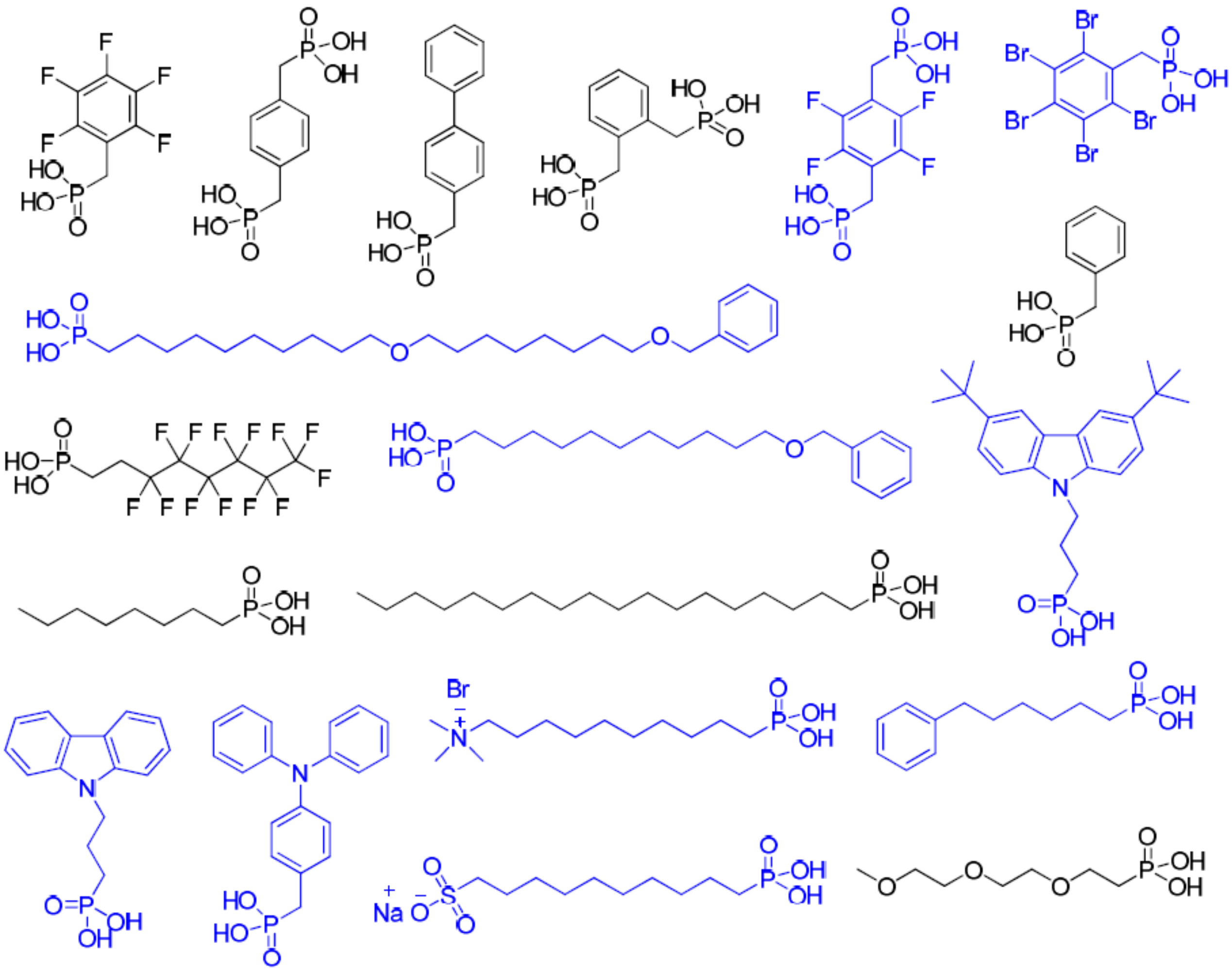
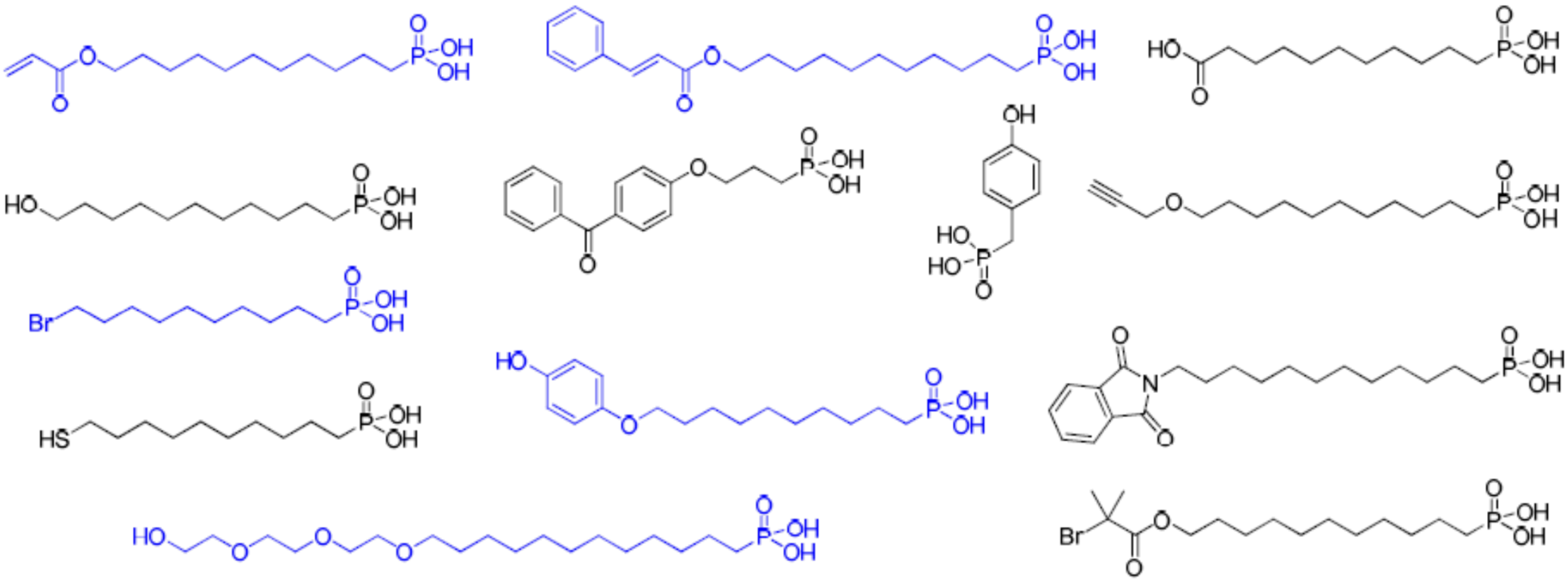
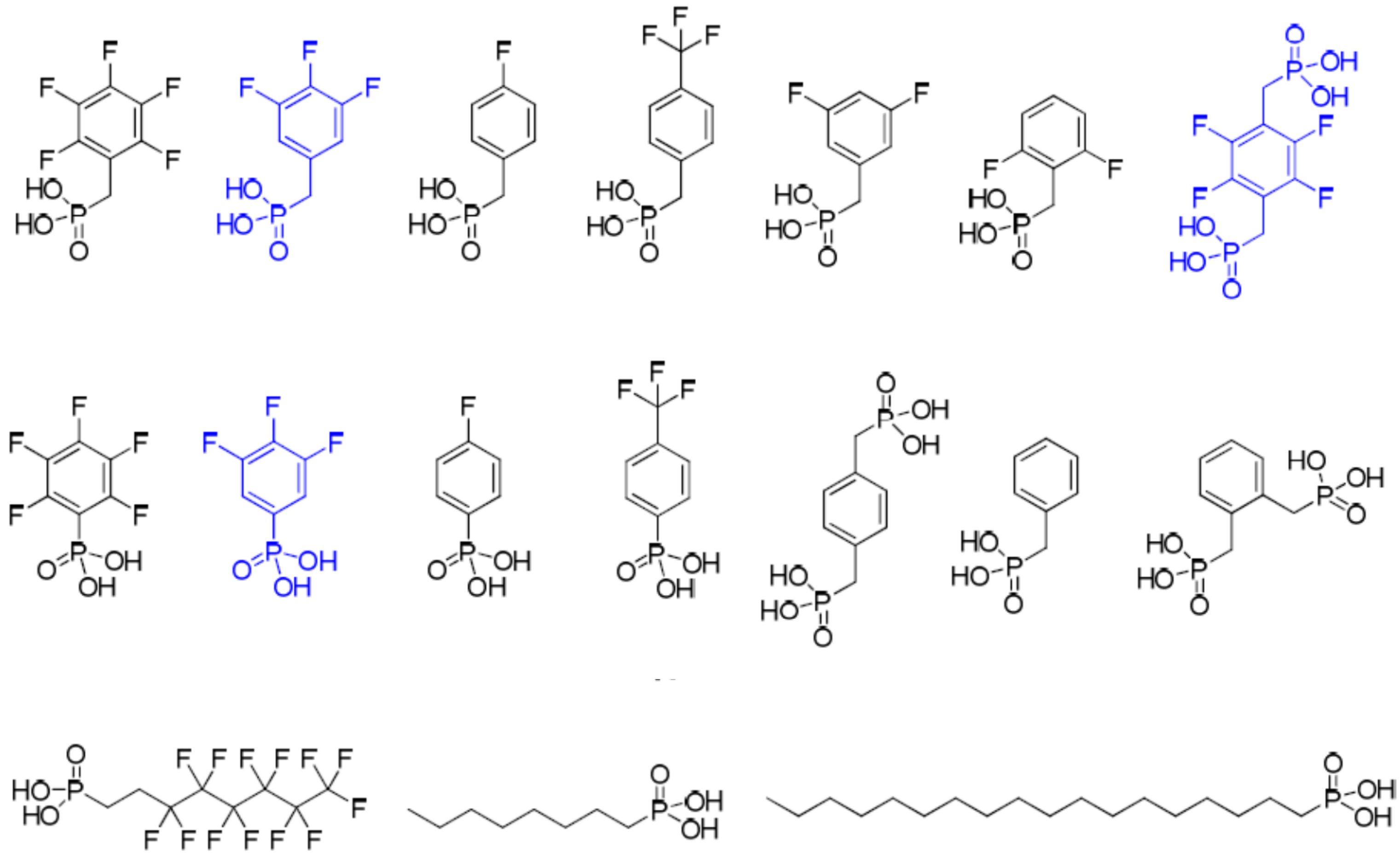
Types of Phosphonic Acids Synthesized



Types of Phosphonic Acids Synthesized

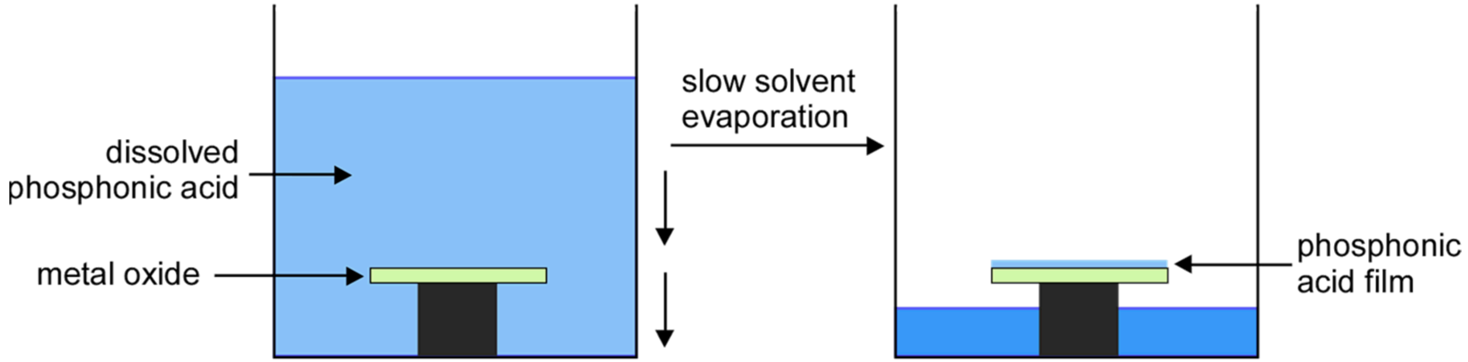


Types of Phosphonic Acids Synthesized



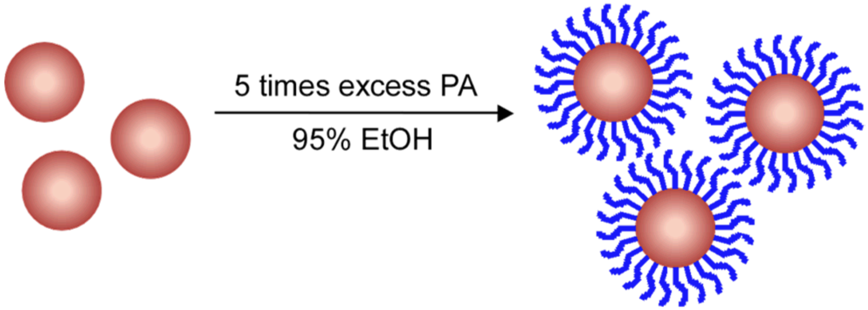
Modifying the Surface

Planar substrates



Important considerations: pre-cleaning of surface, temperature, removal of excess and loosely-bound ligand

Nanoparticles



Important considerations: pre-dispersion of particles, temperature, removal of excess and loosely-bound ligand

Hanson *et al.*, *J. Am. Chem. Soc.* **2003**, *125*, 16074

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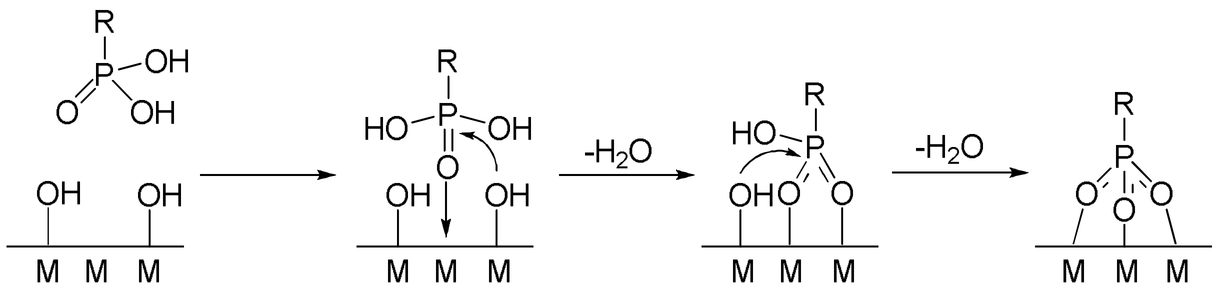
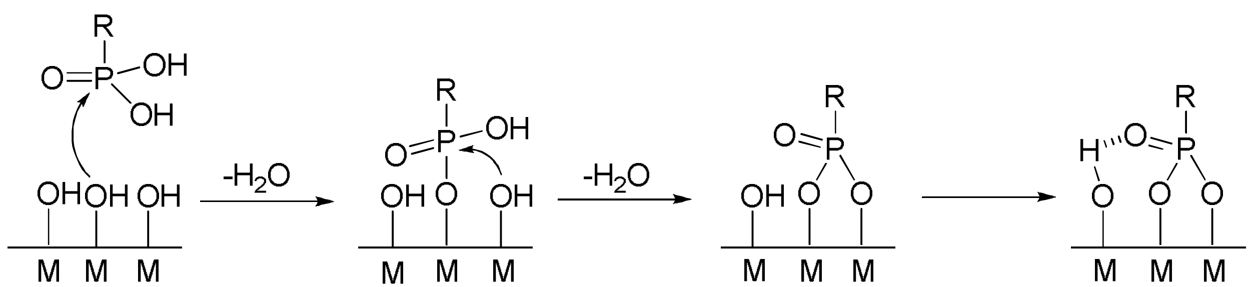
Proposed Mechanism of Attachment



- Coordination of phosphoryl group to Lewis acid site on surface
- Heterocondensation



- Heterocondensation

Important factors: cleanliness of surface, Lewis acidity, surface hydroxyl content, heat

Brodard-Severac *et al.*, *Chem. Mater.* **2008**, *20*, 5191

Guerrero, *et al.*, *J. Mater. Chem.* **2005**, *15*, 3761

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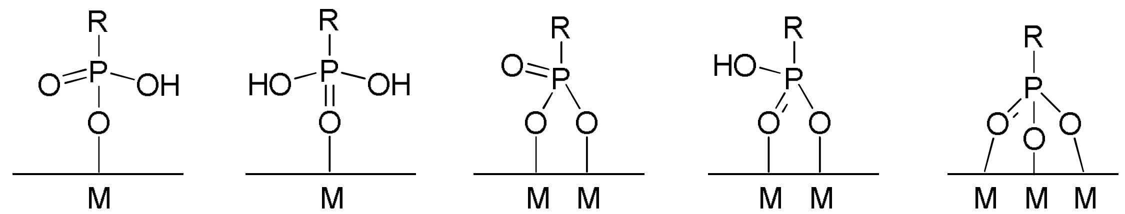
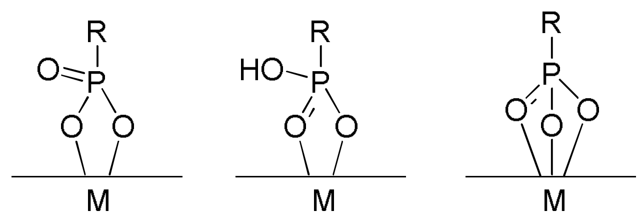
Possible Binding Modes

Monodentate, Bridging Bi- and Tridentate



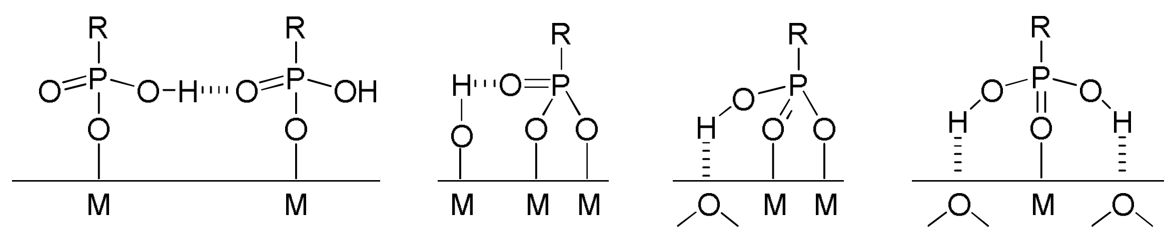
a **b** **c** **d** **e**

Chelating Bi- and Tridentate



f **g** **h**

Some Possible Additional Hydrogen Bonding



i **j** **k** **l**

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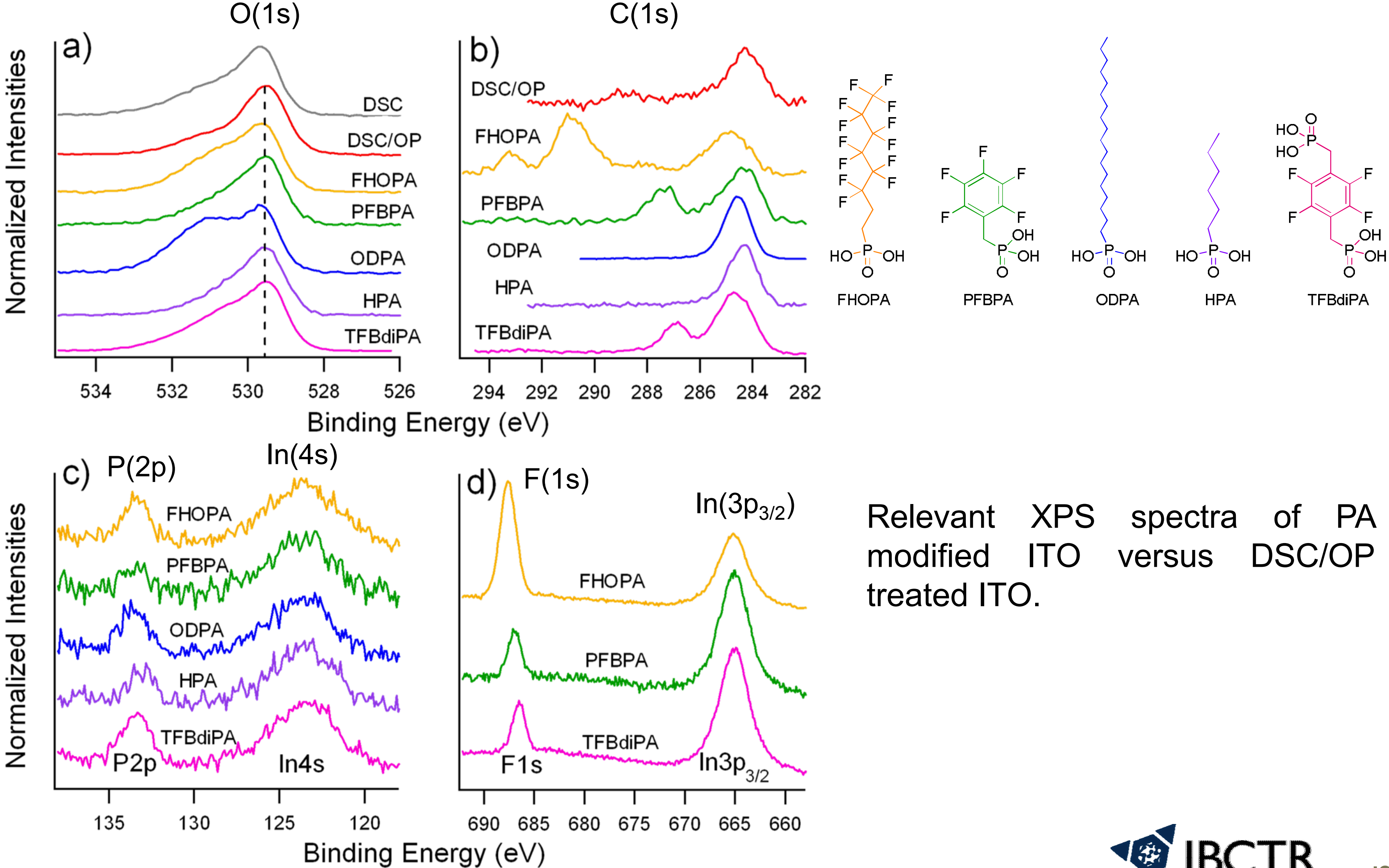
Brodard-Severac *et al*., *Chem. Mater.* **2008**, *20*, 5191

XPS Analysis



Relevant XPS spectra of PA modified ITO versus DSC/OP treated ITO.

Paniagua *et al.*, *J. Phys. Chem. C.* **2008**, *112*, 7809

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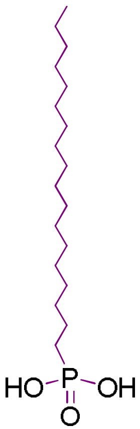
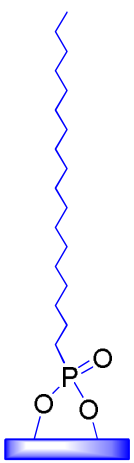
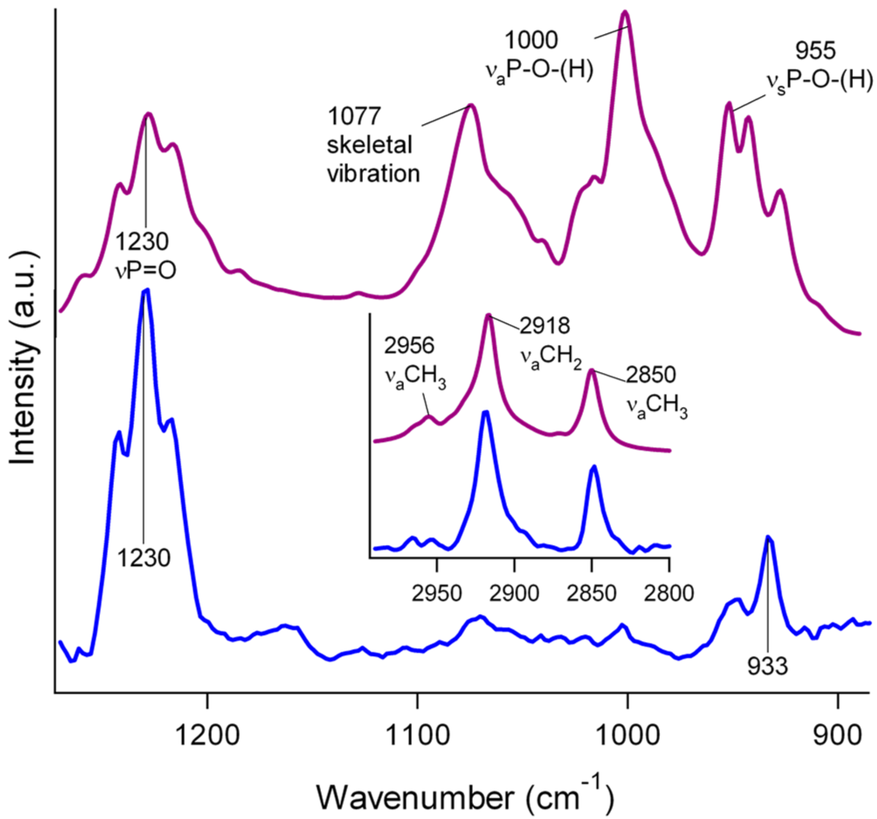
IRRAS Studies



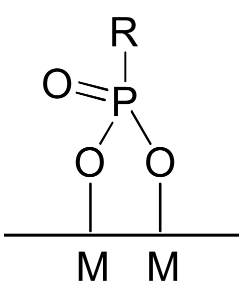
FTIR



PM-IRRAS



- Infrared Reflection Absorption Spectroscopy (IRRAS) can be used to study the binding sites of PAs to surfaces
- IRRAS of ODPA on ITO indicates a primarily bidentate bonding to the surface



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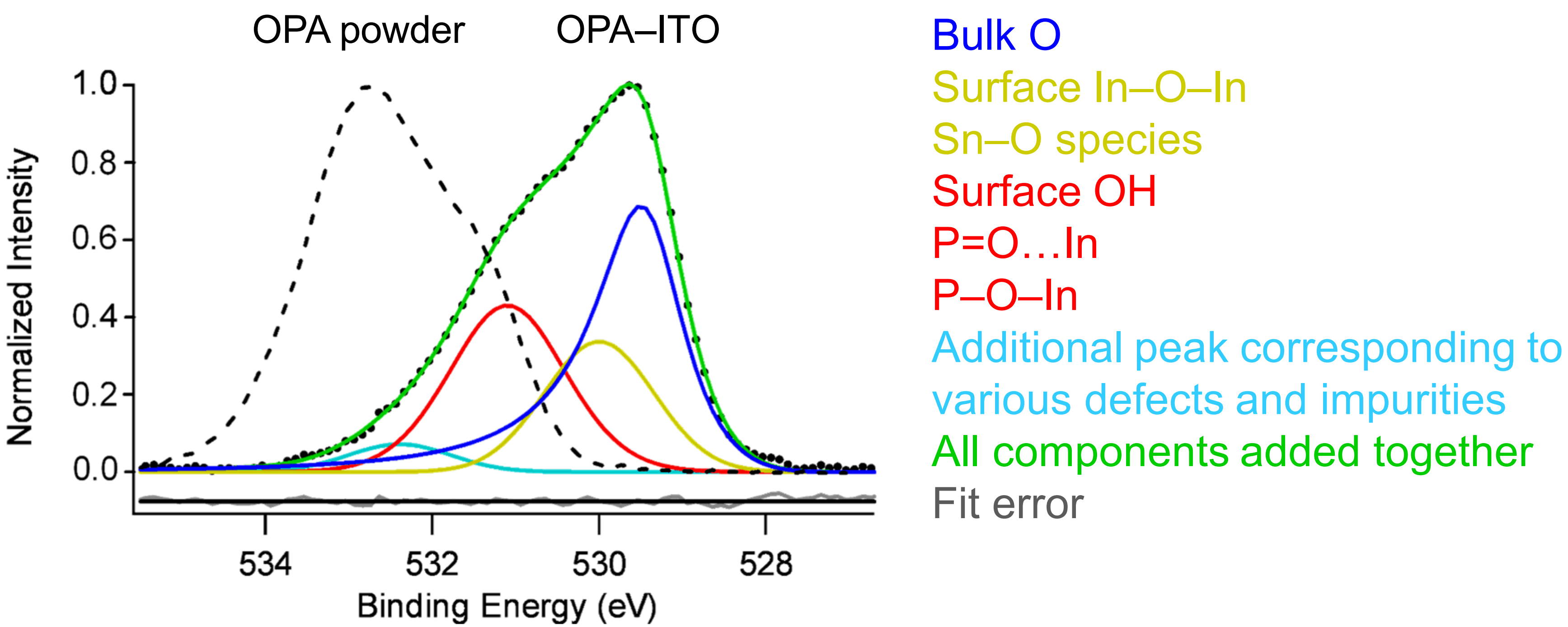
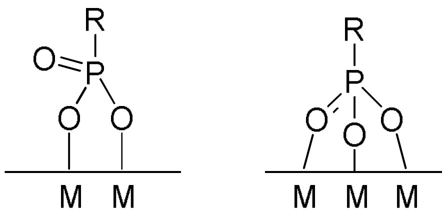
Paniagua *et al*., *J. Phys. Chem. C.* **2008**, *112*, 7809

XPS Analysis



- O(1s) peak of OPA on ITO is comprised of a number of oxygen species
- Deconvolution of this peak can give insight into the binding mode of PAs on ITO
- The absence of any peak at ~ 534 eV (which would correspond to H-bonded configurations) suggests that bidentate and tridentate binding modes are predominant



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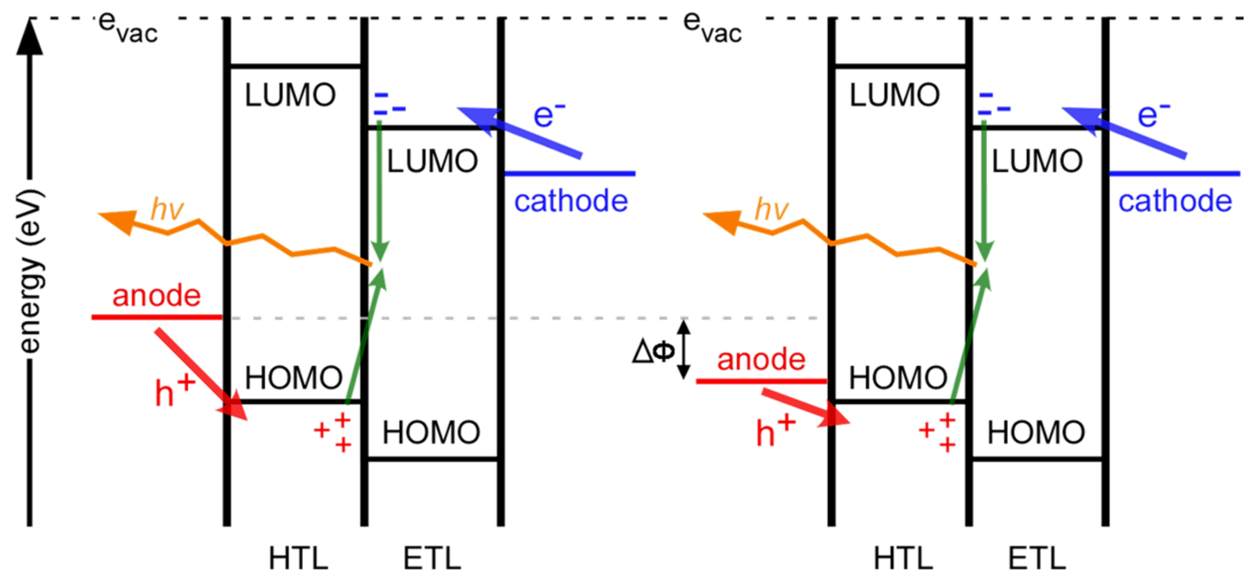
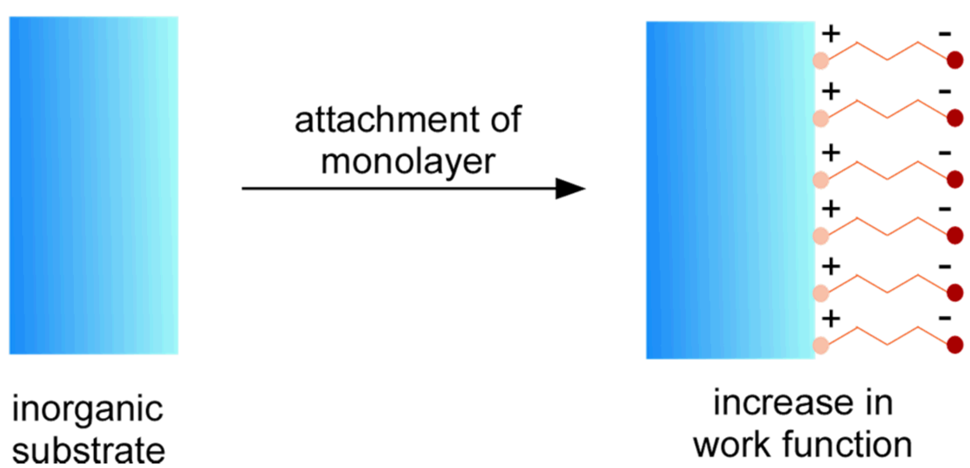
Paramonov *et al*., *Chem. Mater.* **2008**, *20*, 5131

Importance of Work Function





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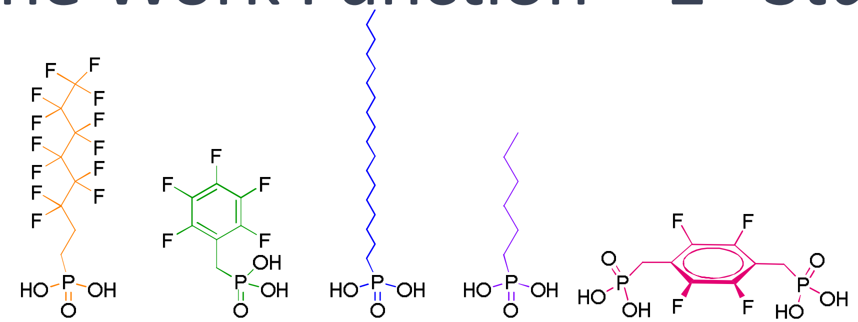
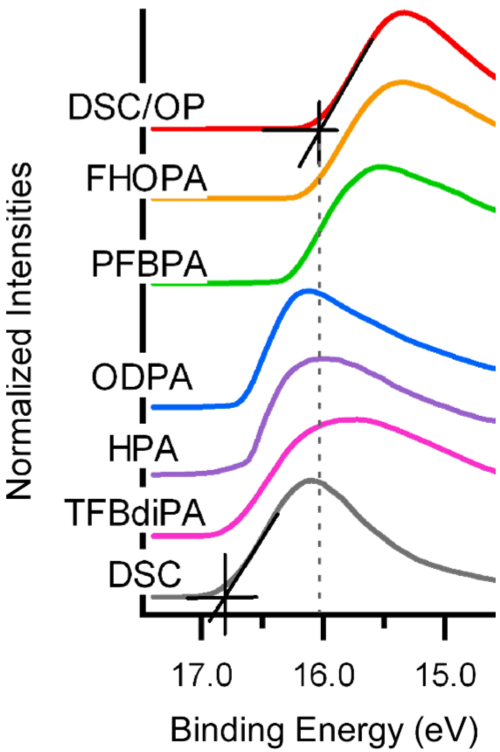
Tuning the Work Function – 1st Study



$$\Phi_m = 21.22 \text{ eV} - B.E.$$

DSC	DSC/OP	FHOPA	PFBPA	ODPA	HPA	TFBdiPA	
4.5	5.1	5.1	4.9	4.5	4.5	4.5	→ **Work Function**



- DSC/OP and FHOPA show the largest increase in work function (+0.6 eV) vs. DSC ITO
- PFBPA shows a slightly smaller increase (0.4 eV)
- ODPA, HPA, and TFBidiPA show no change
- The bond dipole of the PA binding group also plays a role in the overall dipole on the surface

Paniagua *et al.*, *J. Phys. Chem. C.* **2008**, *112*, 7809

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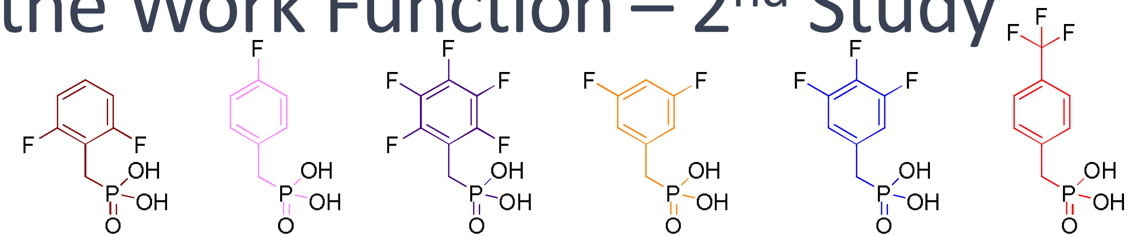
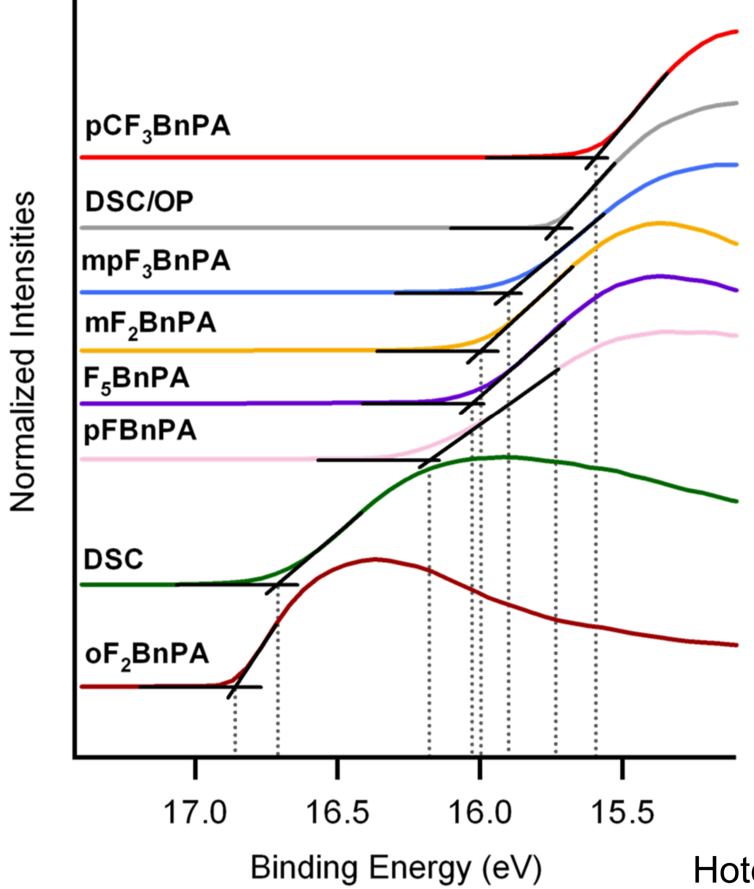
Tuning the Work Function – 2nd Study



DSC	DSC/OP	oF_2BnPA	pFBnPA	F_5BnPA	mF_2BnPA	mpF_3BnPA	CF_3BnPA	
4.5	5.5	4.4	5.0	5.2	5.2	5.3	5.6	⟶ **Work Function**



- pCF_3BnPA shows the largest increase in work function (+1.1 eV) vs. DSC ITO
- pCF_3BnPA shows a slight decrease in work function (-0.1 eV) vs. DSC ITO
- Various other work functions are obtained by varying the fluorination on the ring

Hotchkiss *et al.*, *Adv. Mater.* **2009**, *21(44)*, 4496

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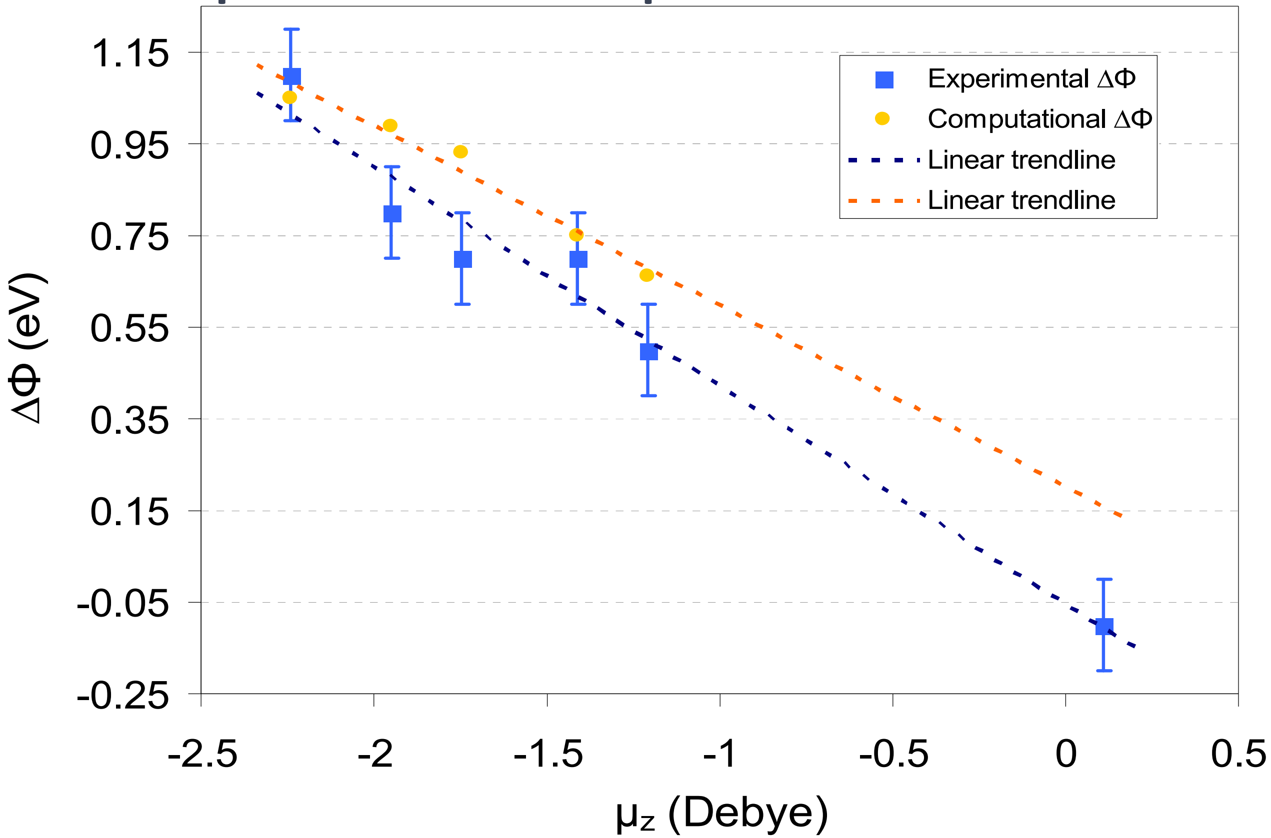
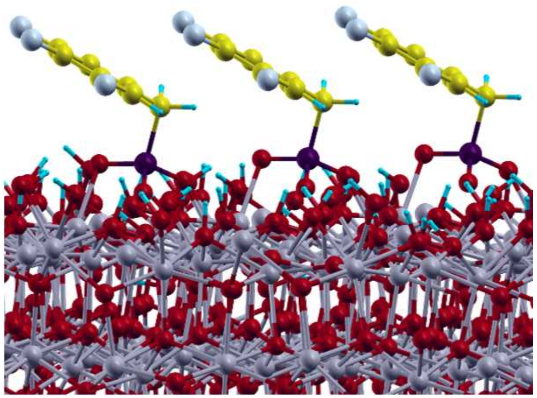
Comparison of Experiment and Theory





The calculated ΔΦ (using a density of coverage of 7.4×10^{13} molecules/cm^2) are slightly larger than those measured experimentally for ITO modified with the same compounds.

The slopes of the experimental data (-0.48 eV/Debye) and the calculated data (-0.39 eV/Debye) are in good agreement.

Hotchkiss *et al*., *Adv. Mater.* **2009**, *21(44)*, 4496

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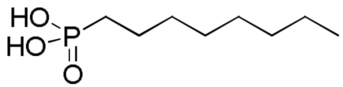
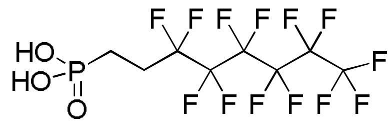
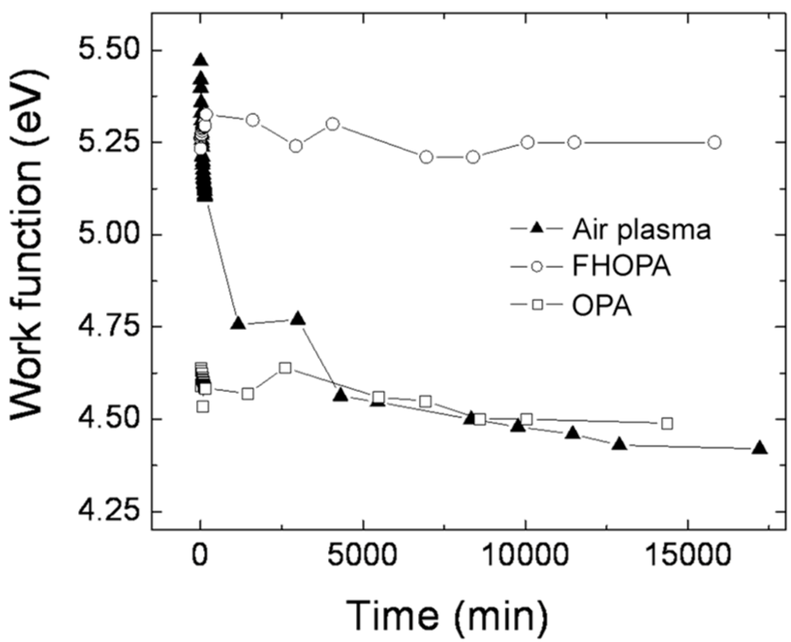
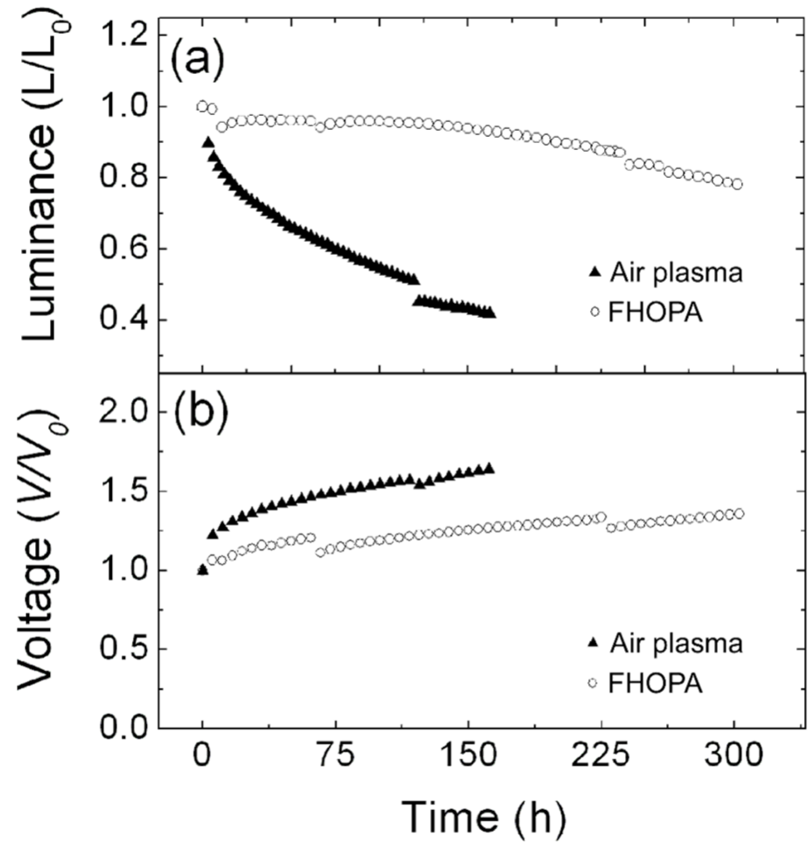
Improved OLED Performance









- Work function change due to OP is reversible
- Work function change due to PA monolayer is stable

- Luminance of fabricated OLEDs shows decreased decay with FHOPA vs. OP treated ITO
- Operating voltage also kept lower

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Sharma *et al*., *Appl. Phys. Lett.* **2008**, *93*, 163308

Surface Energy

- Surface energy is a quantification of the disruption of molecular bonds when a surface is created
- Can be divided into 4 contributing forces:
  - Permanent and induced dipoles, hydrogen bonding (polar component)
  - Instantaneous dipoles (dispersion component)
- Can also think about it in forces of cohesion and adhesion can play a role
- Control over these properties can allow for better interfacial properties between materials

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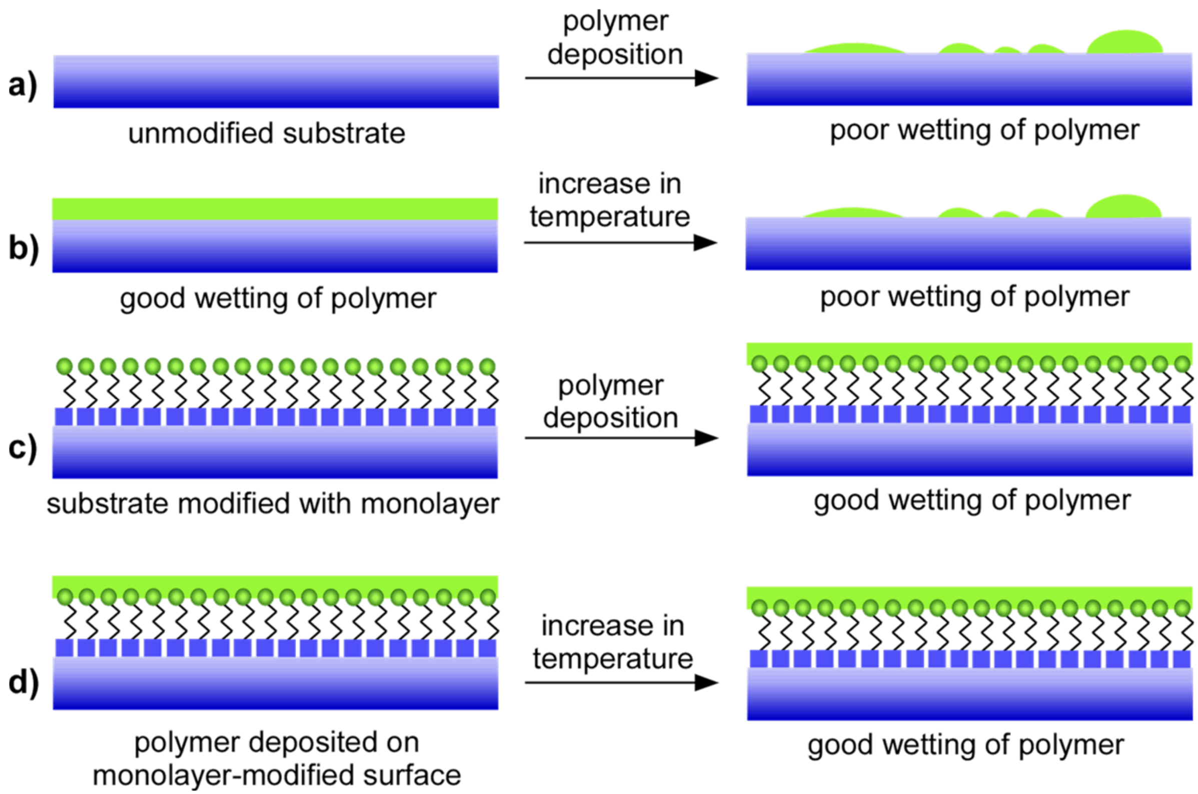
Importance of Surface Energy



- Metal oxides have relatively high surfaces energies and many organic hole-transport materials have relatively low surface energies
- The organic layer can delaminate over time
- Device lifetime and performance could be decreased

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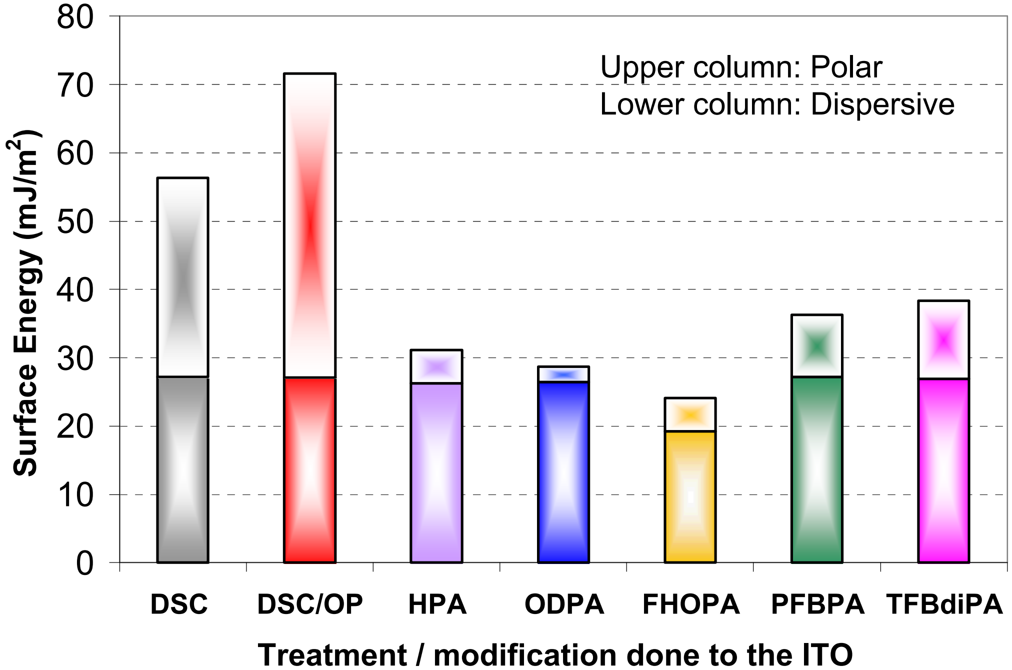
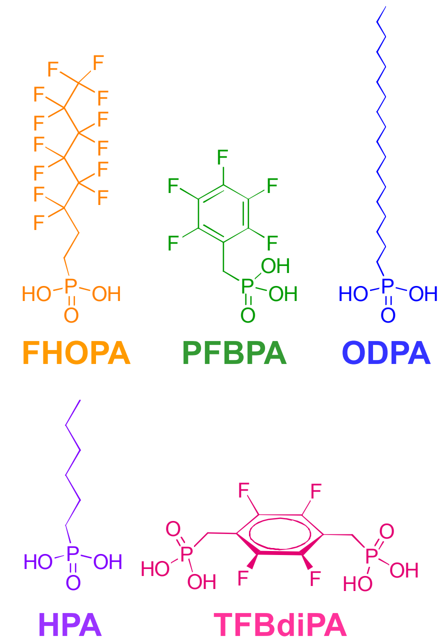
TUNING THE SURFACE ENERGY – 1ST STUDY





Errors on surface energies are ± 1 mJ/m^2

- PA modification of ITO reduces overall surface energy
- Specifically, the polar component is reduced while the dispersive component is kept relatively the same

Many organic hole-transport materials are non-polar

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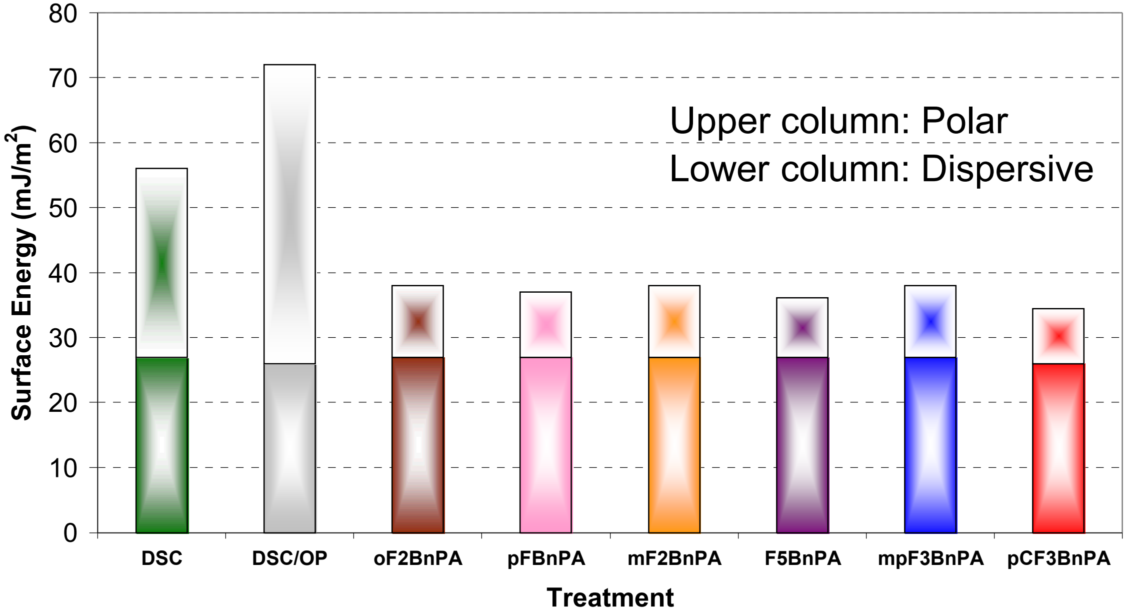
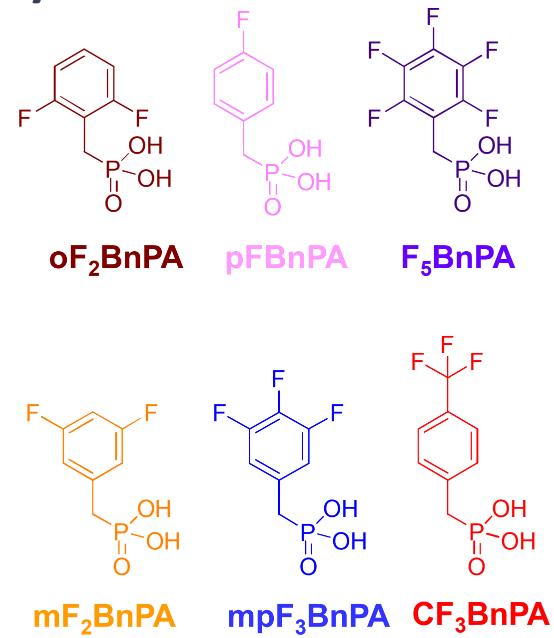
Paniagua *et al*., *J. Phys. Chem. C.* **2008**, *112*, 7809

Tuning the Surface Energy – 2nd Study





Errors on surface energies are ± 1 mJ/m²

- Surface energy can be kept relatively constant (~ 35 ± 2 mJ/m²) regardless of PA modifier used

Work function can be tuned 1.2 eV while keeping the surface energy constant

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Hotchkiss *et al.*, *Adv. Mater.* **2009**, *21(44)*, 4496

Conclusions

- Monolayers can play an important role in the surface properties of materials
- A variety of phosphonic acids (not all shown) can be synthesized with few steps in high yields
- PAs can be used to modify the surfaces of ITO (and other metal oxides)
- PAs bind to ITO *via* bidentate and tridentate bonds
- The functionalized PAs shown can substantially change both the work function and the surface energy of the ITO surface
- Incorporating PA monolayers into OLED devices can improve the luminance and lifetime of the device

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  - Nathan Hankins
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  - Sergio Paniagua (Prof. Neal Armstrong)
  - Dr. Madhava Kosuri (Prof. William Koros)
  - Dr. Asha Sharma (Prof. Bernard Kippelen)
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  - Dr. Chris Corso and Anthony Dickherber (Prof. William Hunt)
  - Bradley MacLeod (Prof. David Ginger)
  - Dr. Bob Norwood
  - Prof. Ken Sandhage
  - Prof. Nils Kröger

Part II – Explosives (Energetic Materials)

- Focused Research
  - Understanding properties
  - New formulations
  - New approaches to research
- Another Level of Rigor
- Opportunities to Support Non-Scientists

Surface Energies of Energetic Materials

- Improved elucidation of the underlying physics which govern the interfacial behavior of explosive materials will enable optimization of explosives detection in checkpoint security applications and improvement in munitions formulation
- Many of these critical interactions have not been evaluated carefully
- Additionally, the relationship between these interactions and the method by which they are characterized has not been examined in detail
- Developing a fundamental knowledge of how various interfacial characterization approaches are related creates a context where results can be appropriately analyzed and utilized

Hoss *et al.*, *J. Colloid Interface Sci.* **2016**, *473*, 28

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Water Droplet on TNT

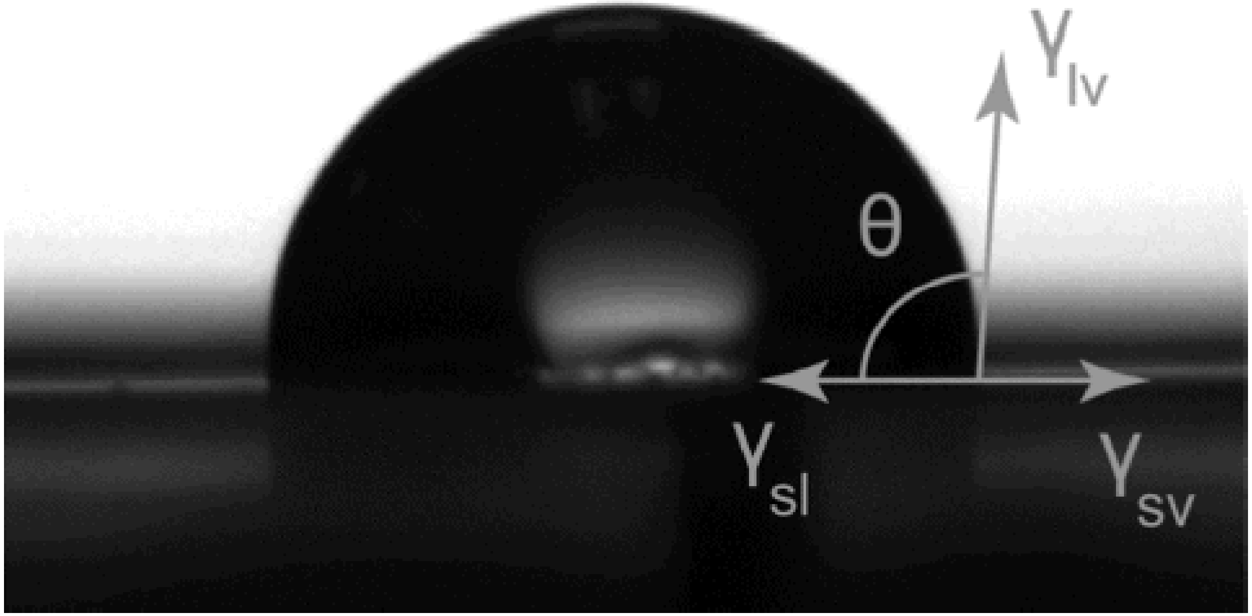

Fig. 1. A droplet of water on a trinitrotoluene (TNT) thin film illustrating the components of Young's equation. In this system, θ is the contact angle, and γ_{lv}, γ_{sv}, and γ_{sl} are the interfacial energies at the water–vapor, TNT-vapor and TNT-water interfaces. The contact angle value is greater than 90°, in agreement with the relatively hydrophobic nature of the TNT thin film.

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Hoss *et al.*, *J. Colloid Interface Sci.* **2016**, *473*, 28

Surface Energies

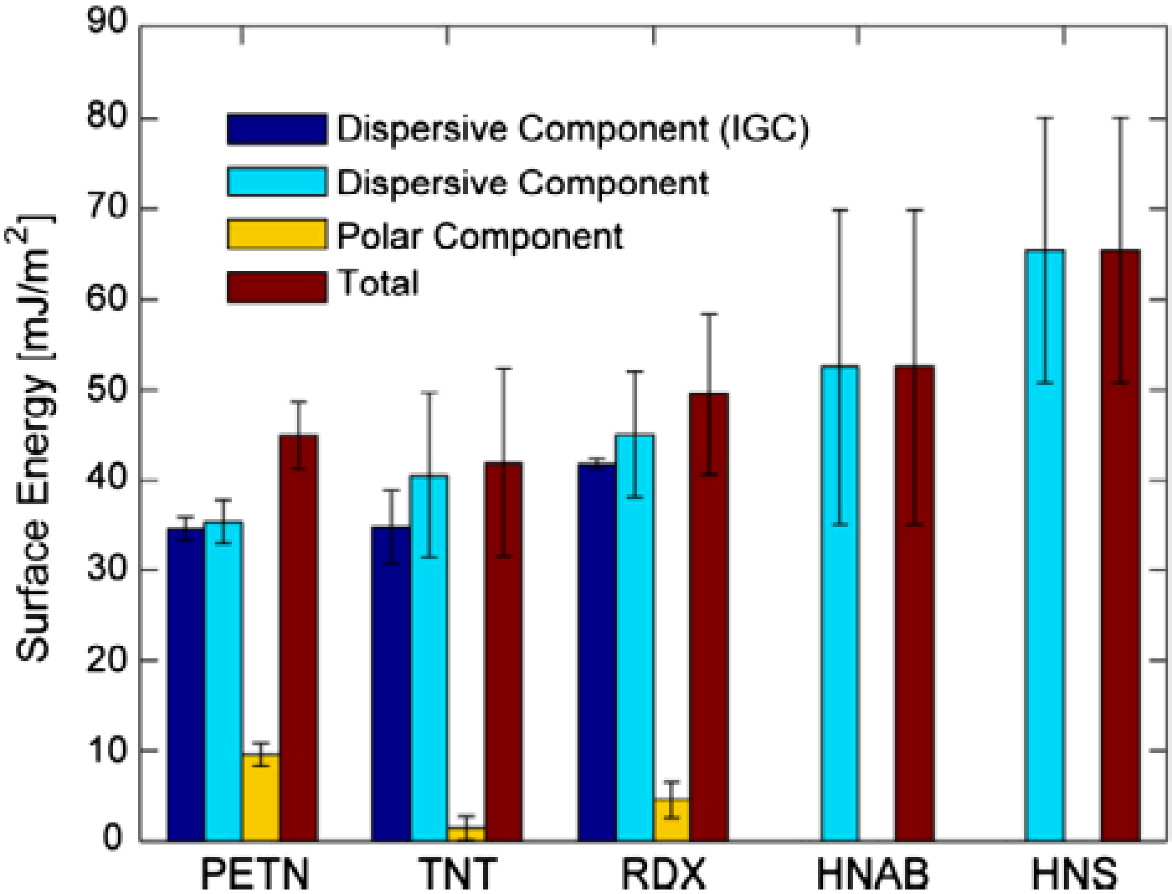

Fig. 3. Surface energy and surface energy components of the energetic materials. The dispersive surface energy components from this study compare well to the dispersive surface energy determined through the IGC method [16]. The dispersive component dominates for each of the films studied. The error bars for the results of this work indicate the 95% confidence interval of regression coefficients. The IGC dispersive component error bars indicate a 95% confidence interval around the mean values.

Hoss *et al*., *J. Colloid Interface Sci.* **2016**, *473*, 28

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Triaminotrinitrobenzene (TATB)

- The molecular crystal explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is attractive from a safety perspective due to its extreme insensitivity to accidental initiation
- Several research groups have demonstrated that formulations and 'neat' pellets pressed from smaller particle TATB powders exhibit increased sensitivity [3–5] and improved detonation spreading
- Sensitivity is inversely linked to the inherent safety of explosive devices, motivating research aimed at optimizing the balance between ease of purposeful initiation and safety
- Our approach was to develop a means to tailor the initiation properties of TATB by controllably modifying the particle size and morphology of the powder.

Hotchkiss *et al.*, *Propellants Explos. Pyrotech.* **2014**, *39(3)*, 402

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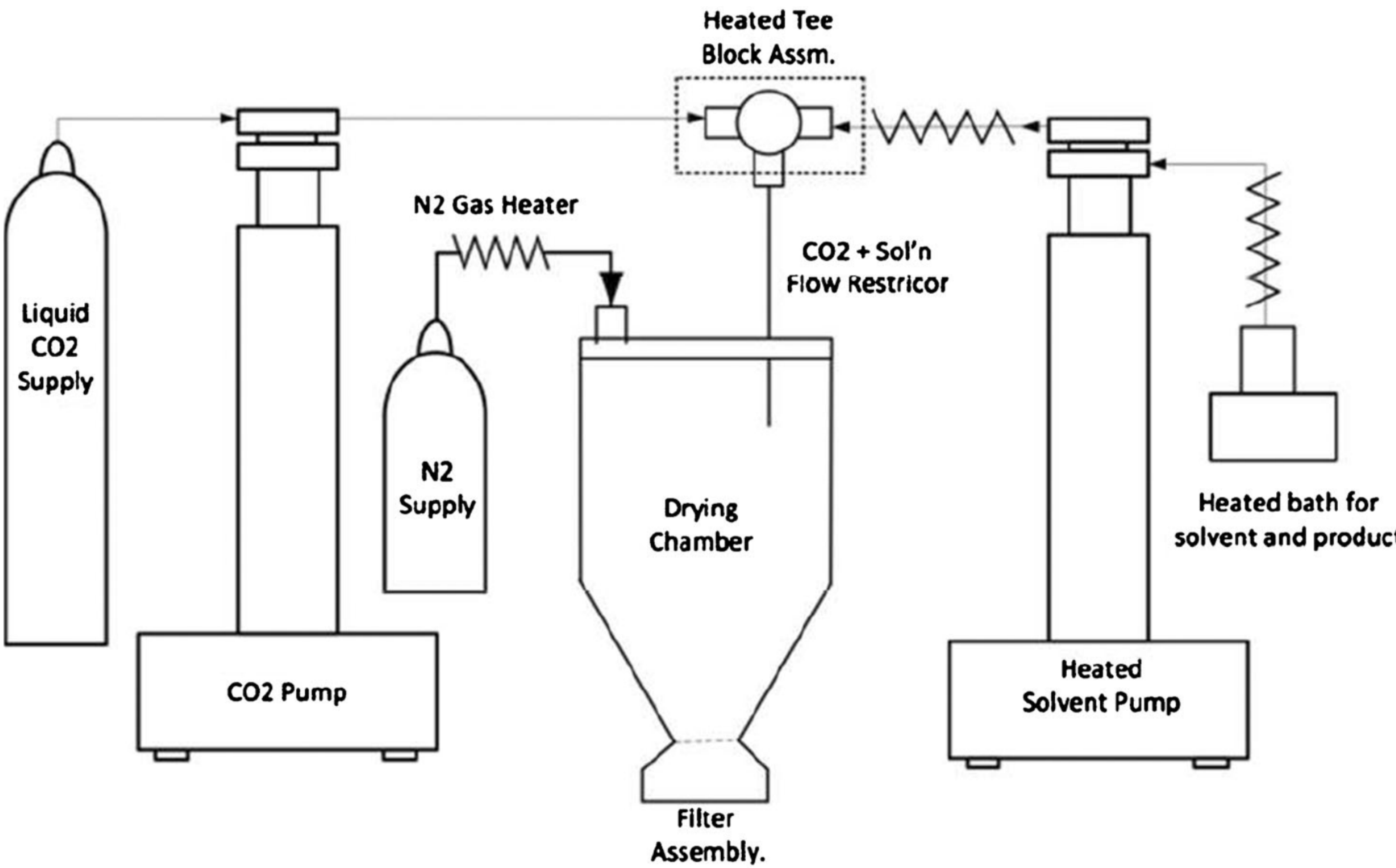
Carbon Dioxide Assisted Nebulization with a Bubble Dryer



Drawing of CAN-BD setup used

Hotchkiss *et al*., *Propellants Explos. Pyrotech.* **2014**, *39(3)*, 402

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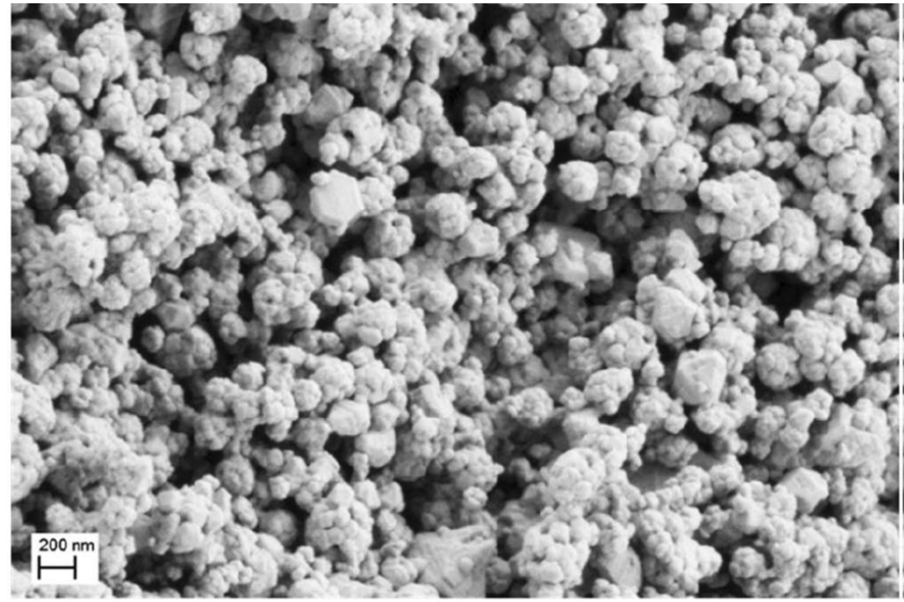
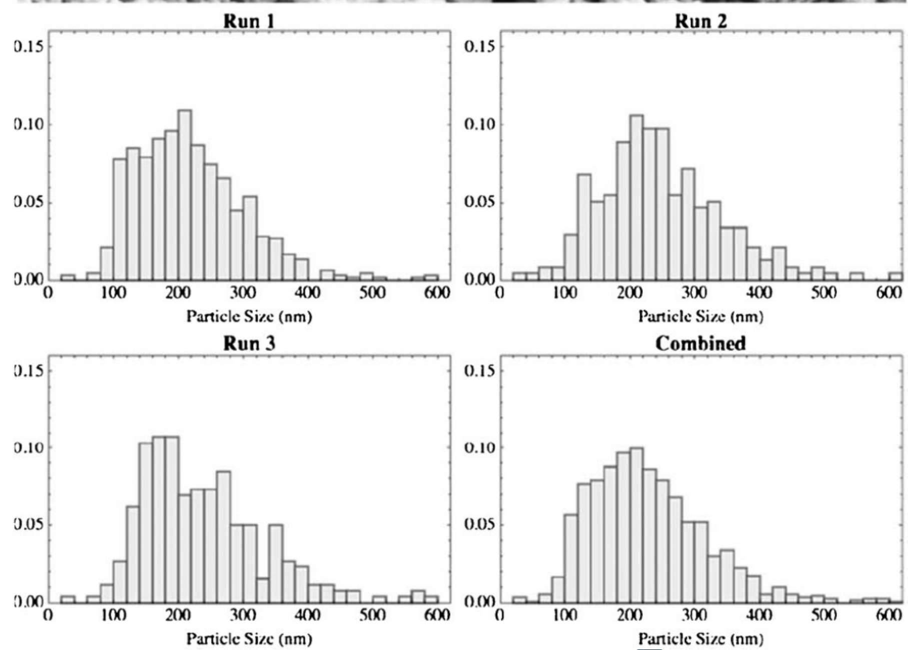
SEM Images

- The CAN-BD process, as currently configured, produces particles of a much more uniform shape and size that traditional crash precipitation methods
- Particle size measurements were conducted on three runs in order to understand reproducibility and then combined for an average distribution
    - Mean particle sizes were found to be 217, 248 and 238 nm for Runs 1, 2 and 3, respectively
    - Similar distributions were found in each run, indicating a well-controlled, reproducible process
    - The combined mean particle size is 228 nm





Hotchkiss *et al.*, *Propellants Explos. Pyrotech.* **2014**, *39(3)*, 402

Combinatorial HME Formulation

- For all intents and purposes, homemade explosives (HMEs) are used for nefarious reasons
- Much of the work to date characterizing HMEs has been on cataloging / understanding their safety and blast properties
- Not as much work has been done to systematically study their physical and chemical properties that determine how to best detect / identify them
  - Too many combinations and permutations, ratios and impurities
  - Expensive
  - Safety concerns considering the amounts that are usually made (see 2nd main bullet)
- A better understanding of potential impurities or degradation products from HMEs may assist in detection or attribution efforts

Why not use automated dispensing methods to formulate HMEs in small amounts in order to study their physical and chemical properties?

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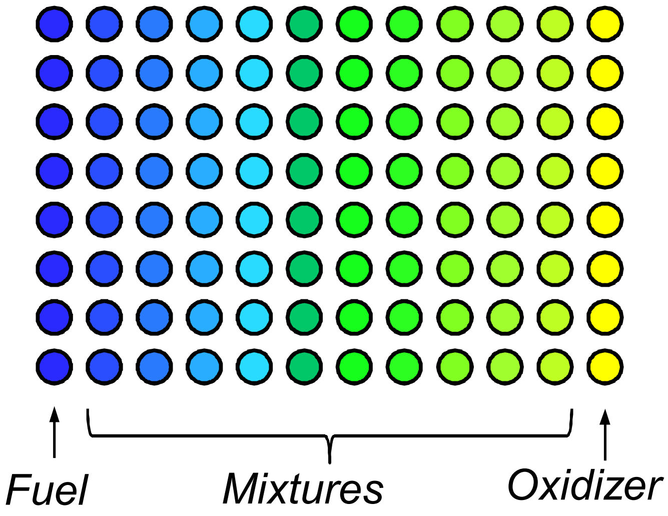
Formulations – 10 mg or Less

- For method and capability development we are focusing on several common fuel/oxidizer mixtures
  - Allowed us to test different deposition / mixing methods for different types of materials
  - Published properties allowed us to compare results
- Keeping printed mixtures to <10 mg reduces safety concerns and waste (most samples consumed by experiments)
- Rigorous experimental design were used to ensure repeatable, reproducible deposition
- Ratios of fuel to oxidizer were systematically varied to understand end effects

96 well plate



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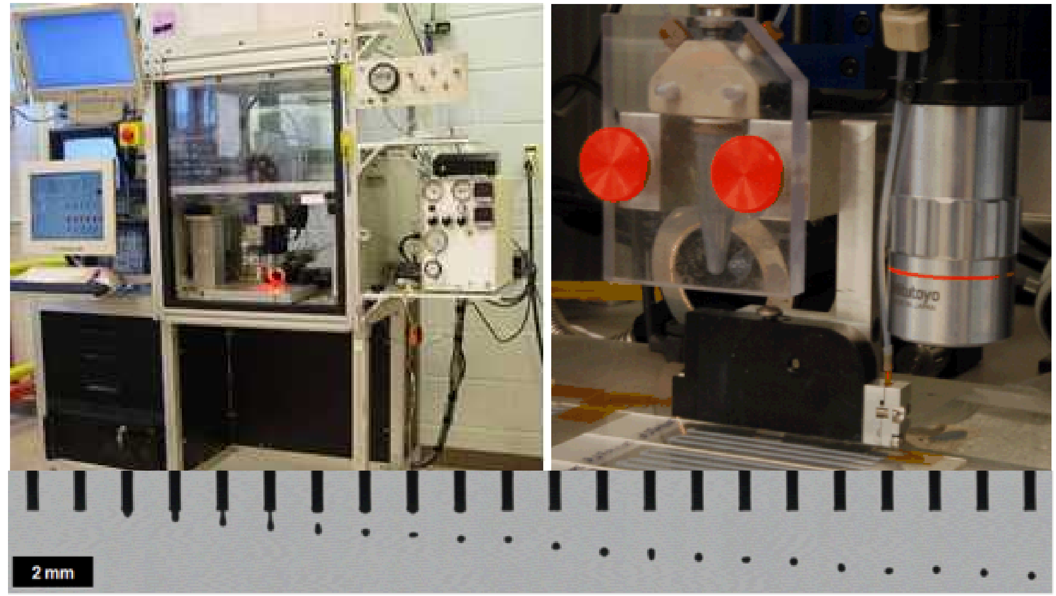
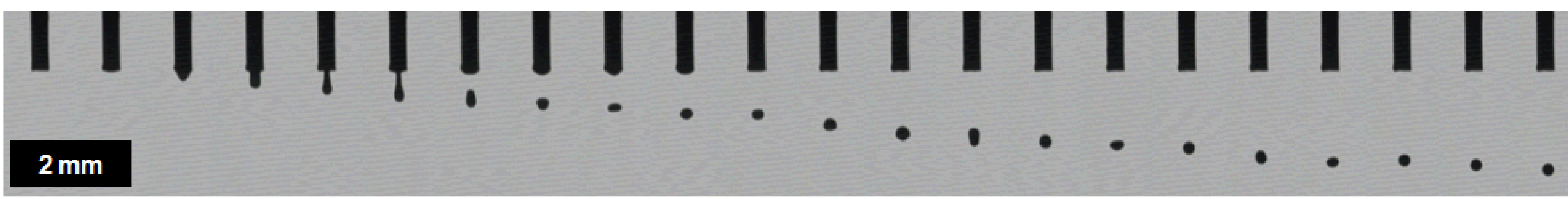
Inkjet Printing System

- Three-axis positioning system
- Microscopes for droplet imaging and registration
- PipeJet™ dispensing mechanism
  - Dosage volumes range from a few nanoliters to several microliters per second
  - Volume dispensed is independent of the liquid's properties like viscosity or surface tension over a wide range
  - Particle laden dispersions can be easily printed – clogging is limited



Inkjet dispensing system showing reservoir, dispensing tip, and registration microscope.



Strobe-illuminated photographs of Al/Bi_2O_3 ink droplet formation. 100 µs between images.

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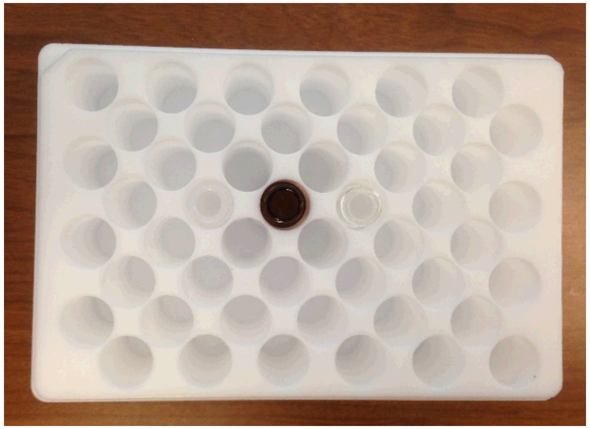
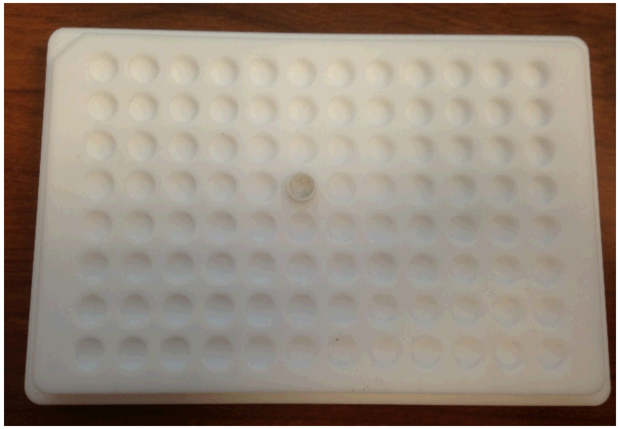
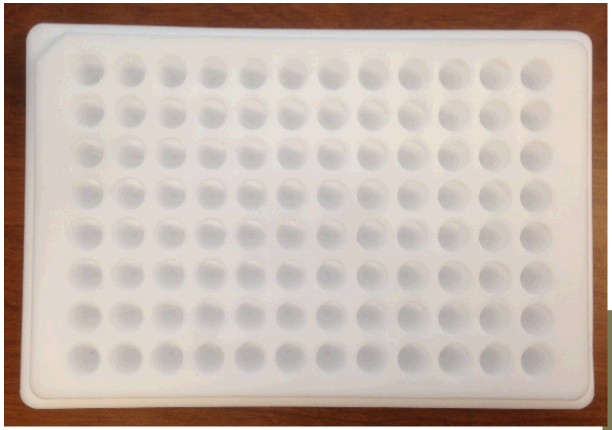
96-Well Plates

- Industry standard 96-well plates are attractive for throughput and standardization
- Eventually can print directly into well plates for a given instrument and analyze in an automated fashion for high throughput
- Large number of samples allows for proper statistics and confidence in results
- For R&D purposes we are used custom-made well plates (PTFE) with same overall dimensions and spacing as ANSI industry standard (9 mm center to center distances, 18 mm for vial-containing 48-well plates)
- Well plates designed for holding containers are designed to have container protrude for easy insertion/removal and potential sealing during aging experiments







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Explosives Vapor Pressures

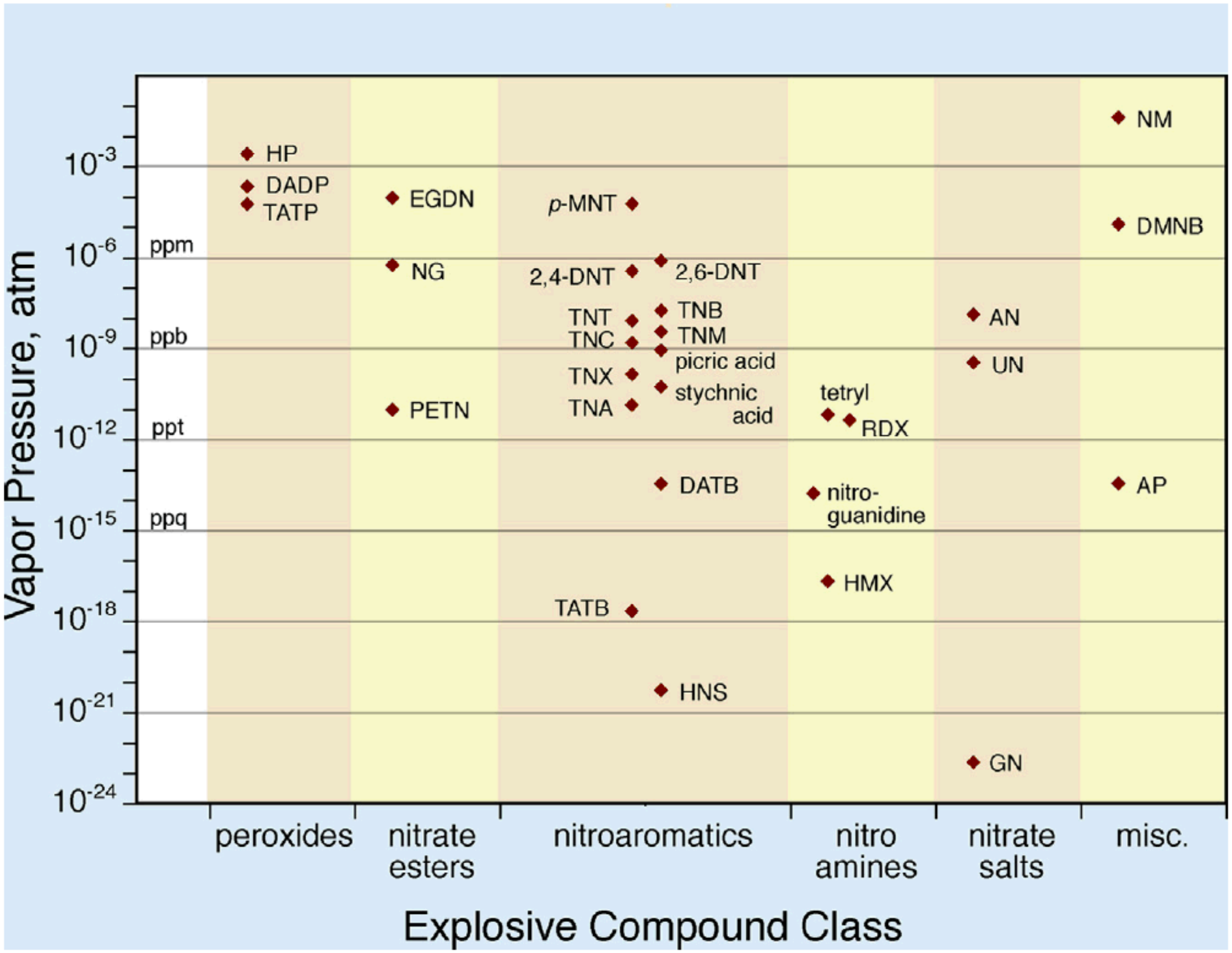

Figure 2. A plot of the average or the preferred explosive VPs at 25°C. These values are from the data presented in Table 3. Values are given in atmospheres on a log scale with horizontal lines placed every three decades. This figure illustrates the relationship of VPs between the various explosive compounds.

Ewing *et al.*, *Trends Anal. Chem.* **2013**, *42*, 35

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Part II Acknowledgements

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Shawn Hightower

EXPLOSIVES TECHNOLOGIES GROUP ETG

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Part III – Cooperative Threat Reduction (CTR)

- Non-laboratory Research
  - No more synthesis – but just as challenging!
    - *Country analyses*
    - *Research on safety/security concepts*
    - *Engagement approaches*
  - Able to utilize past experience
- Opportunity to Support Other Nations
  - Collaboration with many countries
  - Specifically, I work closely with Iraq, Turkey, Yemen, Pakistan

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Innovative solutions for countering biological and chemical threats globally

Strengthen capacities to safely, securely, and responsibly detect, handle, and control dangerous biological and chemical agents

- Promote the responsible use of biological and chemical agents, equipment, and expertise globally
- Improve understanding and management of the risks associated with accidental and deliberate misuse of biological and chemical agents.
- Encourage global partnerships and adherence to international risk management standards




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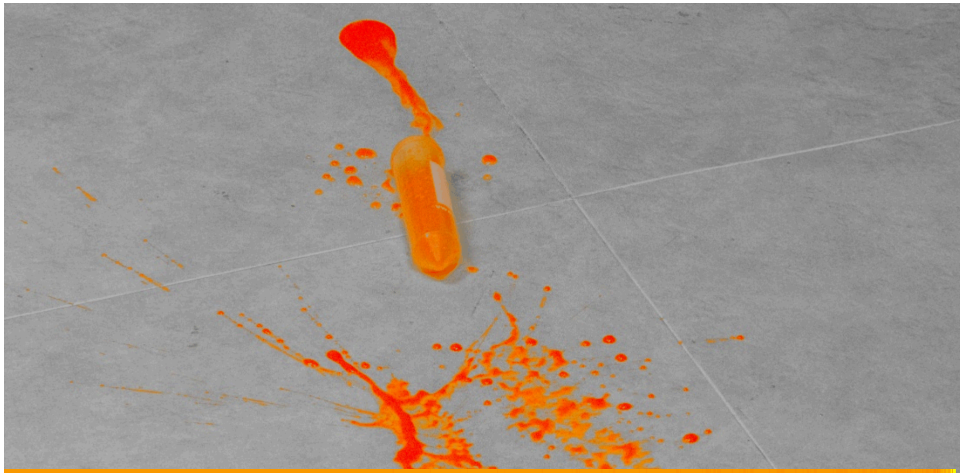
IBCTR core capabilities

Human Capacity Development



Risk Management

Analysis

Health Security

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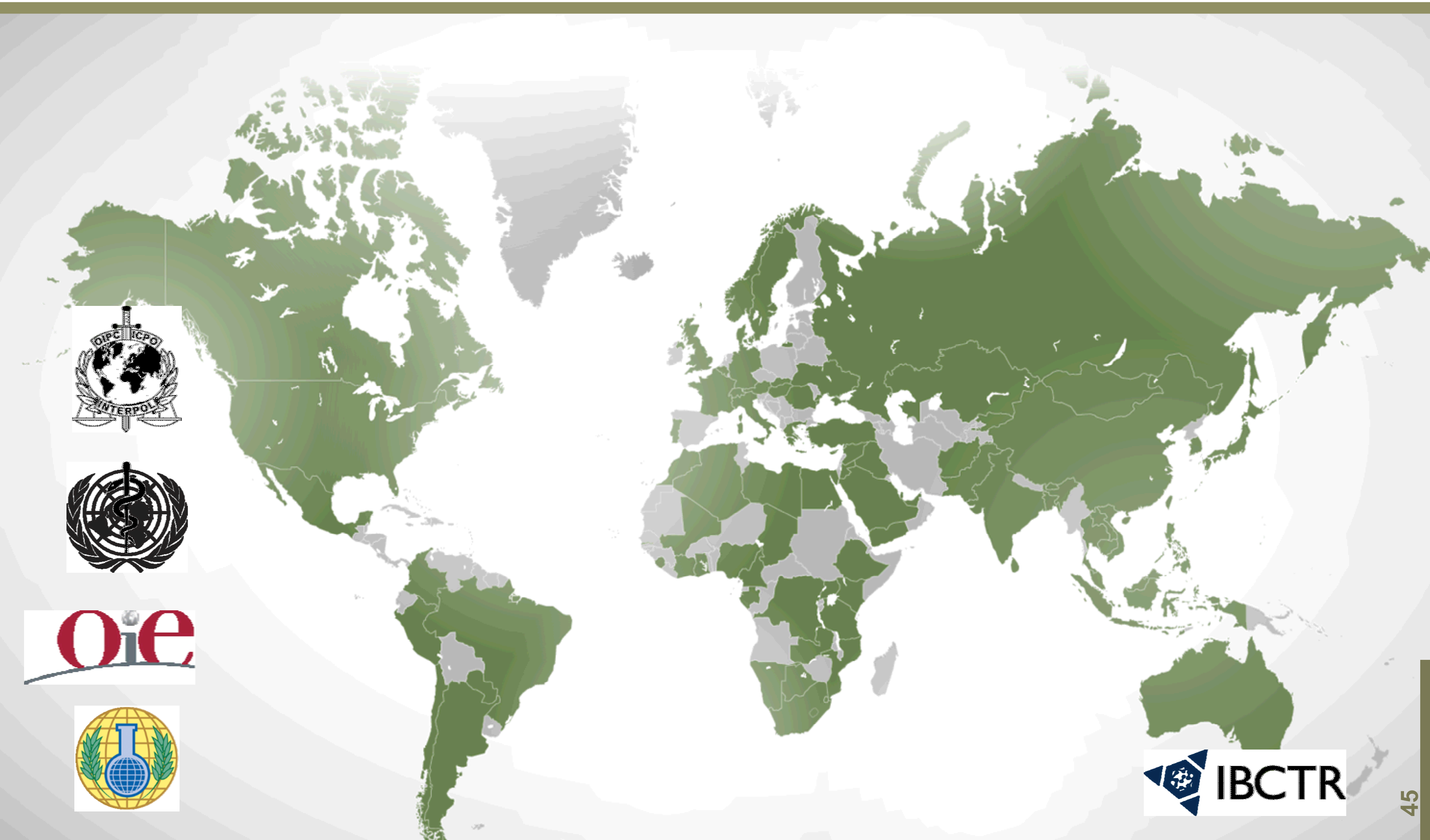
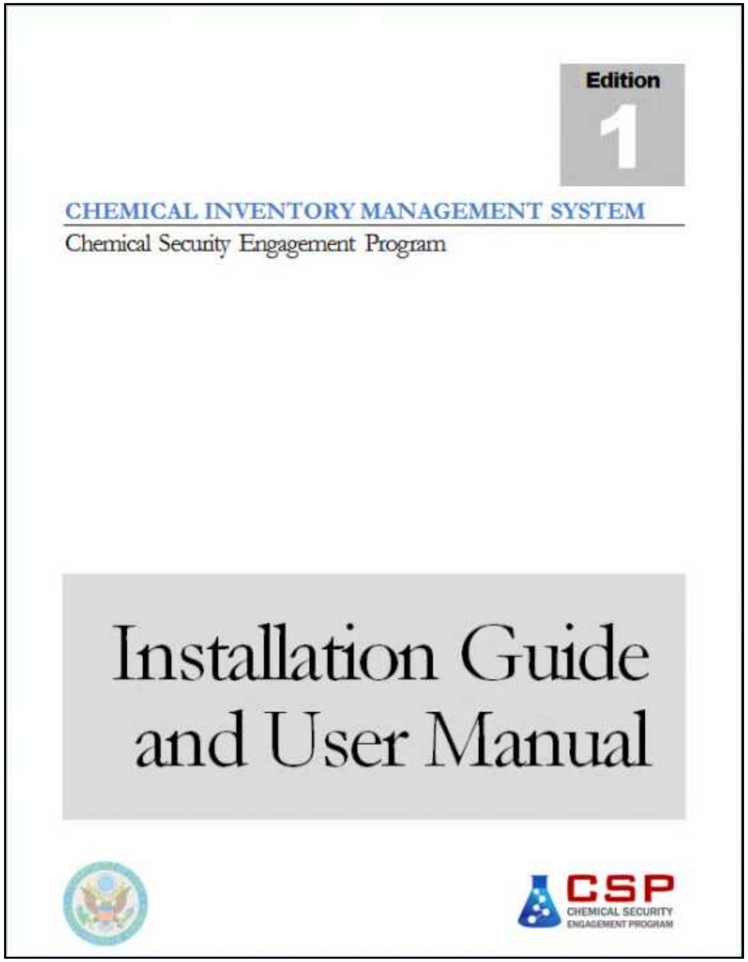
IBCTR’s Global Experience



Inventory Management Tools

Chemical Management Software (CMS)

- Promote a fundamental approach to managing chemicals in the laboratory, focused on security and safety
- Sandia-developed CMS inventory tool
  - *Designed to be used as a simple system at small institutions*
  - *Has access control options, ability to save and share databases, and to flag chemicals of concern*
- Hands-on training on effective chemical inventory management systems
  - *Including: laboratory management best practices for procurement, receiving, tracking, and proper storage of chemicals*


Edition 1

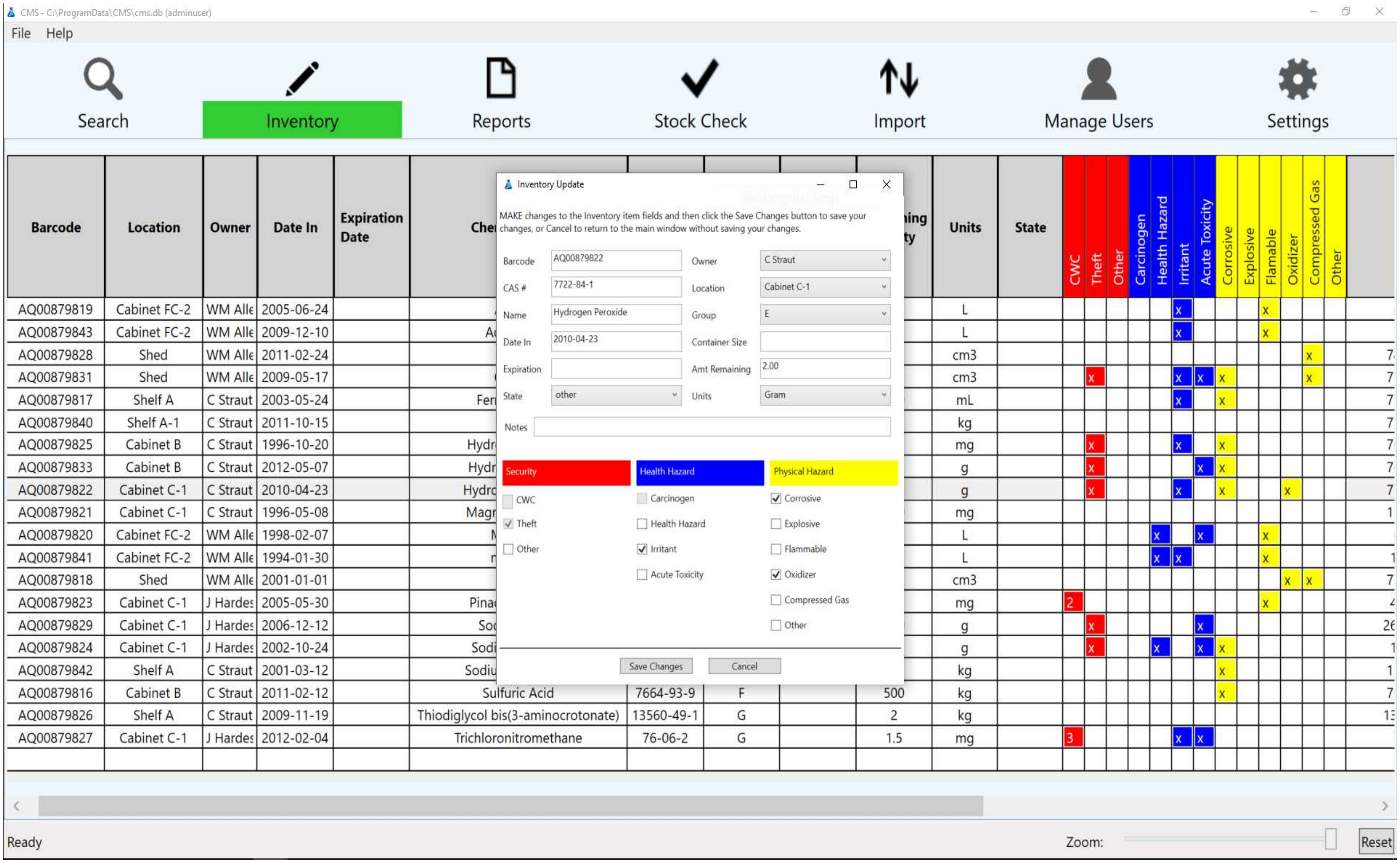
CHEMICAL INVENTORY MANAGEMENT SYSTEM

Chemical Security Engagement Program

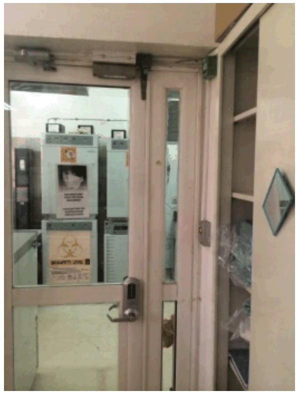
Installation Guide and User Manual

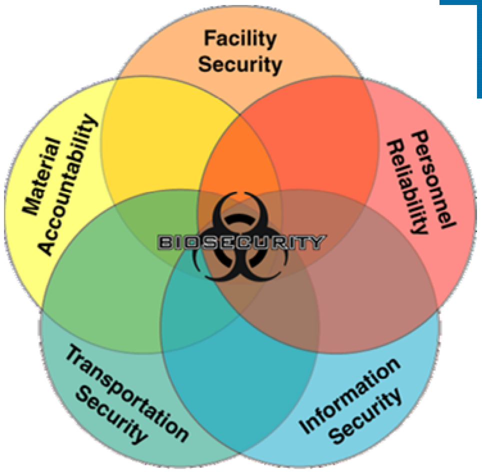
CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM

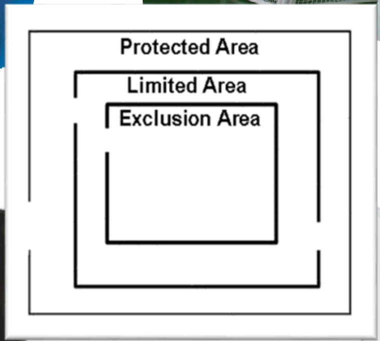
CMS Software Screenshot



Security Upgrades







Reduce the risk of intentional removal (theft) of a valuable biological or chemical material

Implement comprehensive security program

- Includes all five pillars
- Based of identified risks, layered security concept, and local infrastructure

Support safety best practices

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International Nonproliferation Export Control Program (INECP)

MISSION

Strengthen global efforts to prevent proliferation of WMD-related materials, equipment, and technology

AREAS OF ENGAGEMENT

Proliferation Risk Analysis in the Licensing Process

- Ensure the license review process competently assesses proliferation risks associated with end-uses and end-users, and ensure technical specialists are being utilized

Government Outreach and Enterprise Compliance

- Assist governments to establish outreach programs and promote enterprise compliance at key enterprises and technology holders

WMD-related Commodity Identification Training and reach-back for Customs

- Ensure enforcement personnel are sensitized to WMD-related materials and equipment, and have access to technical/analytical resources and support

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CBRNE CIT Course Objectives

Goal: Enable enforcement personnel to better mitigate CBRNE threat by gaining a better understanding of the commodities and circumstances that might indicate non-state actor CBRNE threats

- **Understand WMD/CBRNE core concepts** Understand the types of traditional Weapons of Mass Destruction (WMD)
  - Understand how non-state actor CBRNE weapons can differ from traditional state sponsored WMD weapons
  - Describe consequences of development and potential use of CBRNE weapons by non-state actors/terrorists
  - Illustrate CBRNE threat through case study examples
- **Identify the commodities needed to make CBRNE weapons**
  - Recognize the availability of CBRNE equipment and starter materials
  - Understand that many CBRNE commodities have legitimate commercial/peaceful uses that are not weapons related
  - Identify means by which non-state actors can acquire CBRNE commodities
  - Recognize combinations of commodities that may indicate CBRNE activity
  - Describe how the presence of these commodities in some circumstances may indicate clandestine weapons activities
- **Understand enforcement agencies' role in preventing proliferation of CBRNE weapons**
  - Describe the totality of circumstances principle and how it relates to CBRNE issues and concerns
  - Recognize that law enforcement action can slow or stop CBRNE weapon development and/or deployment

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- The ‘Chem’ Team
  - Christine Straut
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  - Pamela McKinsey
  - Walt Sansot
  - Emily Diez
- The Managers
  - Jen Gaudioso
  - Ben Brodsky
  - Constantine Stewart
  - George Sanzero

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pjhotch@sandia.gov

Questions?

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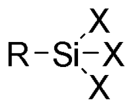
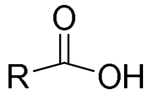
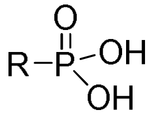
INTERNATIONAL BIOLOGICAL and CHEMICAL THREAT REDUCTION

Backup Slides

Types of Surface Modifiers

$R-SH$	**Noble metals (esp. gold, silver)**
$R-NH_2$	**Cadmium selenide, gold**
 X = H, Cl, OR'	**Various metal oxides (esp. glass, ITO)**
	**Various metal oxides (esp. glass, ITO)**
$R-OH$	**Iron oxide, silicon, glass**
	**Various metal oxides (esp. ITO, TiO_2), cadmium selenide**

Love *et al*., *Chem. Rev.* **2005**, *105*, 1103

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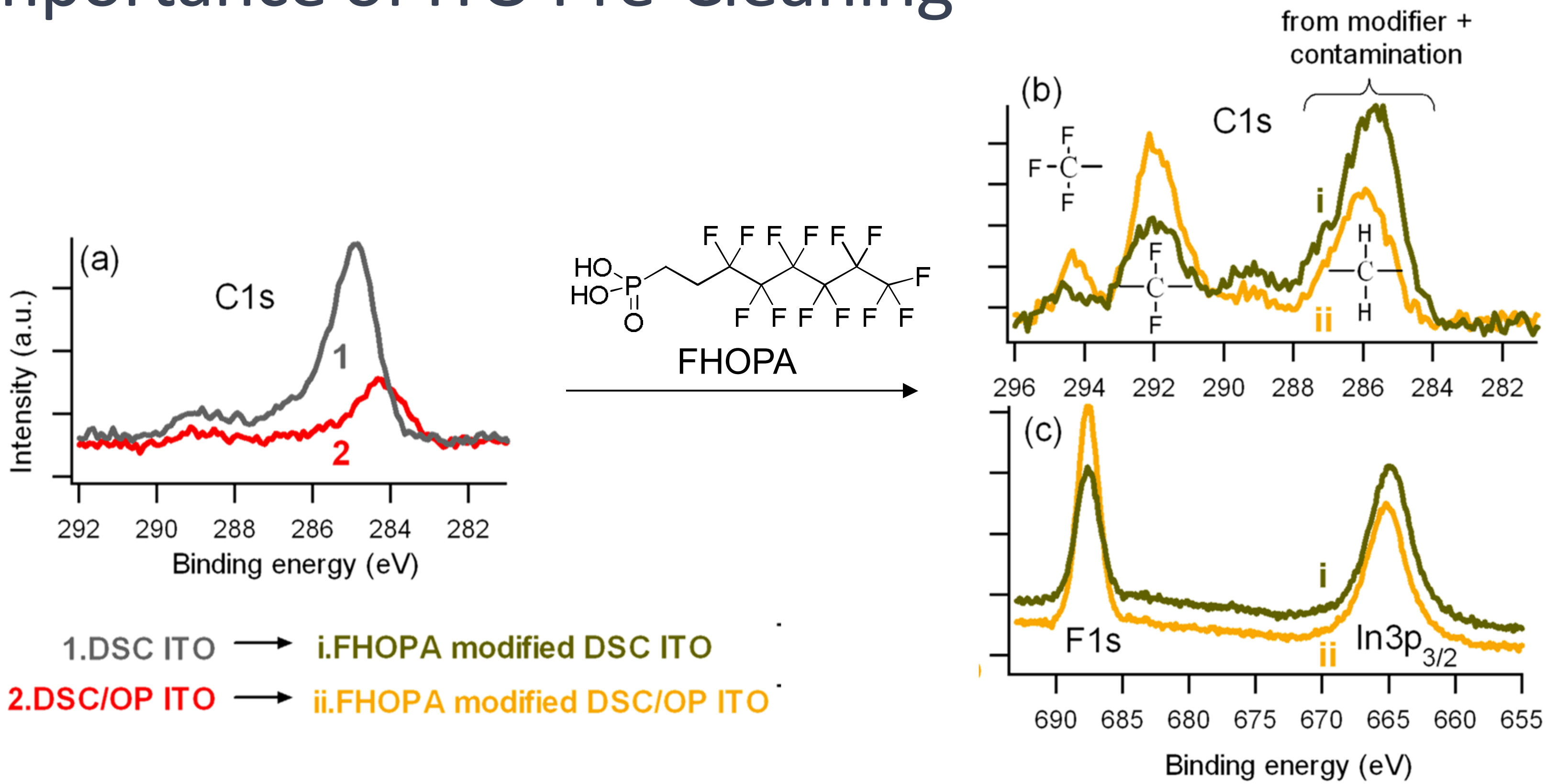
Importance of ITO Pre-Cleaning

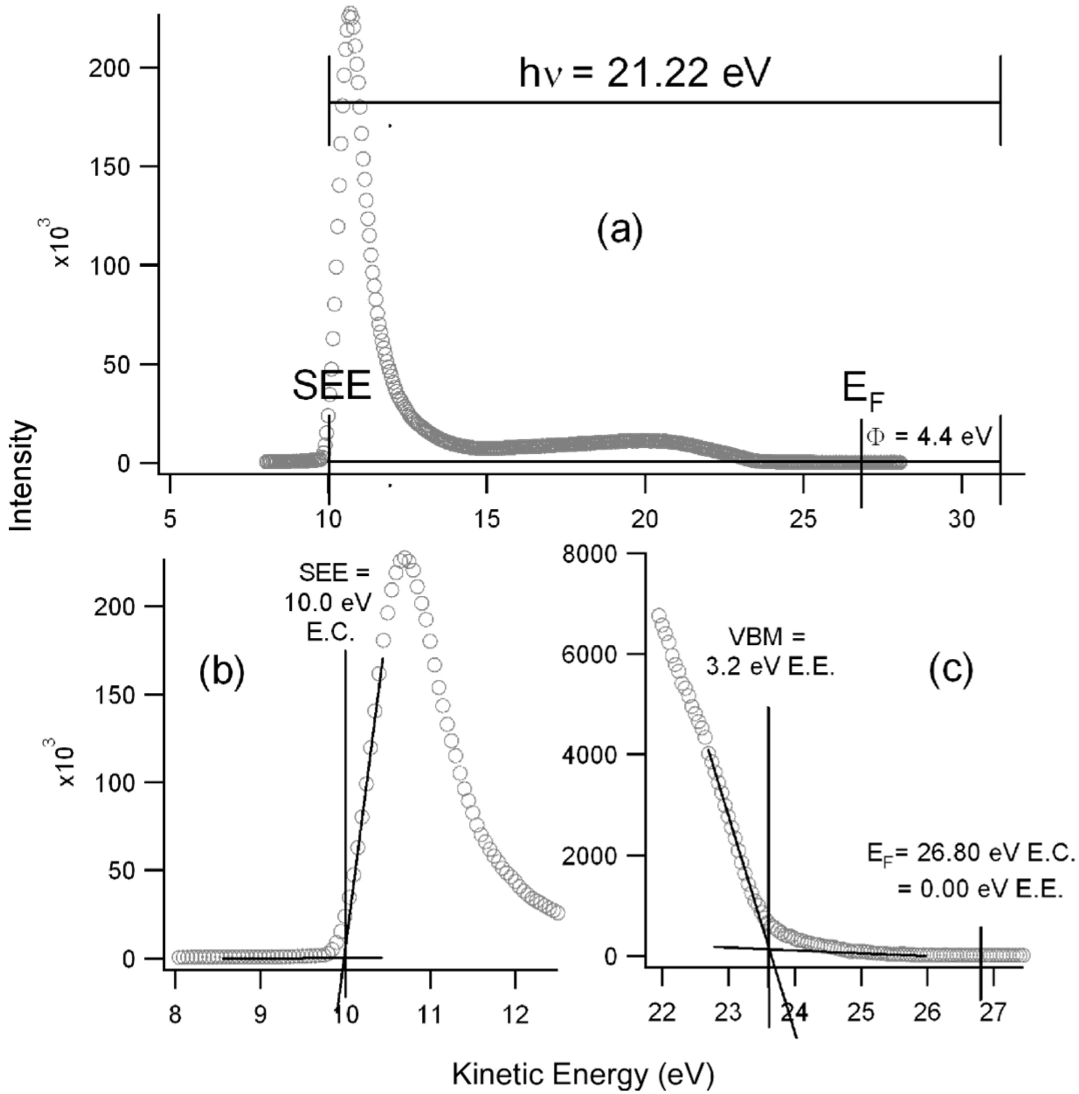


Oxygen plasma (OP) treatment reduces initial surface contamination and increases reactive surface sites over detergent/solvent cleaned (DSC) alone

Data and Figures from S. Paniagua

Paniagua *et al.*, *J. Phys. Chem. C.* **2008**, *112*, 7809

Determination of the Work Function from UPS



$\Phi_m = E_K^{min} + 21.22\text{ eV} - E_K^{max}$

For DSC ITO

$\Phi_m = 10.0\text{ eV} + 21.22\text{ eV} - 26.8\text{ eV}$

$\Phi_m = 4.4\text{ eV}$

Data and Figure from S. Paniagua

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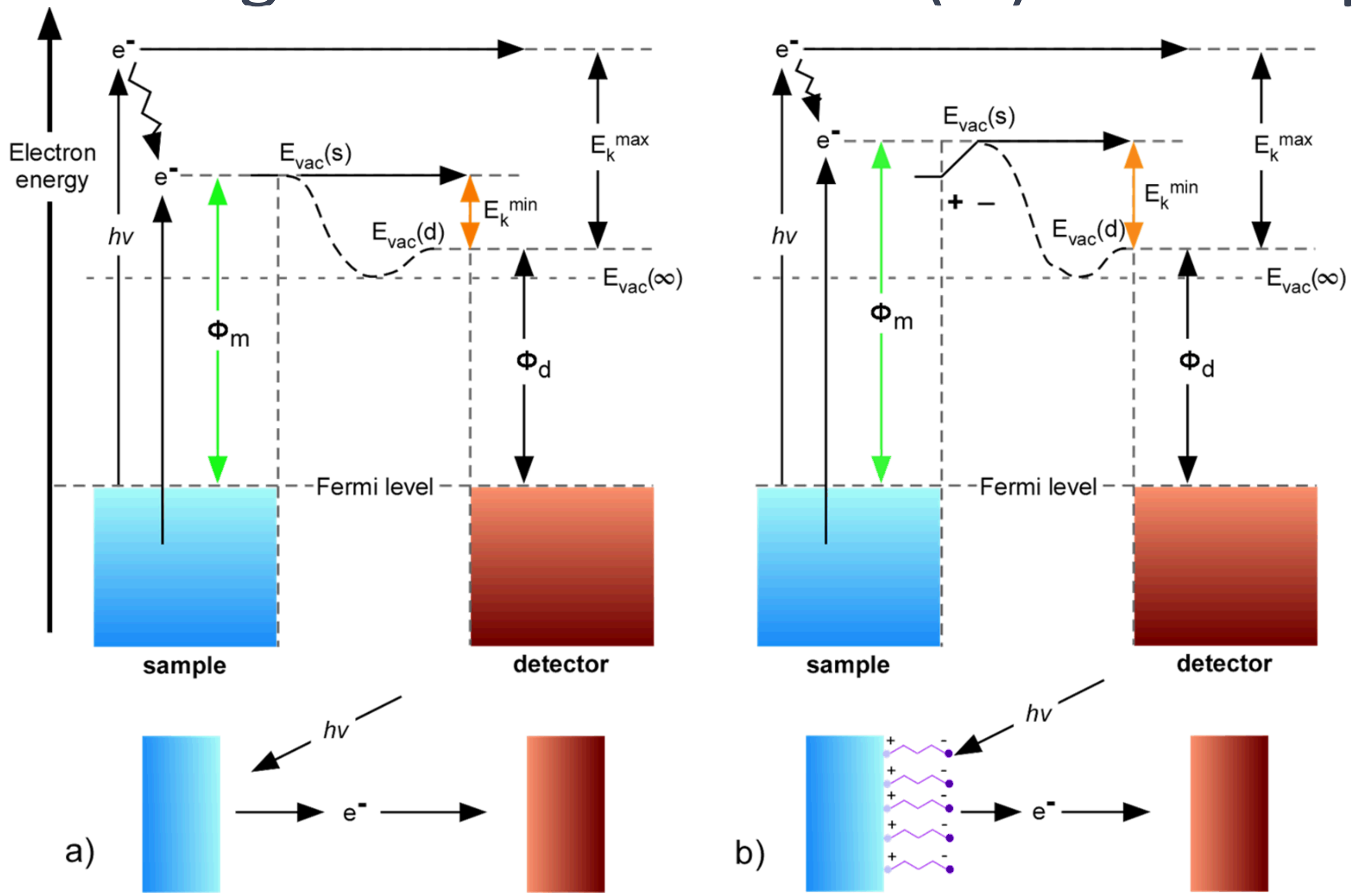
Tuning the Work Function (Φ) with a Dipole



$h\nu$ = energy of incoming light

Φ_m = work function of metal

Φ_d = work function of detector

$E_{vac}(\infty)$ = vacuum level at infinitiy

$E_{vac}(s)$ = vacuum level of the solid

E_k^{max} = primary electrons excited from Fermi level

E_k^{min} = secondary electrons just escaping the solid above $E_{vac}(s)$

- Work function is the energy difference of an electron at the Fermi level vs. a singly ionized solid with the electron at rest at $E_{(vac)}(s)$ just outside the solid
- E_k^{min} and E_k^{max} can be detected by Ultraviolet Photoelectron Spectroscopy (UPS) measurements

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Figure adapted from Cahen *et al*., *Adv. Mater.* **2003**, *15*, 271

IRRAS

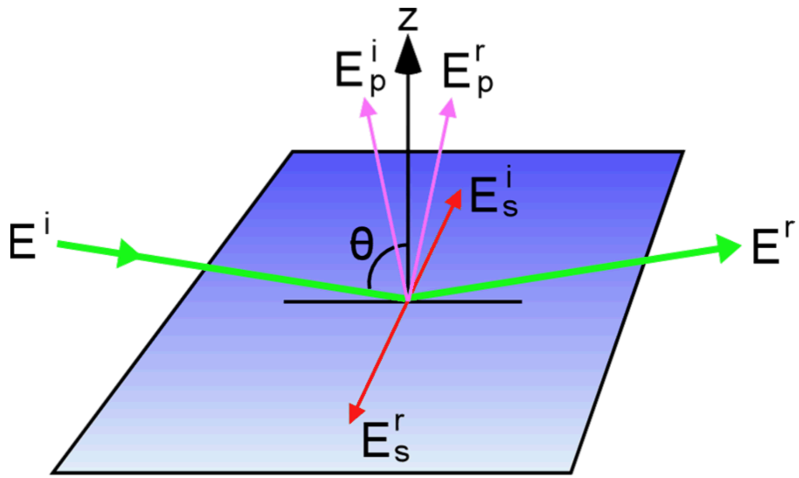


Illustration of the interaction of incoming infrared radiation (E_i) with a highly reflective surface as a grazing angle (θ), where:

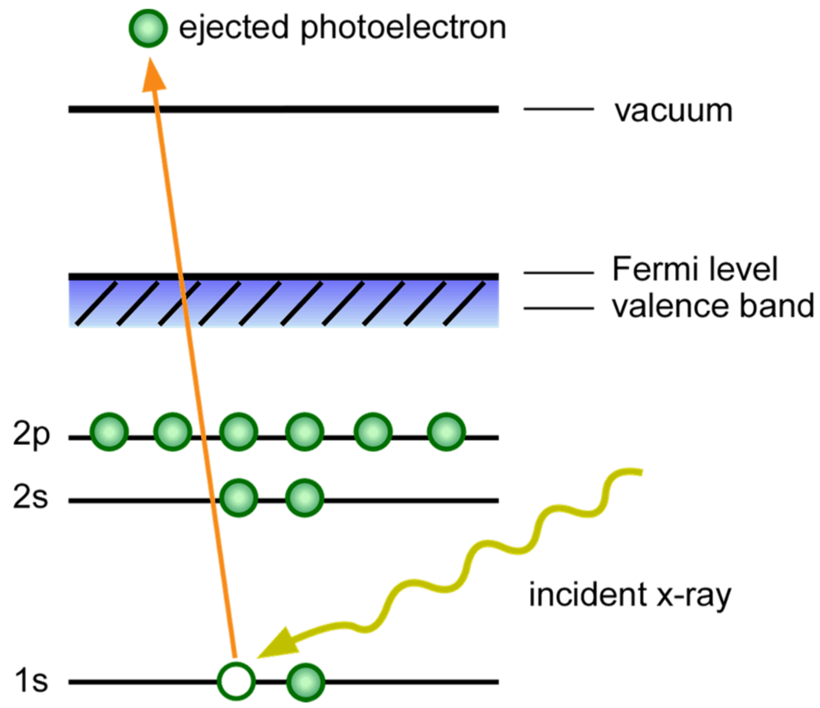
E_r = reflected radiation

$E_s{}^i$, $E_s{}^r$ = the *s* components of the electric fields of incident and reflected radiation.

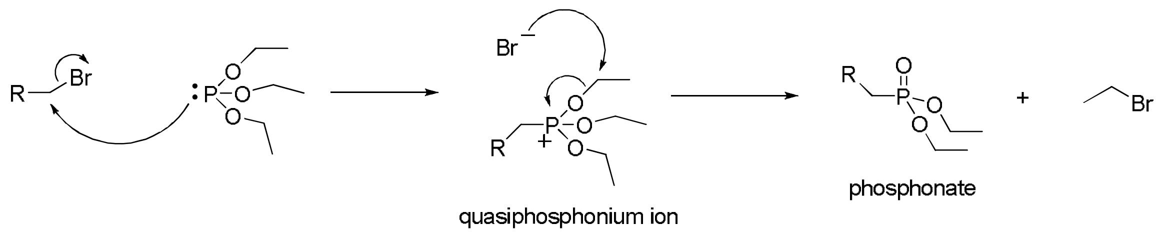
$E_p{}^i$, $E_p{}^r$ = the *p* components of the electric fields of incident and reflected radiation.

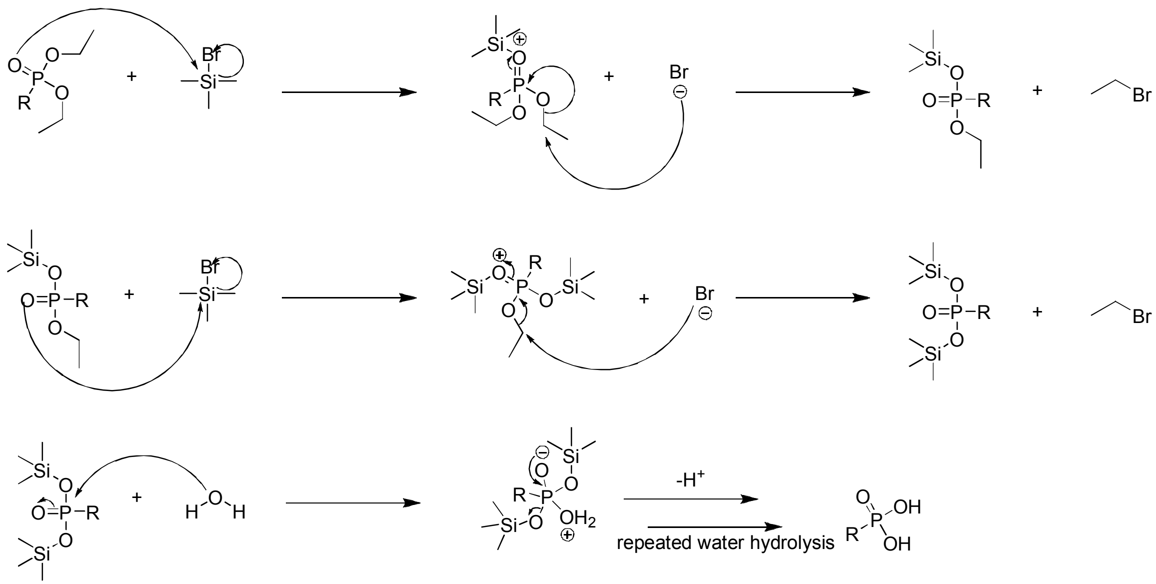
Hayden, B. E., Reflection Absorption Infrared Spectroscopy. In *Vibrational Spectroscopy of Molecules on Surfaces*, Yates, J. T.; Madey, T. E., Eds. 1987; pp 267-344.

XPS

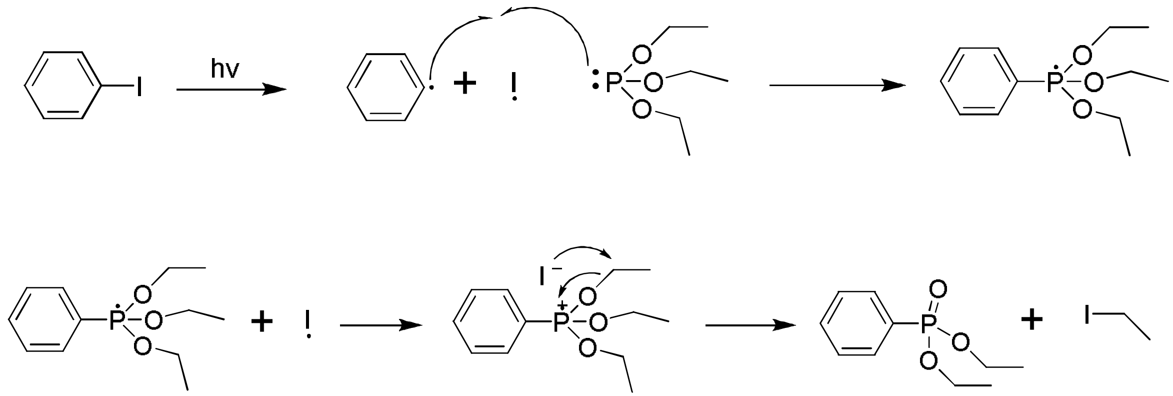

ejected photoelectron
vacuum
Fermi level
valence band
2p
2s
incident x-ray
1s

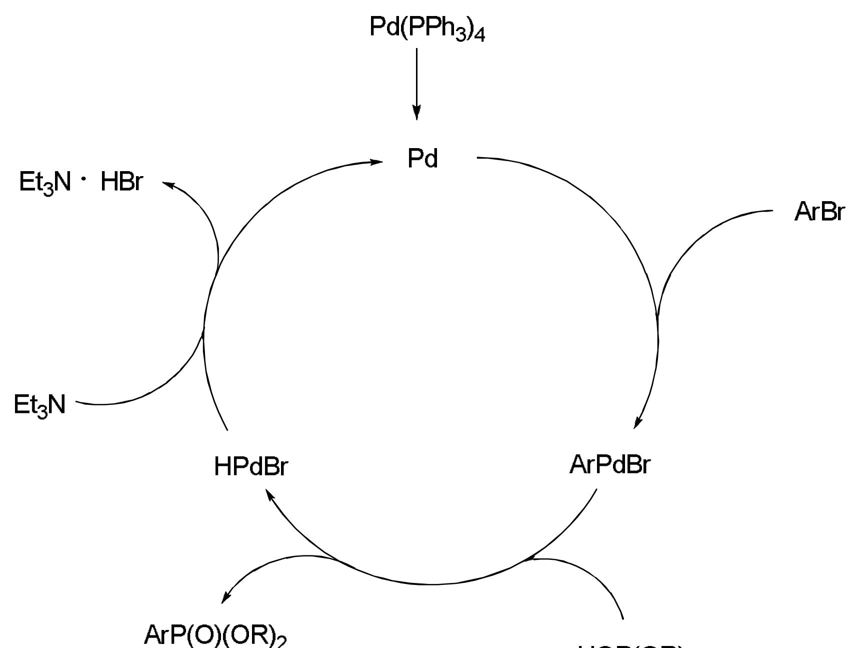
Arbuzov and Hydrolysis Mechanisms



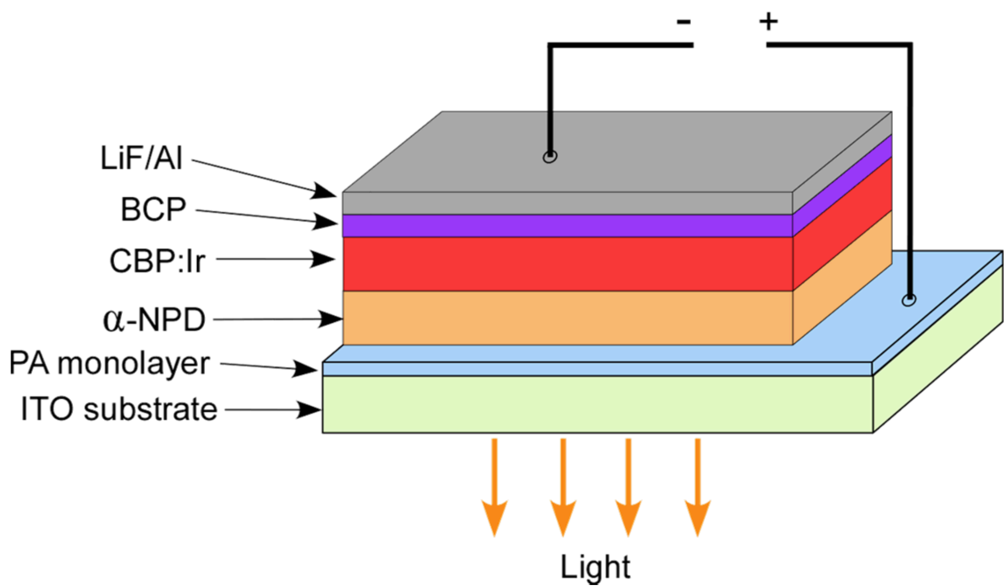


Arylphosphonates





OLED Device Layers



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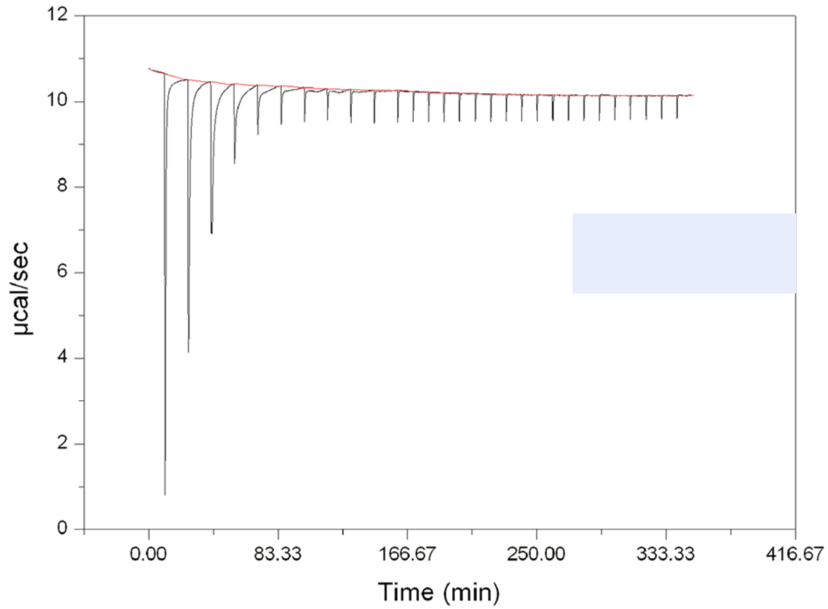
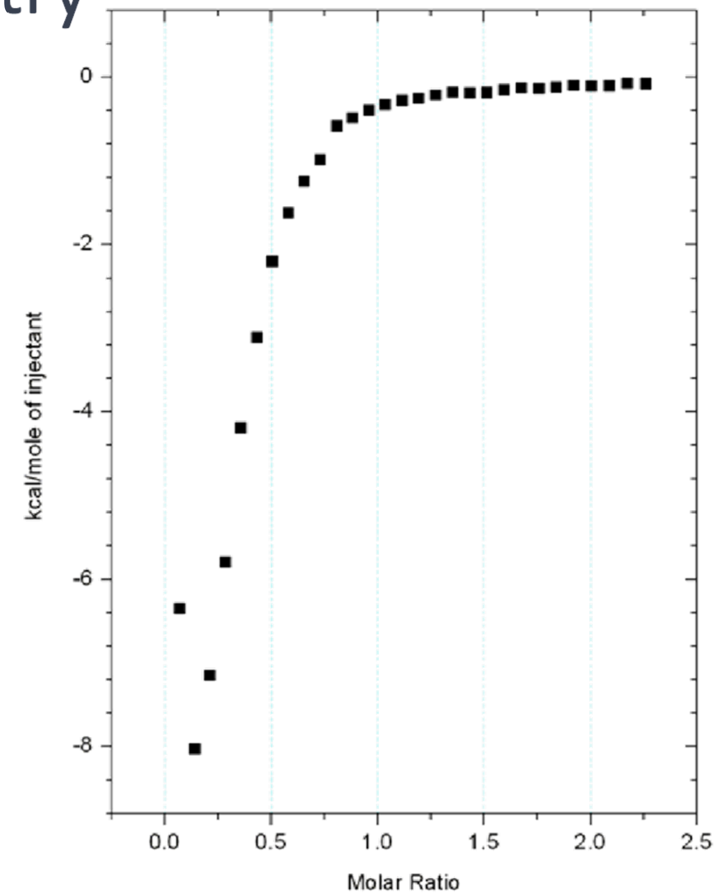
Isothermal Titration Calorimetry



Raw ITC graph – peaks of heat flow corresponding to injections of titrant into sample cell



Corresponding isotherm – integrated peaks from raw ITC graph with respect to time, then take into account concentrations

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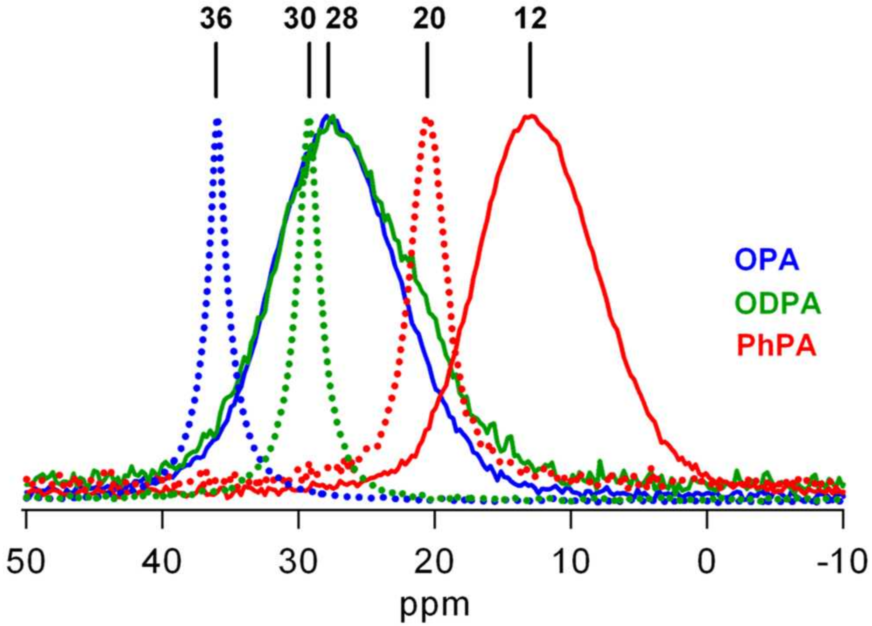
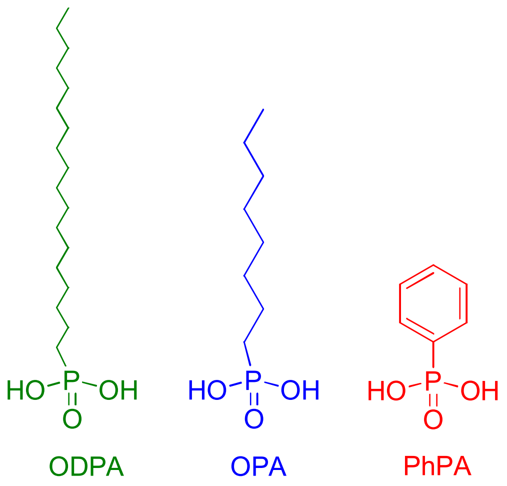
Data collected by N. Hankins

^{31}P MAS NMR





Dashed lines – unbound PA
Solid lines – PA bound to ITO NPs

- 8 ppm shift is seen between unbound PhPA (20 ppm) and OPA (36 ppm) vs. PhPA–ITO (12 ppm) and OPA–ITO (28 ppm), respectively
- Only a 2 ppm difference is seen between unbound ODPA (30 ppm) and ODPA–ITO (28 ppm), indicative of increased hydrogen bonding

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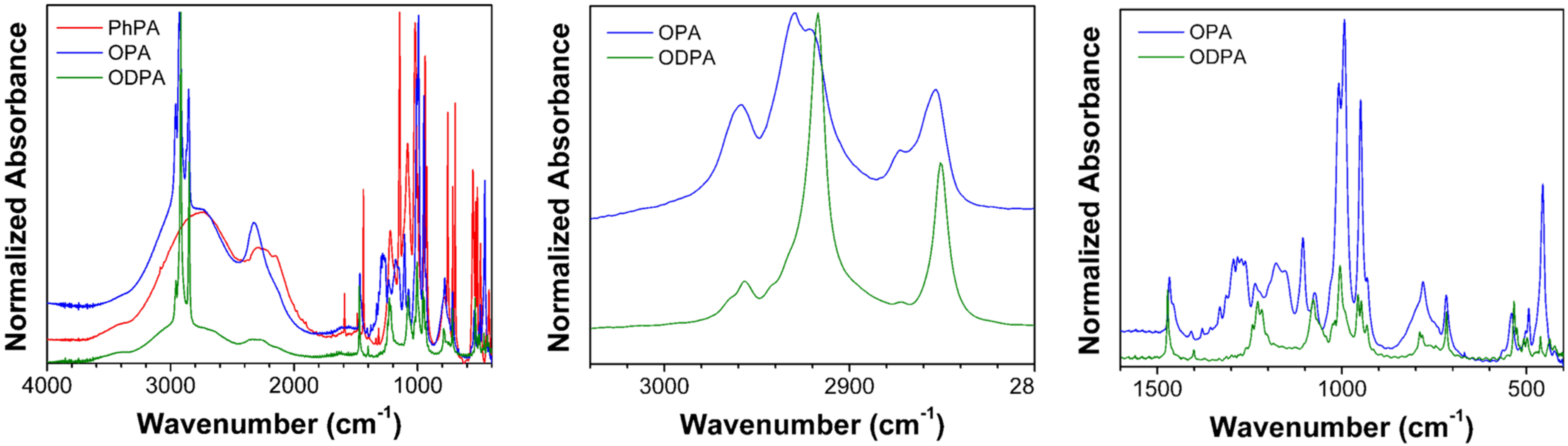
FTIR



IR indicates more hydrogen bonding in ODPA than in OPA

P–O stretching in P–OH (~ 2800 cm^{-1}) shows decreased intensity in ODPA

O–H out of phase deformation (~2350 cm^{-1}) is decreased intensity in ODPA

P=O stretch (~1250 cm^{-1}) is different in ODPA and OPA

P–O–H stretching (~1000 and ~940 cm^{-1}) have decreased intensity in ODPA

C–H stretching indicates higher degree of packing of the alkyl chains in ODPA

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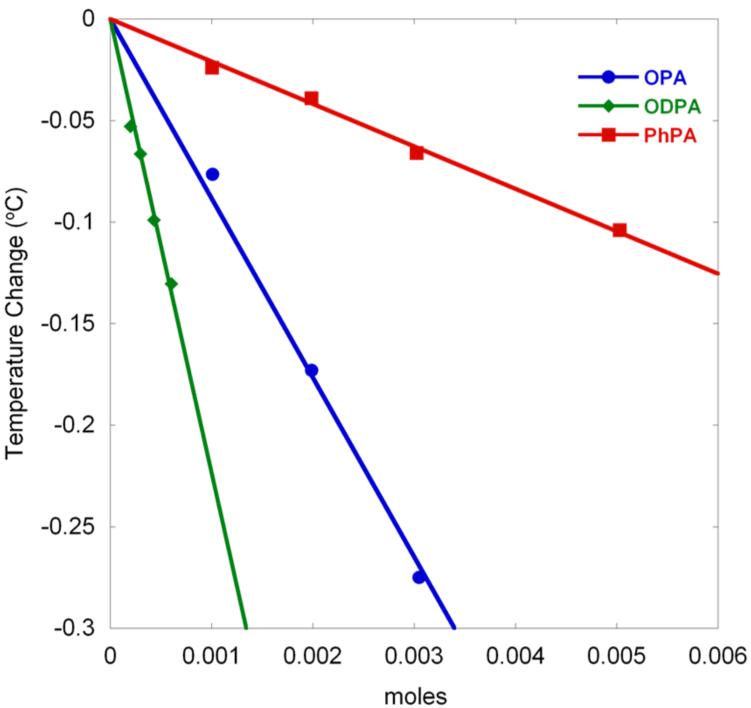
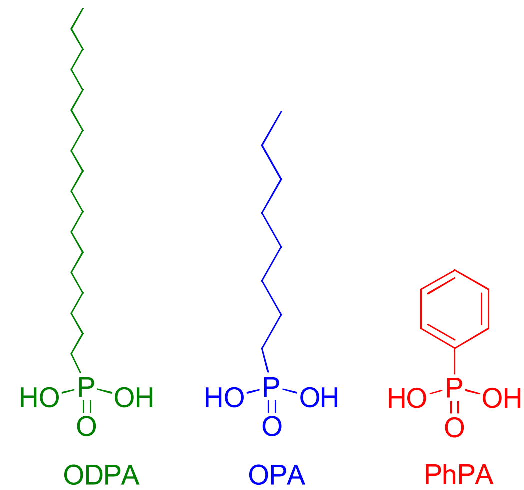
Data and Figures from P. Kim

Determination of the Binding Energy

Enthalpies of solution from solution calorimeter





ΔH_{dil} – negligible

E_S – 55 mJ/m^2

E_{SAM} – approximated (paraffin – 25 mJ/m^2, polystyrene – 32.4 mJ/m^2)

	ΔH_{sol} (kJ/mol)	ΔH_r (kJ/mol)	D (kJ/mol)
PhPA	- 10.8 ± 0.5	- 44 ± 0.6	52 ± 1
OPA	- 45.3 ± 3.0	- 41 ± 0.5	82 ± 4
ODPA	- 114.8 ± 7.0	- 49 ± 1.0	159 ± 8

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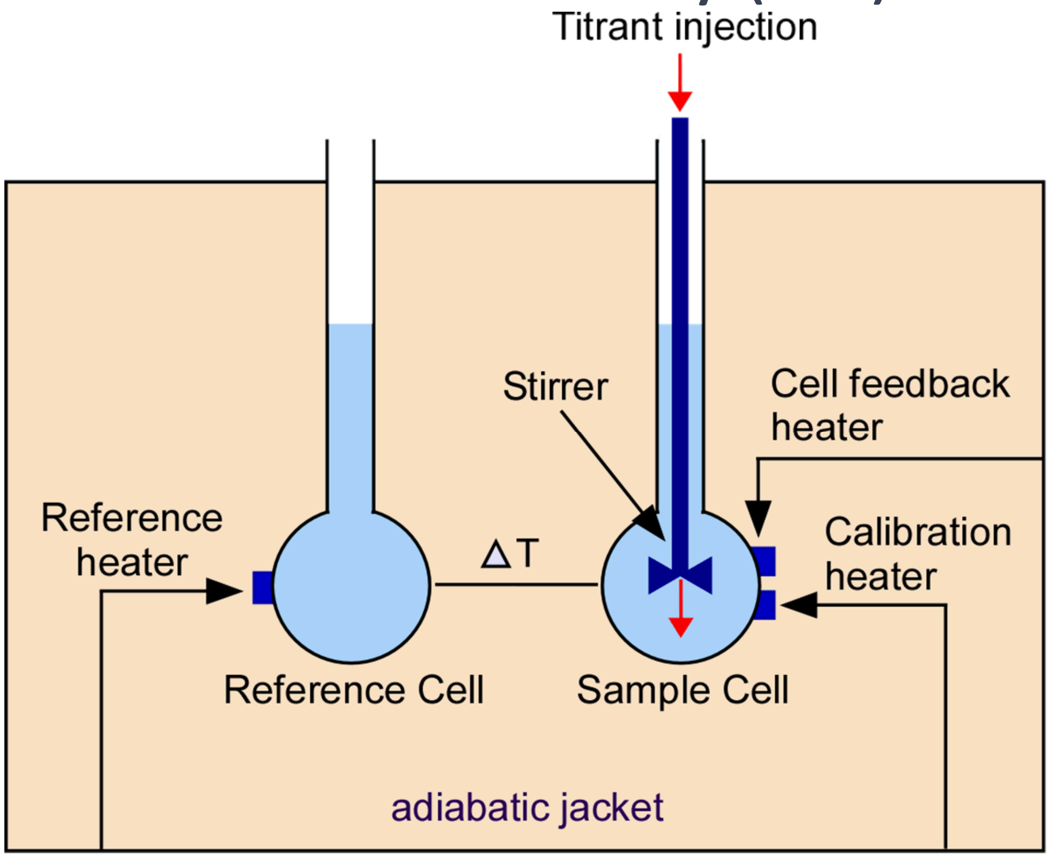
Isothermal Titration Calorimetry (ITC)



- Inject ligand into solution of nanoparticle (with stirring)
- Reaction produces heat (exothermic)
- Feedback power to sample cell is decreased
- Negative peaks seen in raw ITC graph

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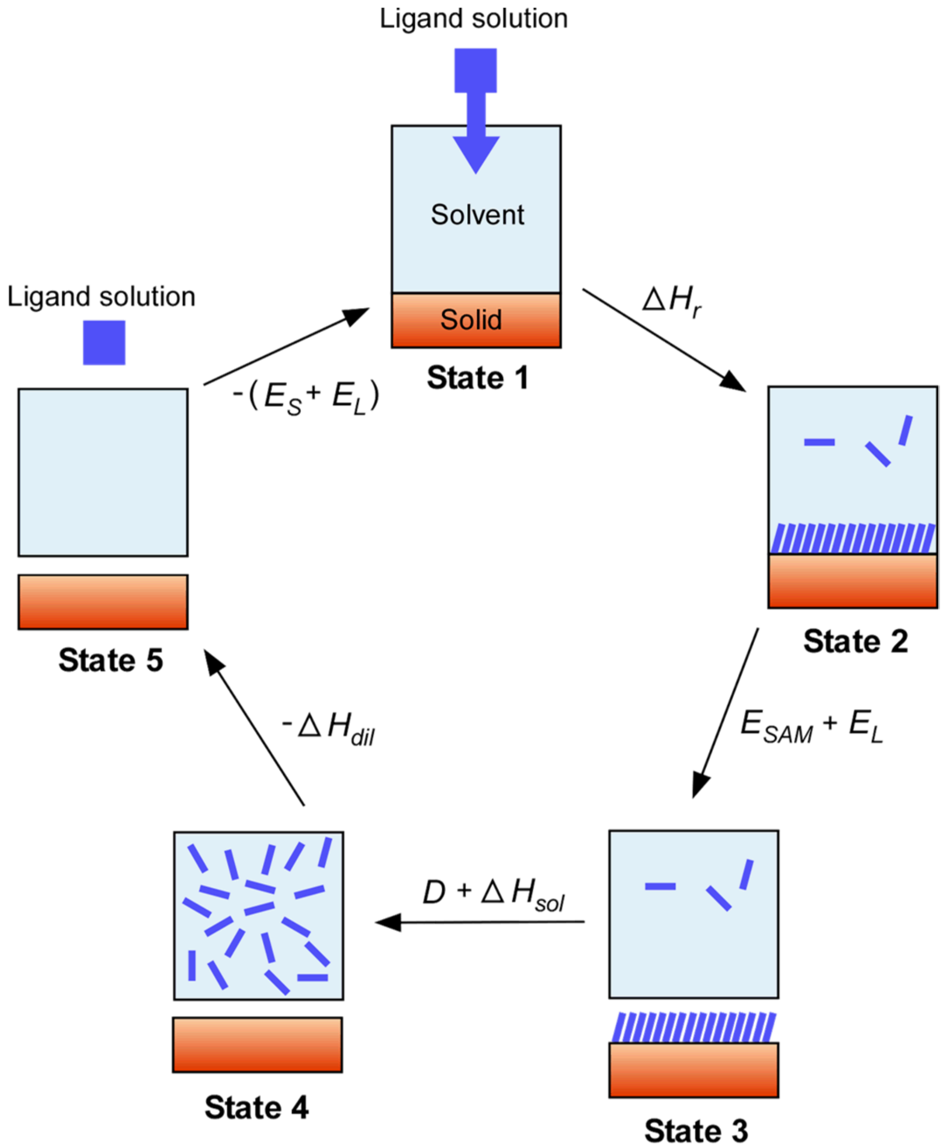
Determination of Binding Energies



ΔH_r – reaction enthalpy
D – binding energy
ΔH_{sol} – enthalpy of dissolution
ΔH_{dil} – enthalpy of dilution
E_S – surface energy of bare solid
E_{SAM} – surface energy of monolayer
E_L – surface energy of solvent

$$\Delta H_r = -D - (\Delta H_{sol} + \Delta H_{dil}) - (E_S - E_{SAM})$$

- *D*, binding energy, can be calculated from the equation if the other values are known
- Ferreira found $D \sim 55$ kJ/mol for alkyl PAs on TiO_2 and ZrO_2 NPs

Ferreira *et al.*, *J. Colloid Interface Sci.* **2005**, *286*, 258