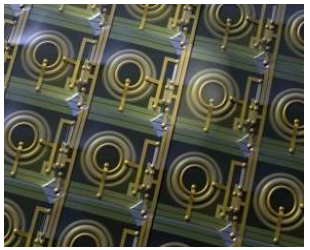
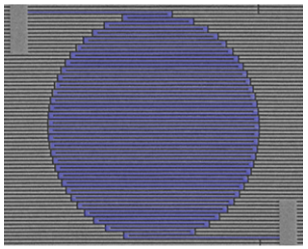
OSA Photonic Detection Technical Group

About Us

The Photonic Detection technical group is part of the Photonics and Opto-Electronics Division of the Optical Society. This group focuses on the detection of photons as received from images, data links, and experimental spectroscopic studies to mention a few. Within its scope, the PD technical group is involved in the design, fabrication, and testing of single and arrayed detectors.





This group focuses on materials, architectures, and readout circuitry needed to transduce photons into electrical signals and further processing. This group's interests include: (1) the integration of lens, cold shields, and readout electronics into cameras, (2) research into higher efficiency, lower noise, and/or wavelength tunability, (3) techniques to mitigate noise and clutter sources that degrade detector performance, and (4) camera design, components, and circuitry.

Executive Board

Shayan Garani Srinivasa, Chair (Indian Institute of Science), shayan.gs@dese.iisc.ernet.in
Francesco Marsili, Vice Chair (JPL), francesco.marsili.dr@jpl.nasa.gov
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OSA Photonic Detection Technical Group

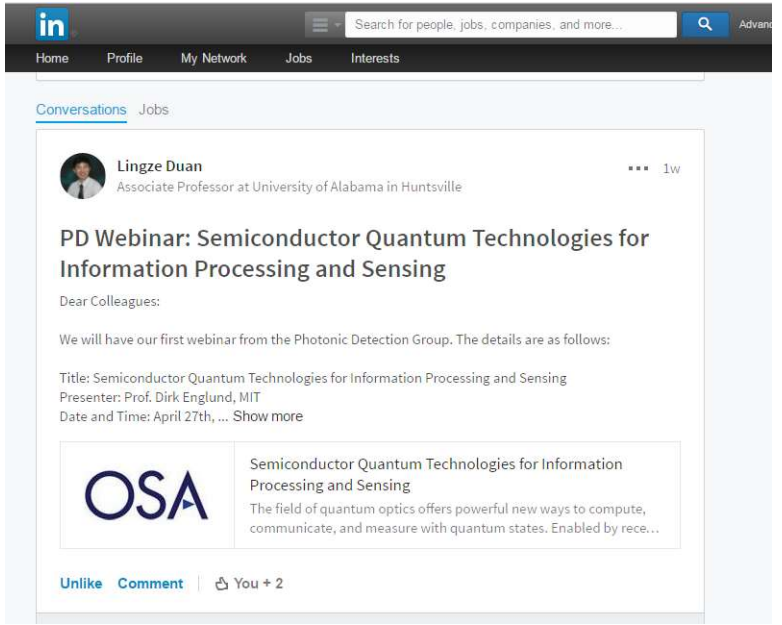
Find us online

OSA Homepage

www.osa.org/PD

LinkedIn Group

www.linkedin.com/groups/Photonic-Detection-Technical-Group-8297763/about



OSA Photonic Detection Technical Group

Planned Technical Group Activities

Our activities include:

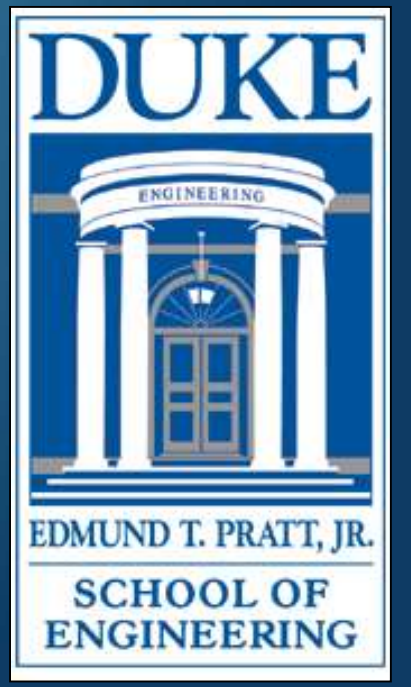
- Special sessions at leading OSA conferences. We had a successful panel discussion at OSA FiO 2015.
- Webinars. We have planned about 3-4 webinars for 2016.
- Proposal on a journal special issue covering PD activities.
- Interaction with local sections and student chapters. We are in the process of setting this up.
- Proposal for the creation of student poster awards at OSA meetings.
- Road map towards solving outstanding research problems.

Outreach:

- Regular communications (distribution list announcements and listservs)
- Create and maintain an active/engaged social media/networking functions (e.g., SharePoint, Google Plus, Twitter, Facebook, and/or LinkedIn).

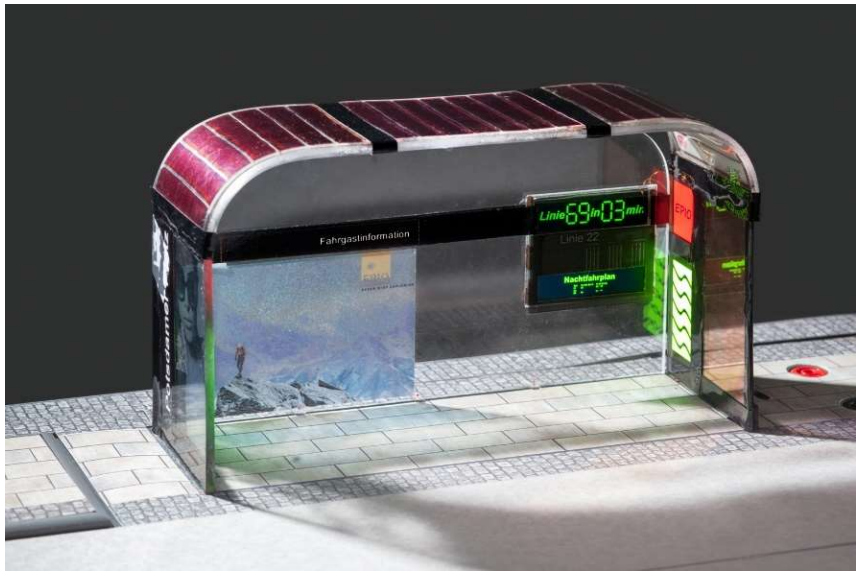
Novel route of hybrid thin film deposition for applications in opto-electronics and energy devices

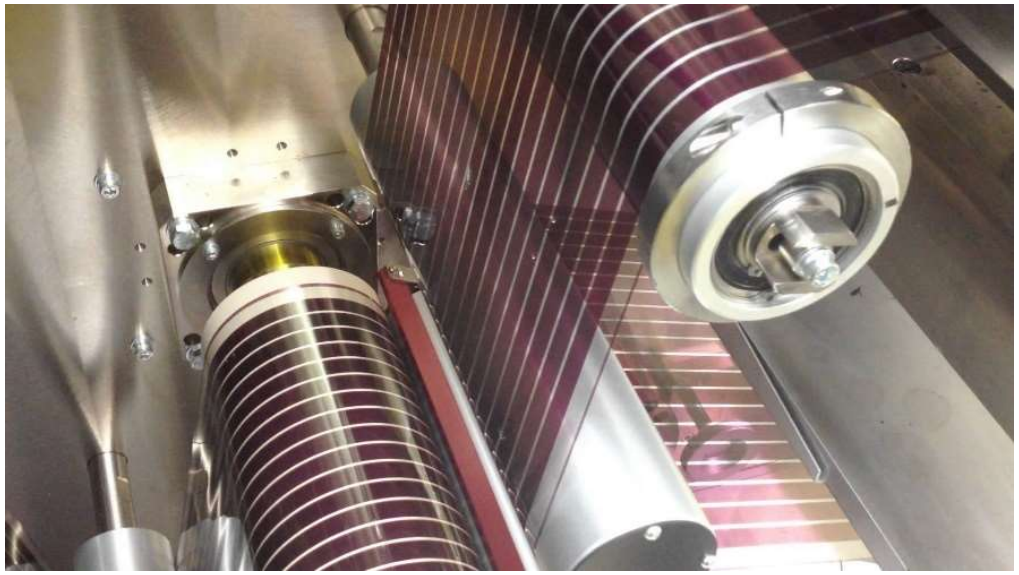
Adrienne D. Stiff-Roberts
Department of Electrical and Computer Engineering
Research Triangle Materials Research Science and Engineering Center (RT-MRSEC)
Duke University
Durham, NC 27708

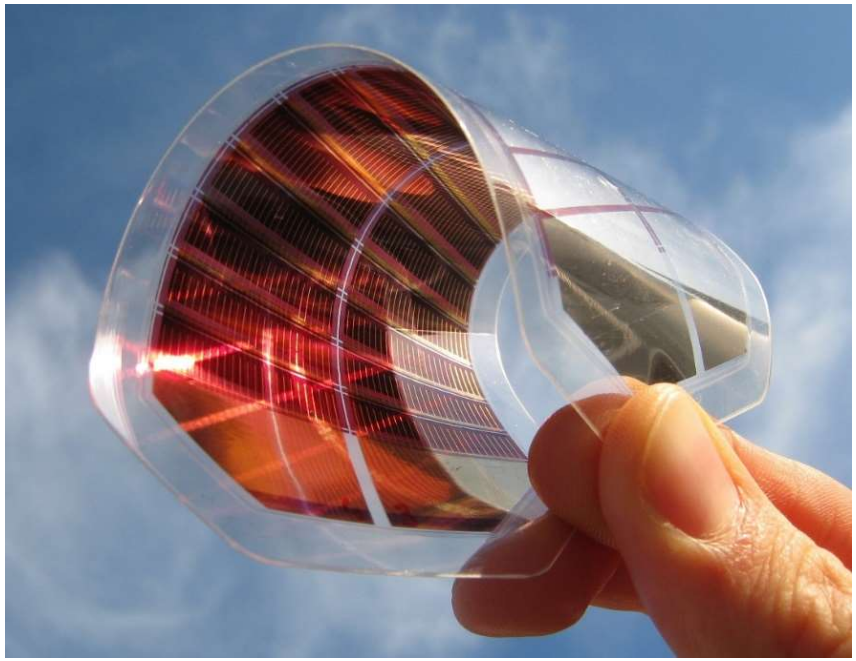


OSA Photon Detection Group Webinar
July 14, 2016

Organic and Hybrid Optoelectronic Devices







Organic and hybrid materials are attractive for optoelectronic devices due to inexpensive and sustainable raw materials, structural flexibility, light weight, and broad range of material properties and functionality.

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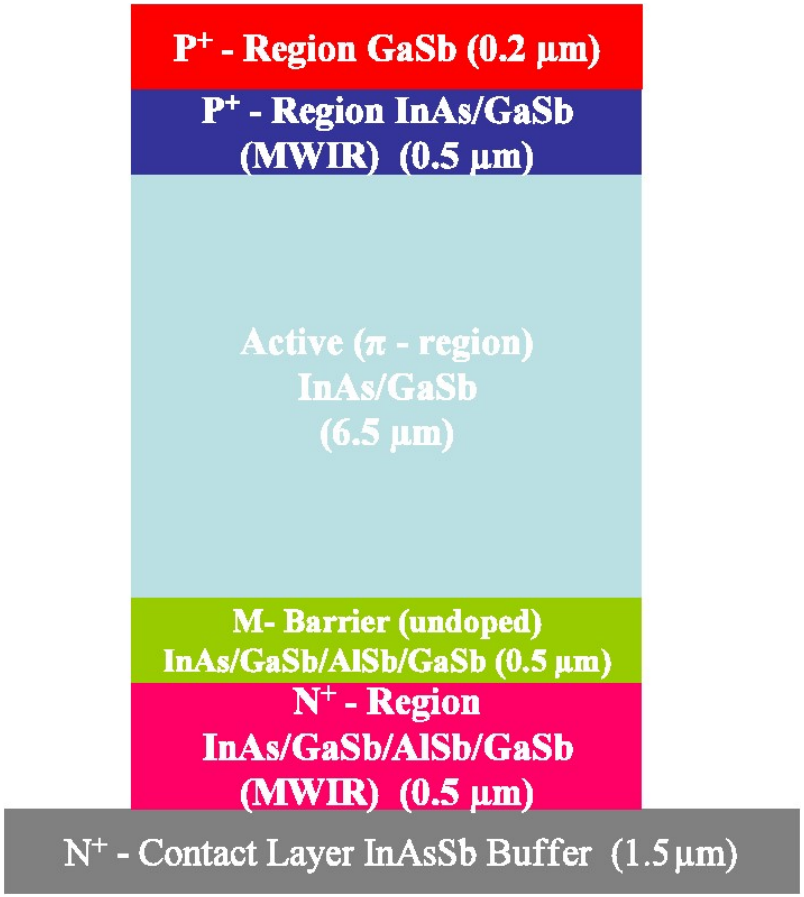
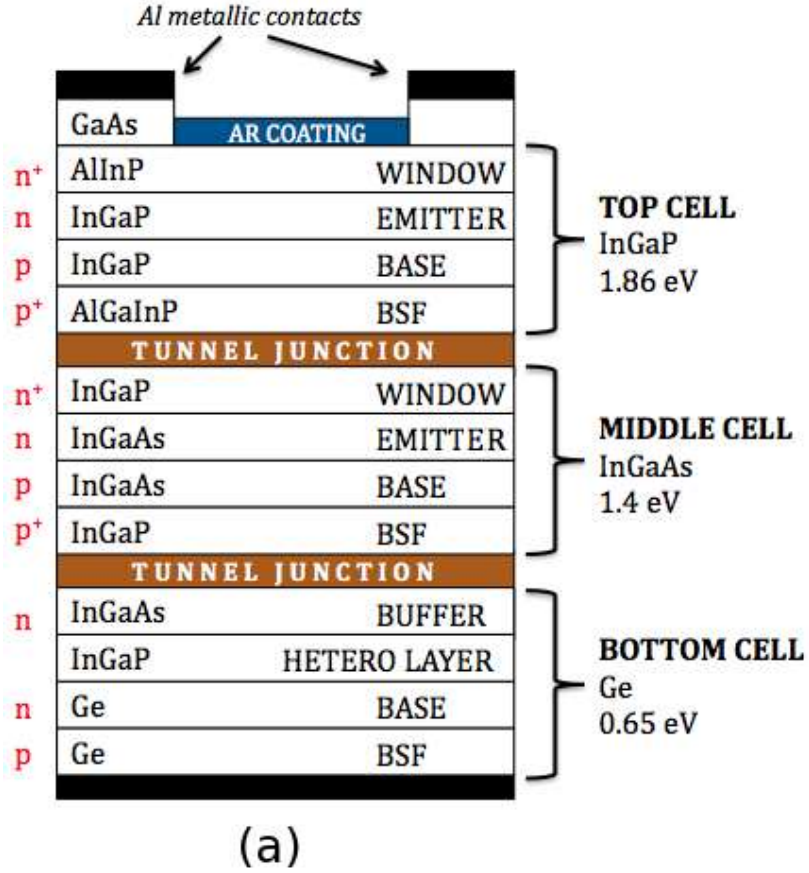
Inorganic Optoelectronic Heterostructures

- Type II Strained-Layer Superlattice IR Photodetector



http://opticalengineering.spiedigitallibrary.org/article.aspx?articleid=1306494

- Multi-junction Solar Cell



http://en.wikipedia.org/wiki/Multijunction_photovoltaic_cell

Inorganic optoelectronic devices benefit from well-established deposition techniques that enable heterostructure design.

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Solution-Processed Deposition

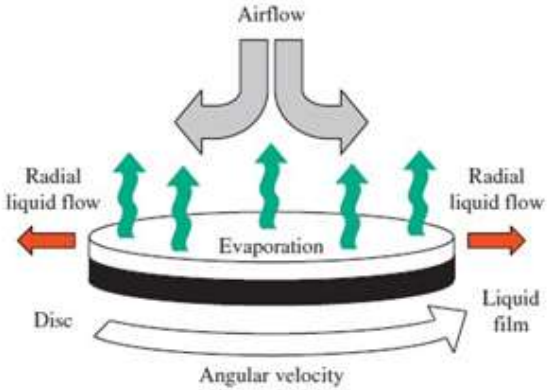
Most organic materials are soluble in organic solvents and can be deposited by solution-processed deposition techniques, which are simple methods to deposit organic thin films with low cost and on a large scale.

Solution-processed depositions involve three steps:

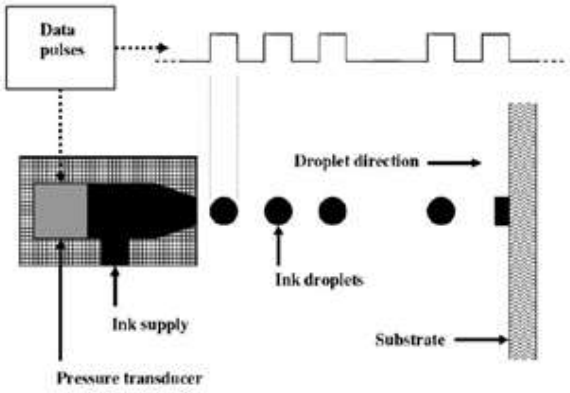
a) **Preparation of target materials solution.**

b) **Spread the solution onto the substrate.**

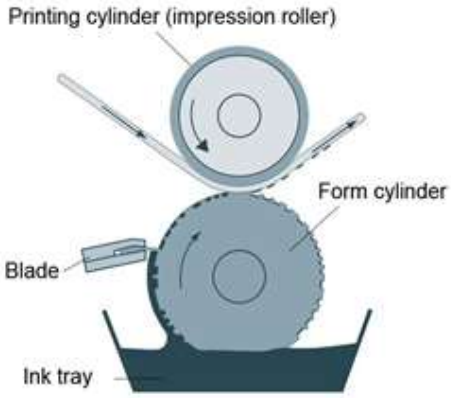
c) **Evaporation of the solvent and film formation.**



Spin-casting



Ink jet printing



Gravure printing

Krebs, F.C., Fabrication and processing of polymer solar cells: A review of printing and coating techniques. Solar Energy Materials and Solar Cells, 2009. 93(4): p. 394-412.

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Solution-Processed Deposition

Disadvantages:

1. Phase separation in blended films driven by solvent evaporation process.
2. Not able to deposit blended films comprising two materials with different solubility characteristics. (e.g., hydrophilic and hydrophobic materials)
3. Not able to deposit multi-layer films comprising different materials with the same solubility characteristics in each layer.

Depositing films in a "dry" state could potentially address these challenges.

→ Thermal evaporation is appropriate for organic small molecules that are thermally robust, but not for macromolecules and polymers that can decompose at elevated temperatures.

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What is MAPLE?

1993 – Pulsed Laser Deposition (PLD) of insoluble polymers (e.g. PTFE)[a] reported

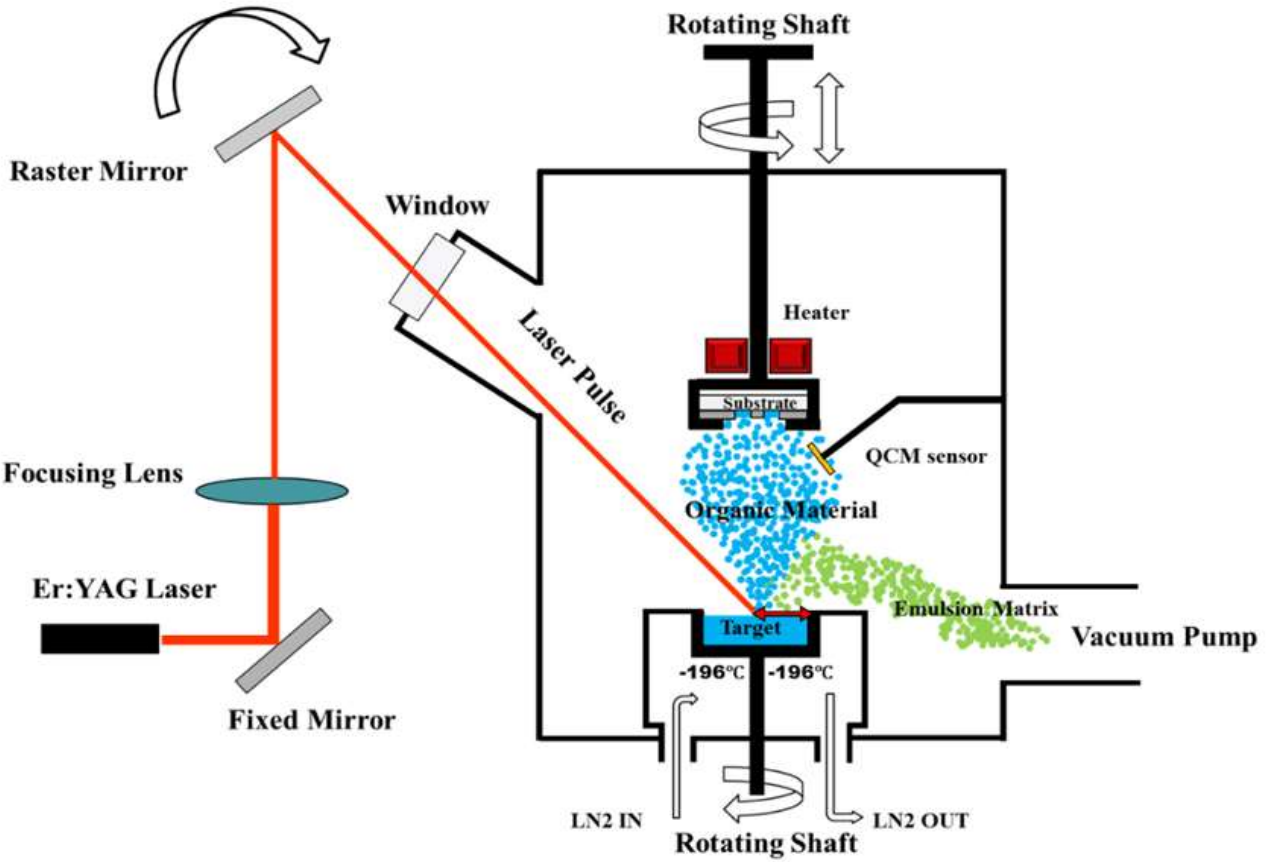
1999 – MAPLE created at Naval Research Laboratory[b]

2002 – UV-MAPLE: Photochemical degradation reported due to UV light[c]

2004 – **Resonant Infrared MAPLE (RIR-MAPLE)** introduced[d], decouples polymer and solvent absorption

2007 – Stiff-Roberts Group uses emulsions of multiple solvents as RIR-MAPLE target

Matrix-**A**ssisted **P**ulsed **L**aser **E**vaporation



(a) Blanchet, et al., Science **262** (1993) 719
(b) Pique, et al., Thin Solid Films **355-356** (1999) 536
(c) Bubb, et al., J. Appl. Phys. **91** (2002) 2055
(d) Toftmann, et al., Thin Solid Films **453-454** (2004) 177

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What is MAPLE?

Matrix-Assisted Pulsed Laser Evaporation

MAPLE enables:

- tailored material composition
- novel film structure
- heterostructure design
- use of same process, regardless of thin-film material or substrate

Parameter Space:

1. Target composition
2. Chamber pressure
3. Substrate temperature
4. Growth distance
5. Fluence

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Outline

- Emulsion-based, Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation (RIR-MAPLE)
- Deposition of Hybrid Nanocomposites
- Optical Coatings
- Photodetectors
- Solar Cells
- Conclusions
- Acknowledgements

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Emulsion-based, Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation (RIR-MAPLE)

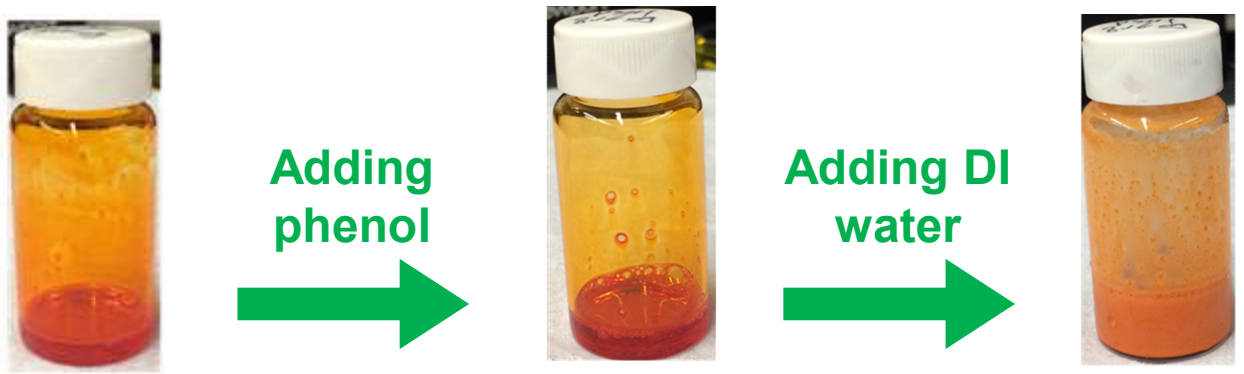
Emulsion-Based RIR-MAPLE

Unique RIR-MAPLE Techniques Developed by Stiff-Roberts Group

Emulsion Host Matrix

The emulsion host matrix contains: primary solvent, secondary solvent, DI water (containing surfactant).

- **Primary solvent** is used to dissolve the target organic materials.
- **Secondary solvent** is mainly used to prevent frozen target sublimation under the vacuum, and also enrich the OH concentration in the emulsion.
- **DI water (containing surfactant)** is used to enrich the OH concentration to absorb the laser energy.



R. Pate and A. D. Stiff-Roberts, *Chemical Physics Letters*, vol. 477, pp. 406-410, August 2009.

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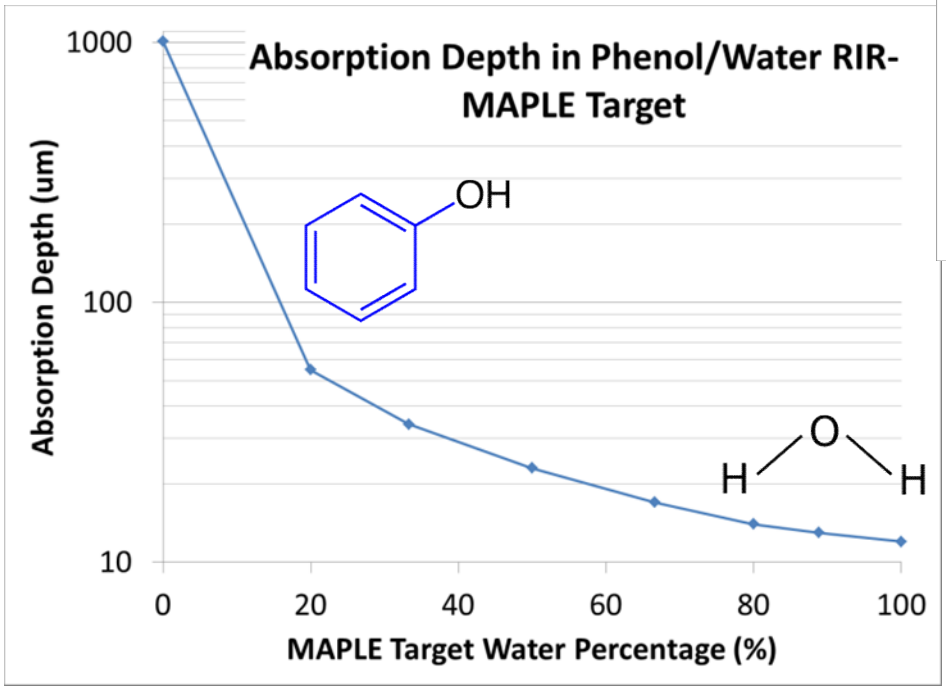
Emulsion-Based RIR-MAPLE

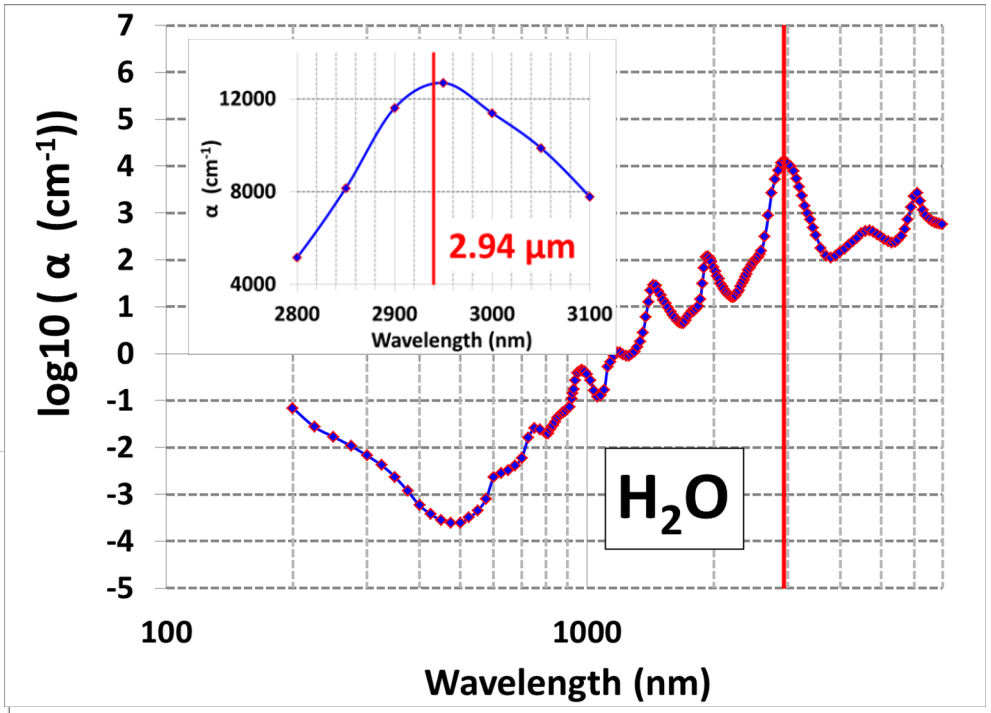
Unique RIR-MAPLE Techniques Developed by Stiff-Roberts Group

Emulsion Host Matrix

- The laser energy is resonant with hydroxyl bond (O-H) vibrational modes.
- The concentration of hydroxyl bonds in the target can be tuned by using oil-in-water emulsions.



R. Pate and A. D. Stiff-Roberts, *Chemical Physics Letters,* vol. 477, pp. 406-410, 2009



G. M. Hale and M. R. Querry, *Appl. Opt.,* vol. 12, pp. 555-563 (1973)

The emulsion approach decouples the organic-based target material from the laser energy.

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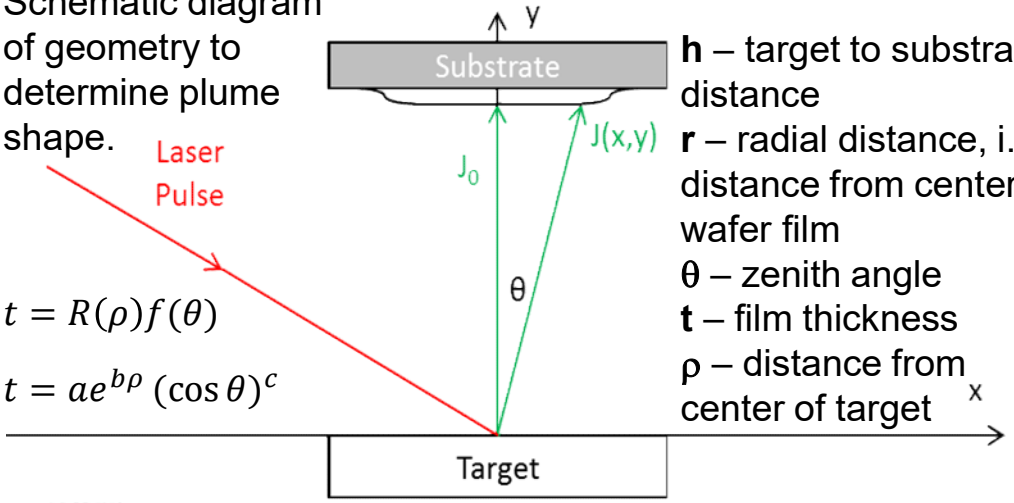
Emulsion-Based RIR-MAPLE

Unique RIR-MAPLE Techniques Developed by Stiff-Roberts Group

Laser-Induced Material Plume

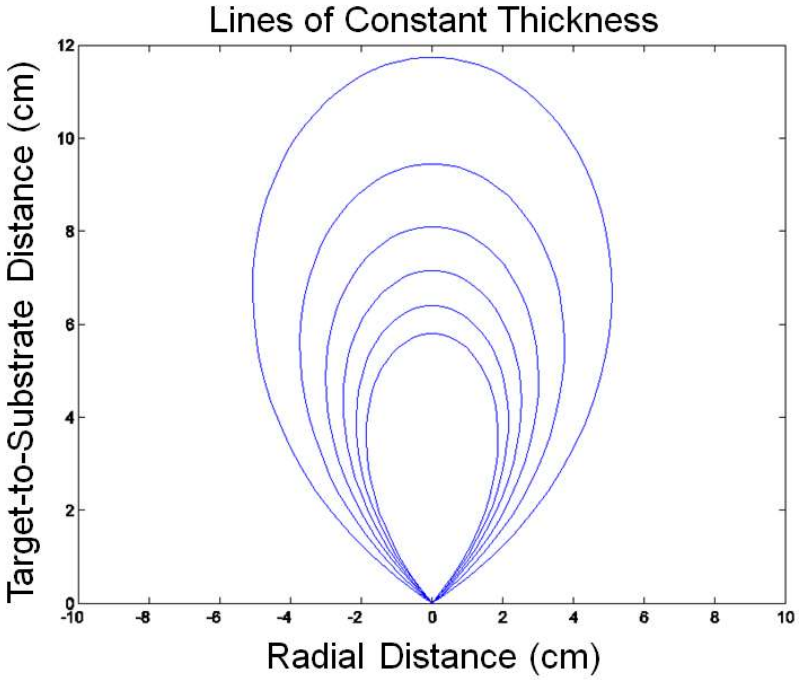
Schematic diagram of geometry to determine plume shape.

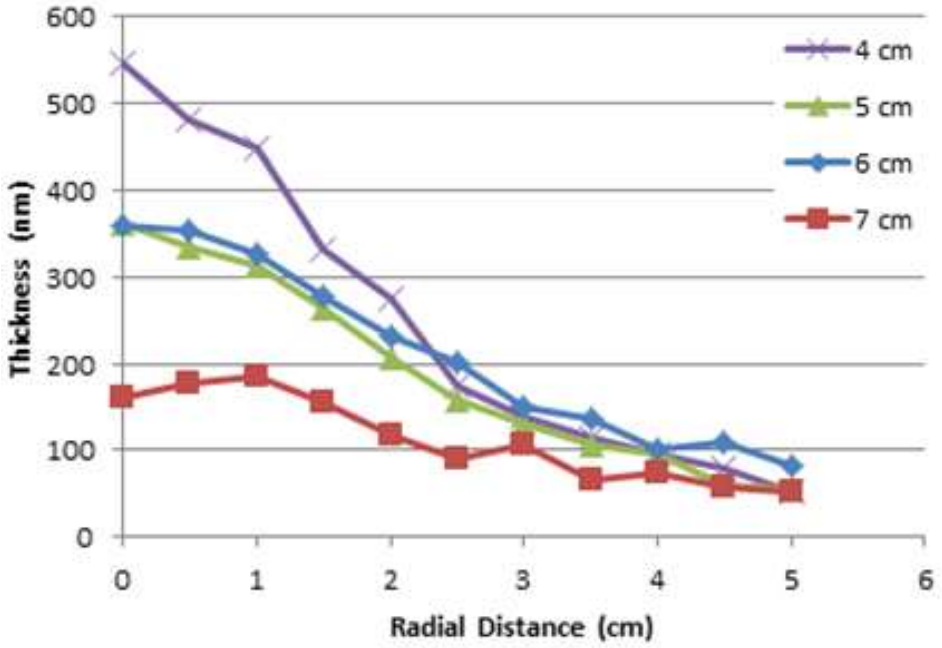


$$t = R(\rho)f(\theta)$$

$$t = ae^{b\rho}(\cos\theta)^c$$

h – target to substrate distance
r – radial distance, i.e. distance from center of wafer film
θ – zenith angle
t – film thickness
ρ – distance from center of target





A natural parameter to use as a representation of the plume is the mass flux, J(x,y), as a function of the axis normal to the target surface (y-axis) and the axis parallel to the target surface (x-axis).

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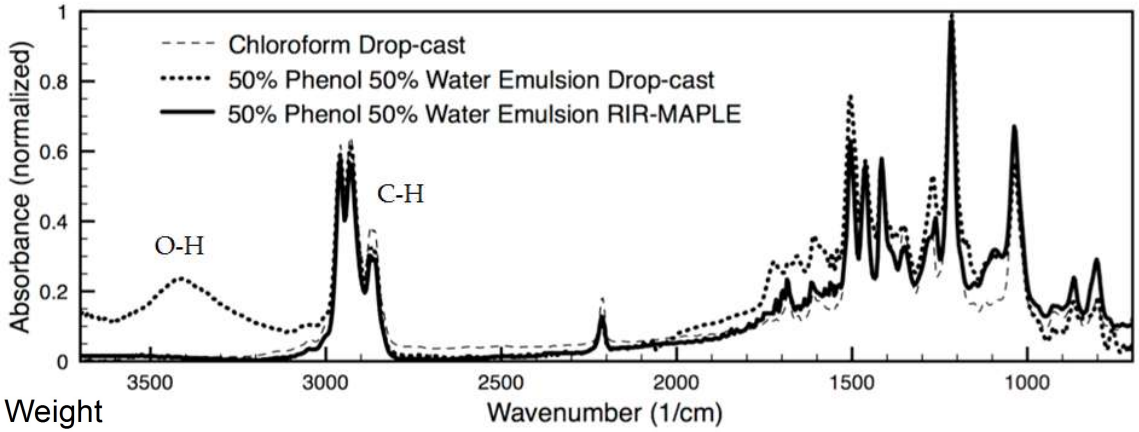
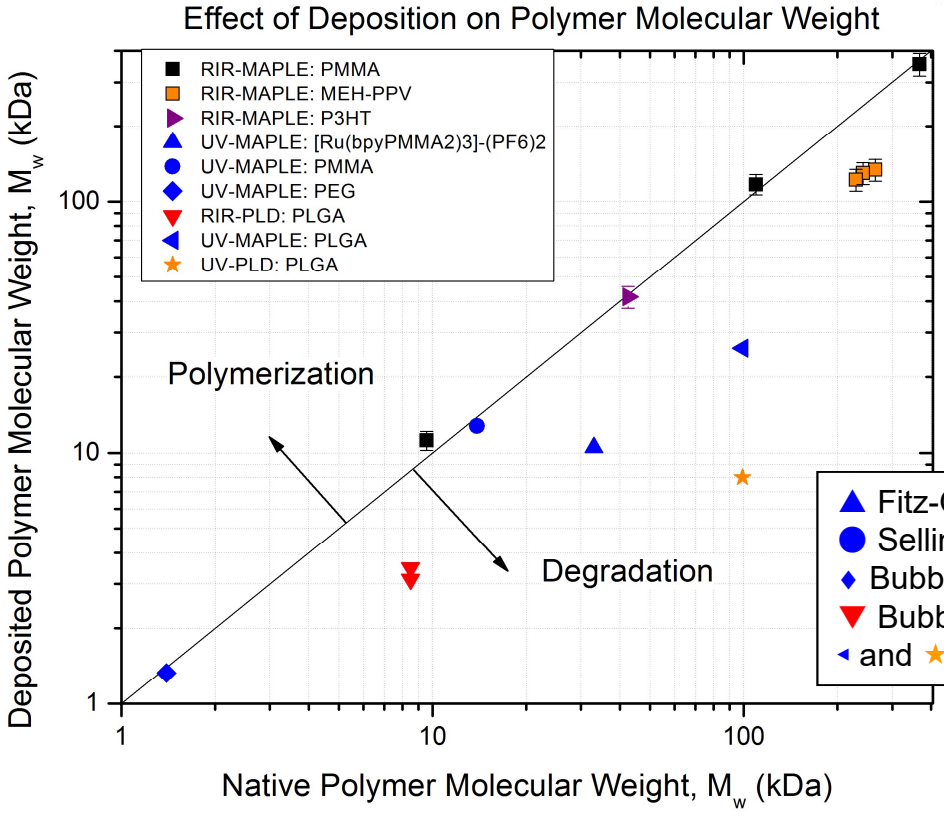
Emulsion-Based RIR-MAPLE

Unique RIR-MAPLE Techniques Developed by Stiff-Roberts Group

Emulsion Host Matrix

R. Pate, K. R. Lantz, and A. D. Stiff-Roberts, *IEEE J. of Sel. Top. Quantum Electron. (Semiconductor Photonic Materials)*, vol. **14** , 1022 (2008).





Photochemical and structural degradation are minimal in polymer films deposited by RIR-MAPLE (confirmed by FTIR absorbance and gel permeation chromatography measurements).

▲ Fitz-Gerald et al., Appl. Phys. A, 80, 1109-1113 (2005)
● Sellinger et al., Thin Solid Films, 516, 6033-6040 (2008)
♦ Bubb et al., J. Appl. Phys., 91, 2055-2058 (2002)
▼ Bubb et al., Appl. Phys. A, 123-125 (2002)
◂ and ★ Mercado et al., Appl. Phys. A, 81, 591-599 (2004)

R. McCormick, J. Lenhardt, and A. D. Stiff-Roberts, *Polymers*, **4**, 341 (2012).

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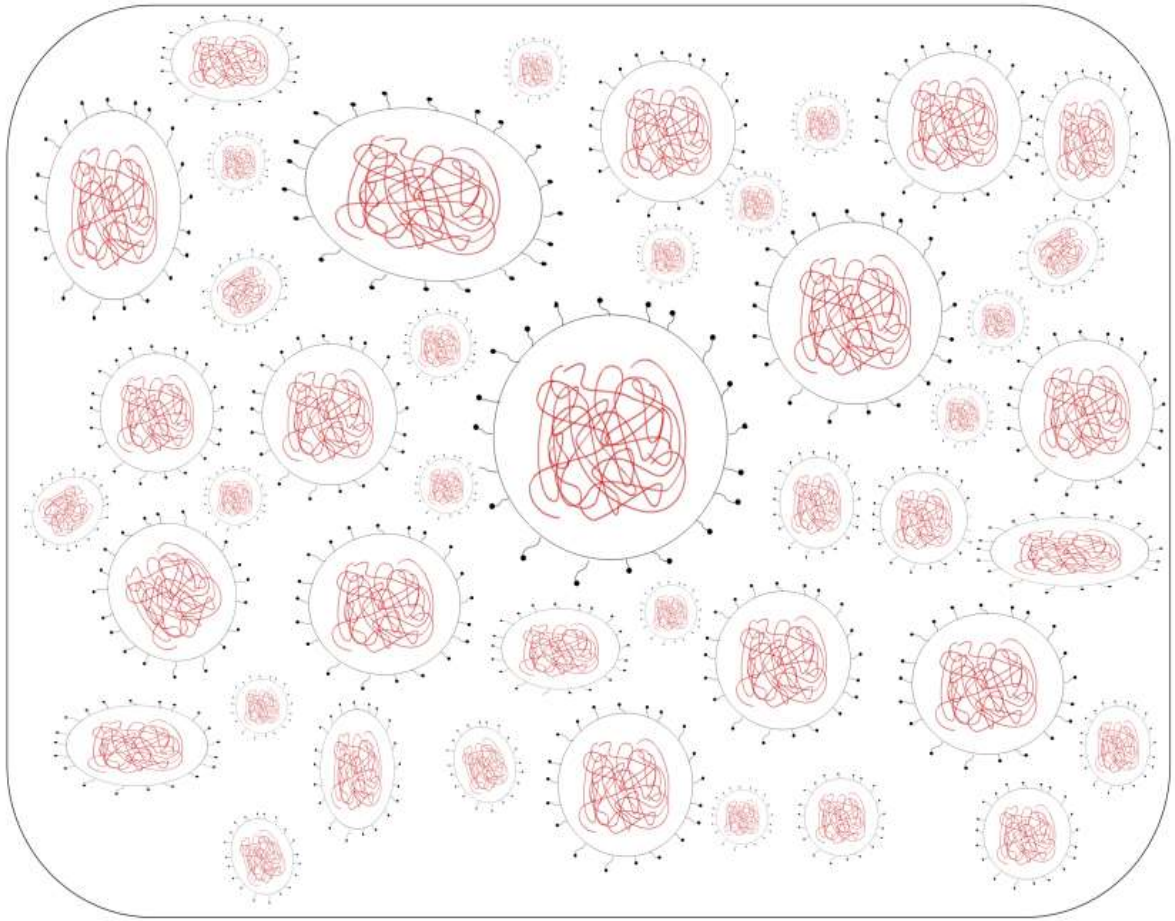
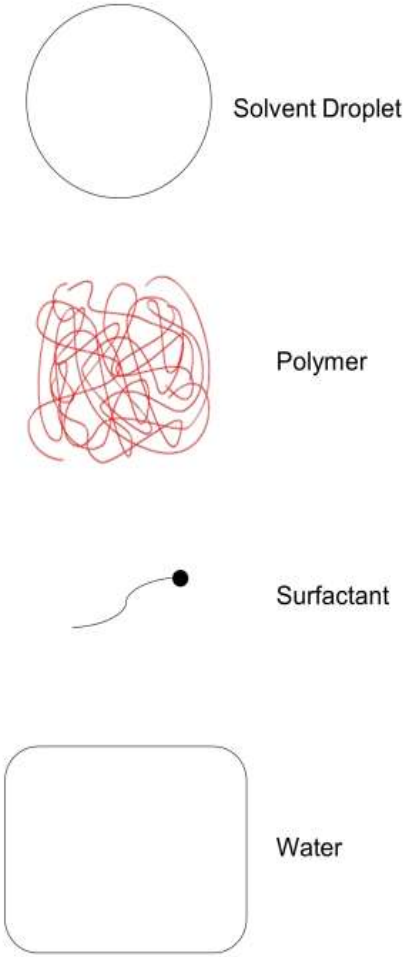
Emulsion-Based RIR-MAPLE

Unique RIR-MAPLE Techniques Developed by Stiff-Roberts Group

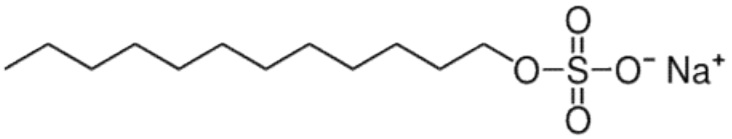
Emulsion Host Matrix





The standard recipe typically results in an oil in water (O/W) emulsion.

Sodium Dodecyl Sulfate (SDS)



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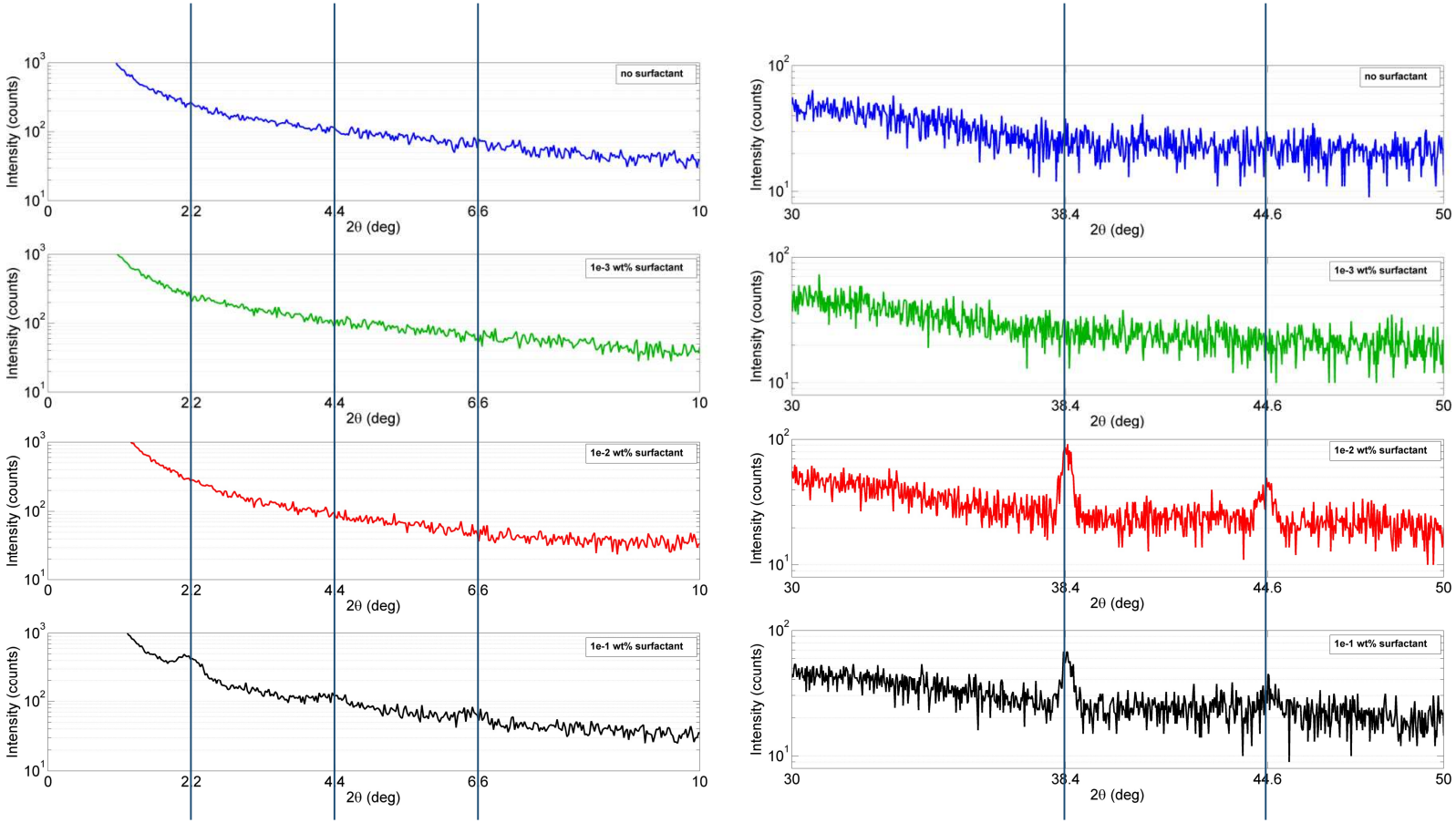
Effect of Surfactant

No SDS

1E-3 wt%

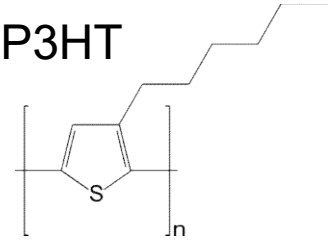
1E-2 wt%

1E-1 wt%



- XRD analysis of four different amounts of surfactant.
- Result: 1E-3 wt% = no structural peak, still creates stable emulsion

P3HT



A. D. Stiff-Roberts, R. D. McCormick, and W. Y. Ge, *Proceedings of SPIE*, vol. 9350, pp. 935007, March 2015.

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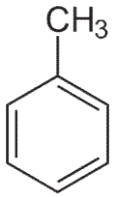
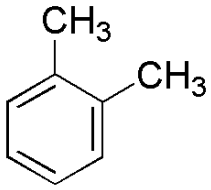
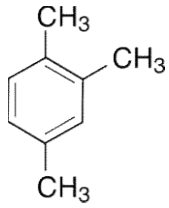
Effect of Primary Solvent

Alkyl aromatic solvents



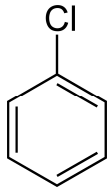


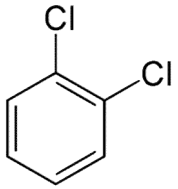


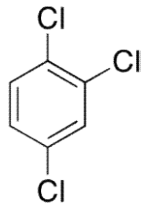
Name	Methylbenzene (Toluene)	1,2 Dimethylbenzene (Xylene)	1,2,4 Trimethylbenzene (Pseudocumene)
RED (Relative Energy Difference)	1	0.93	1.13
Vapor Pressure (Kpa), 25°C	2.9	0.93	0.88
Solubility in water (g/100g)	0.0526	0.0178	0.0057

Decreasing vapor pressure and solubility-in-water

Chlorinated aromatic solvents







Name	Chlorobenzene (CB)	1,2 Dichlorobenzene (ODCB)	1,2,4 Trichlorobenzene (TCB)
RED	0.89	0.79	0.74
Vapor Pressure (Kpa), 25°C	1.2	0.16	0.038
Solubility in water (g/100g)	0.0472	0.0156	0.00488

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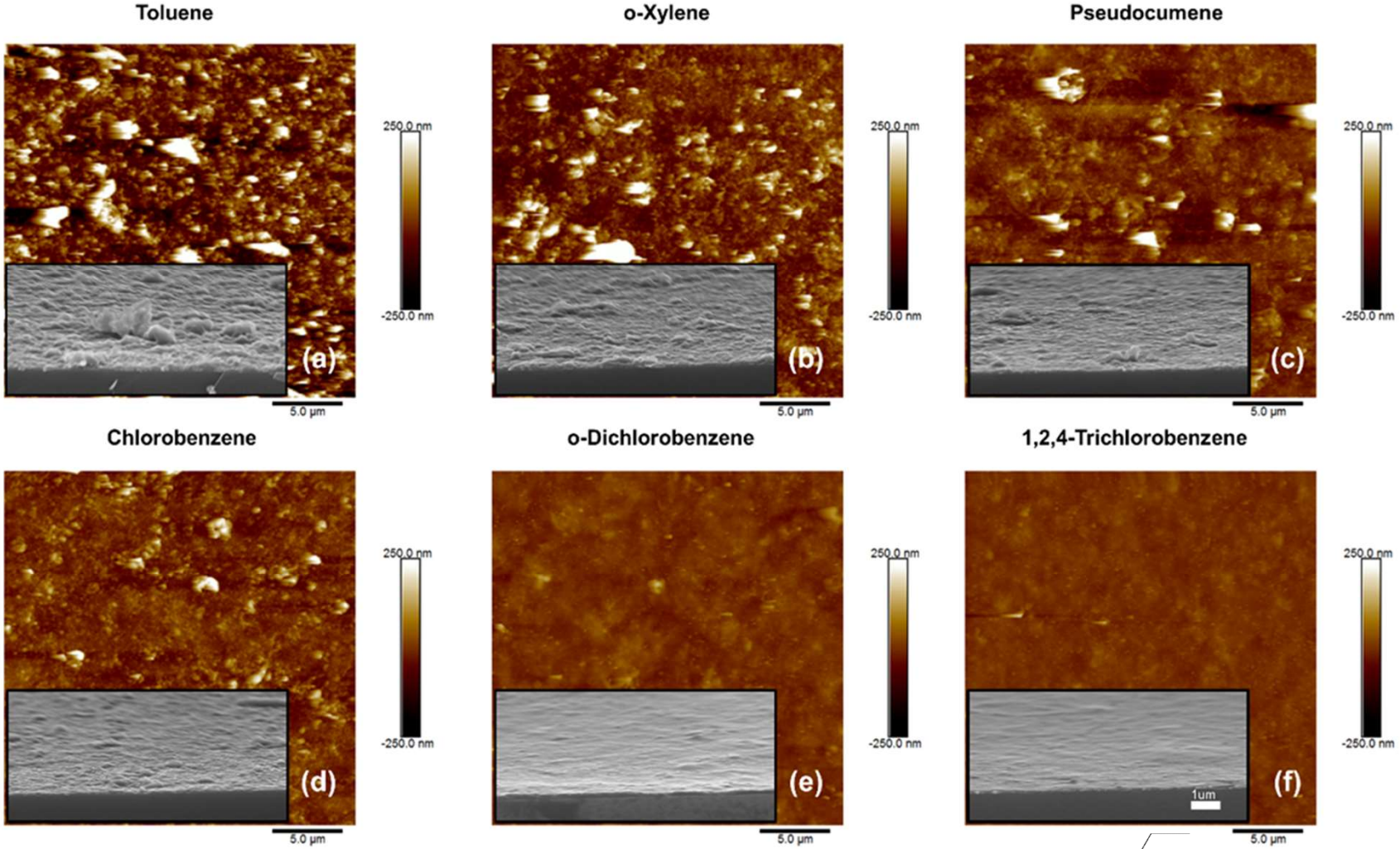
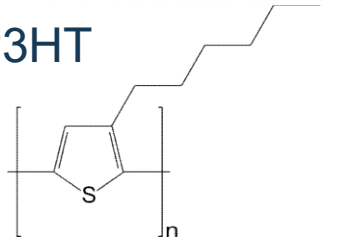
Effect of Primary Solvent - P3HT Deposition



P3HT



* Manuscript submitted.

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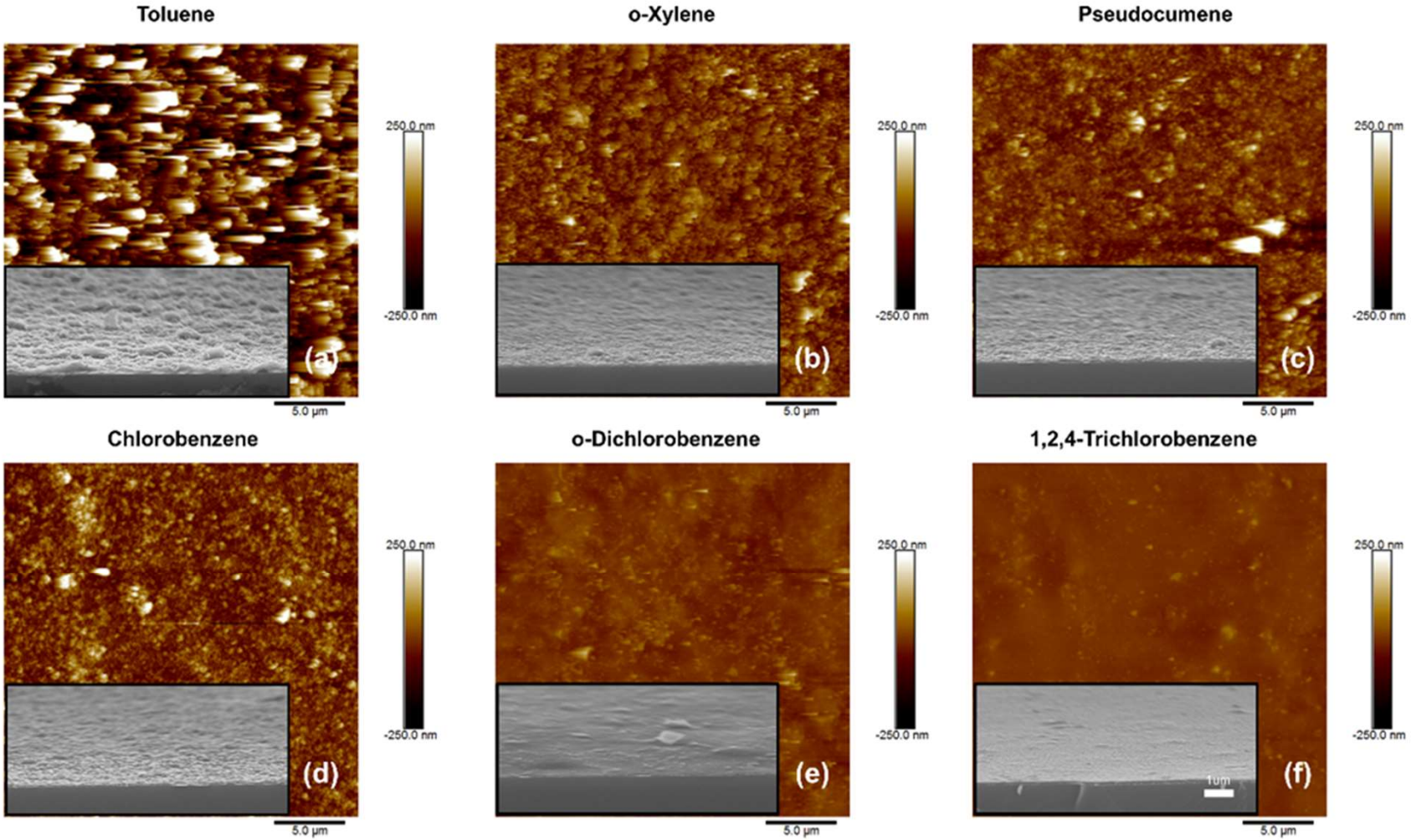
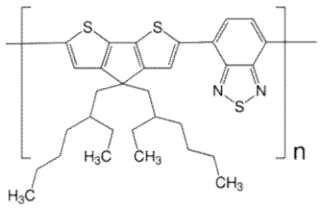
Effect of Primary Solvent - PCPDTBT Deposition





PCPDTBT

* Manuscript submitted.

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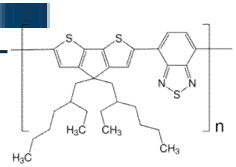
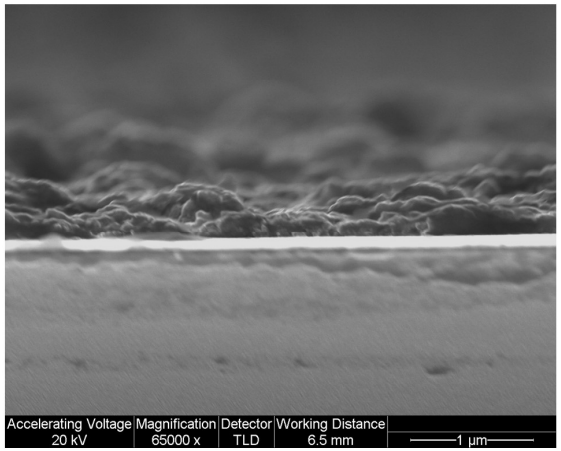
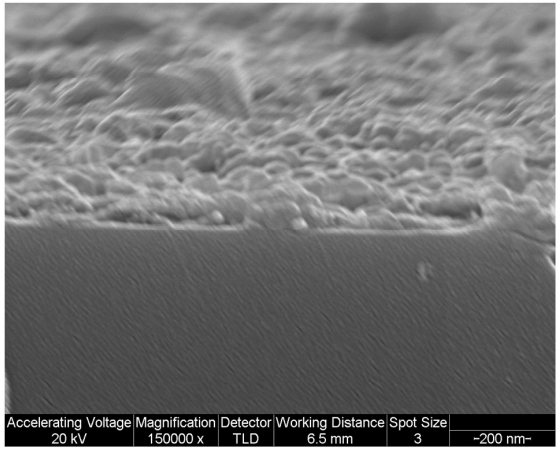
Effect of Primary Solvent - PCPDTBT Deposition

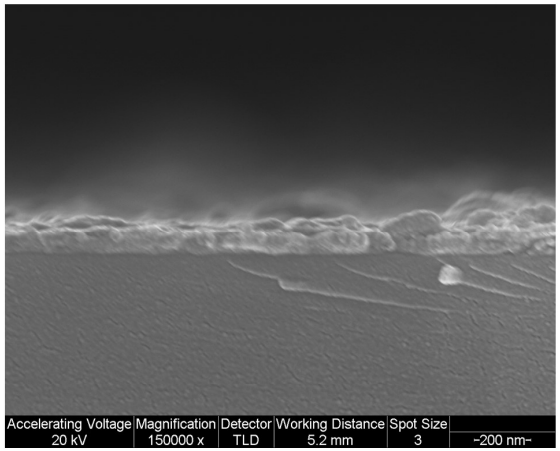
PCPDTBT



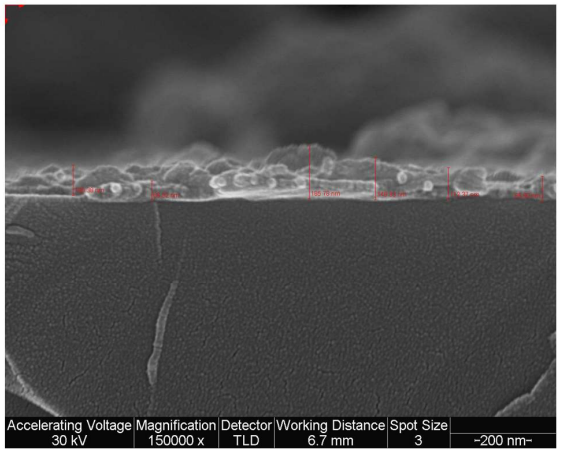
Alkyl aromatic solvents

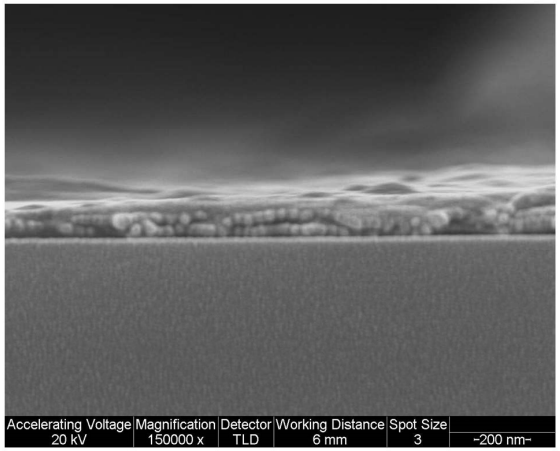


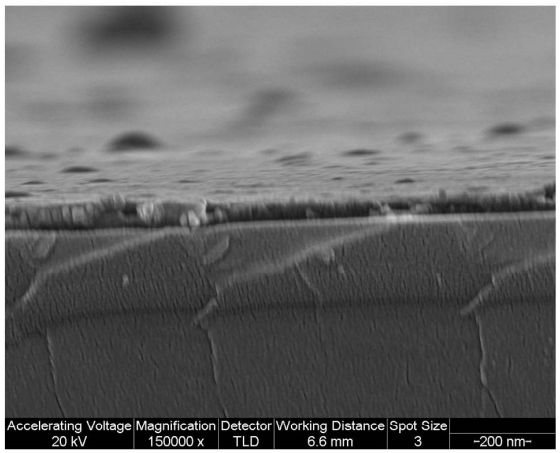




Chlorinated aromatic solvents





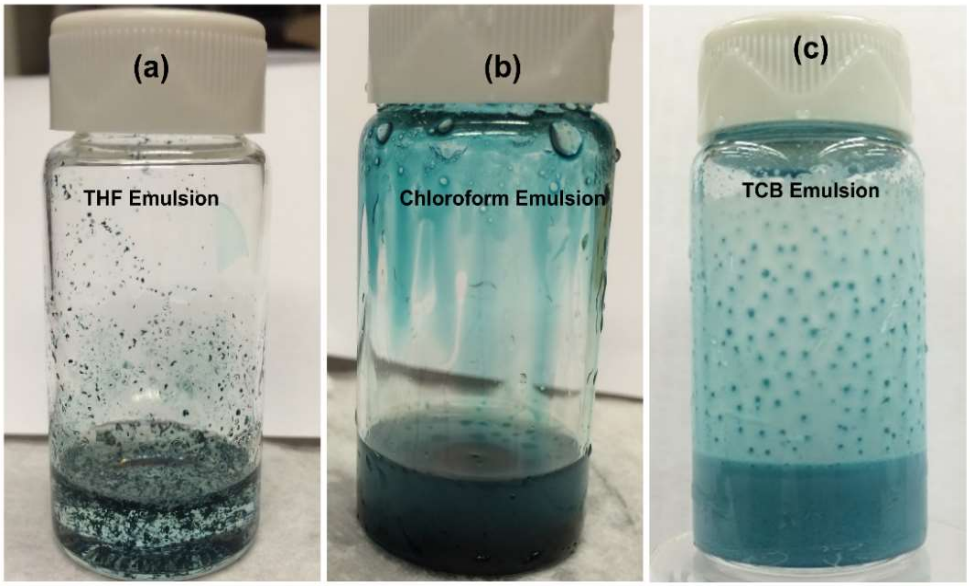


Decreasing vapor pressure and solubility-in-water

* Manuscript submitted.

Effect of Primary Solvent - Growth Mechanisms

Solubility-in-Water



Solubility-in-water: 30 g/100g
RED: 0.77

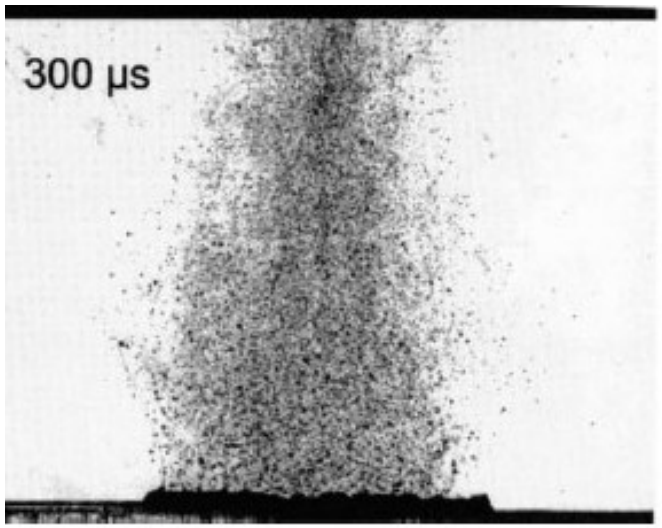
Solubility-in-water: 0.792g/100g
RED:0.61

Solubility-in-water: 0.00488 g/100g
RED:0.74

For lower solubility-in-water, the emulsified particle size decreases. The polymer films are formed by discrete polymer clusters resulting from direct transfer of emulsified particles by laser irradiation of the target.

* Manuscript submitted.

Vapor Pressure



Nahen K, Vogel A; Plume dynamics and shielding by the ablation plume during er:yag laser ablation. J. Biomed. Opt. 0001;7(2):165-178.

For lower vapor pressure, fewer solvent molecules are created for the same incident laser energy. As a result, solvent molecules in the plume are less likely to get trapped in the deposited film, leading to more tightly packed films.

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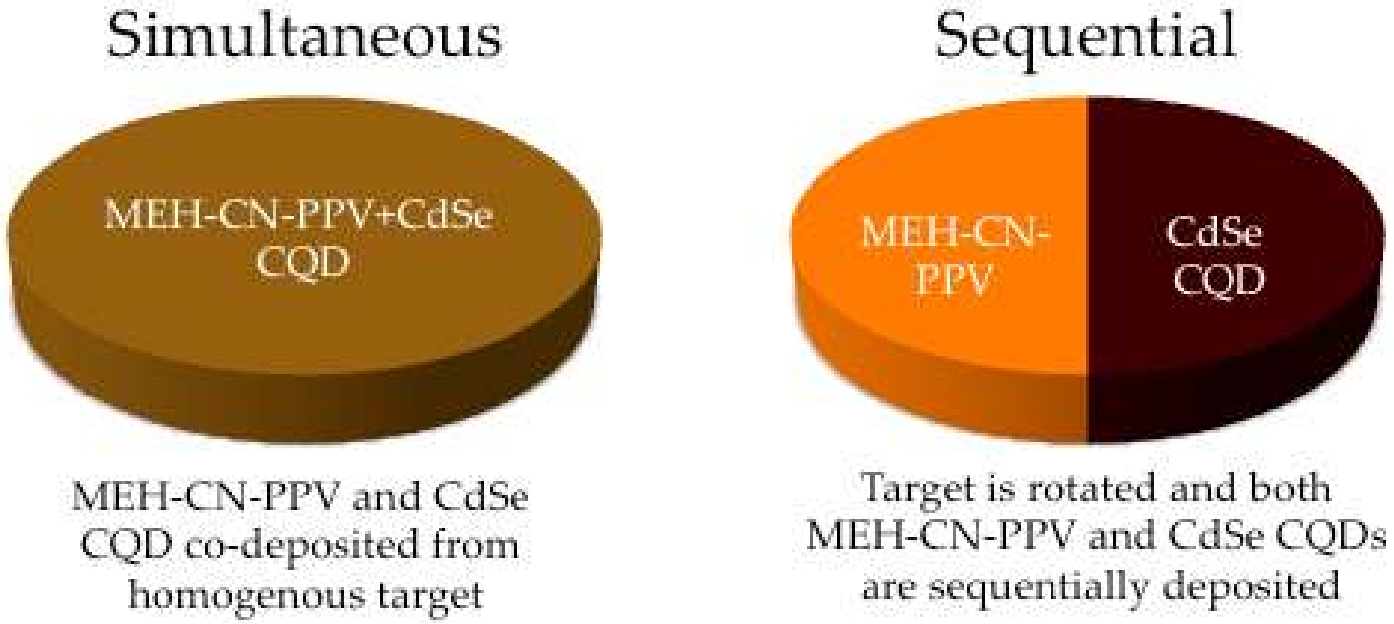
Deposition of Hybrid Nanocomposites

Deposition Modes for Blended Films



Advantages of sequential deposition:

- Provides co-deposition, but different solvents chosen to optimize solubility and film morphology of each component
- Sequential deposition reduces the impact of solubility characteristics of one component on the deposition of another component.

R. Pate, K. R. Lantz, and A. D. Stiff-Roberts, *Thin Solid Films*, **517**, 6798 (2009).

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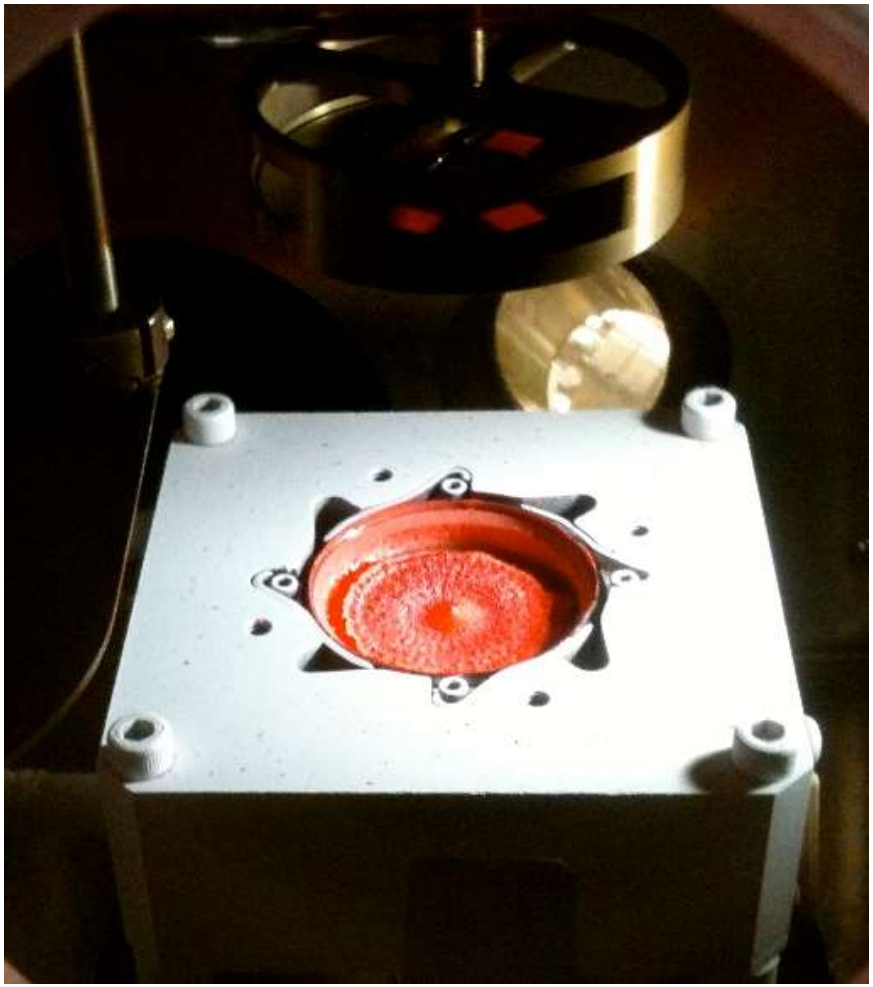
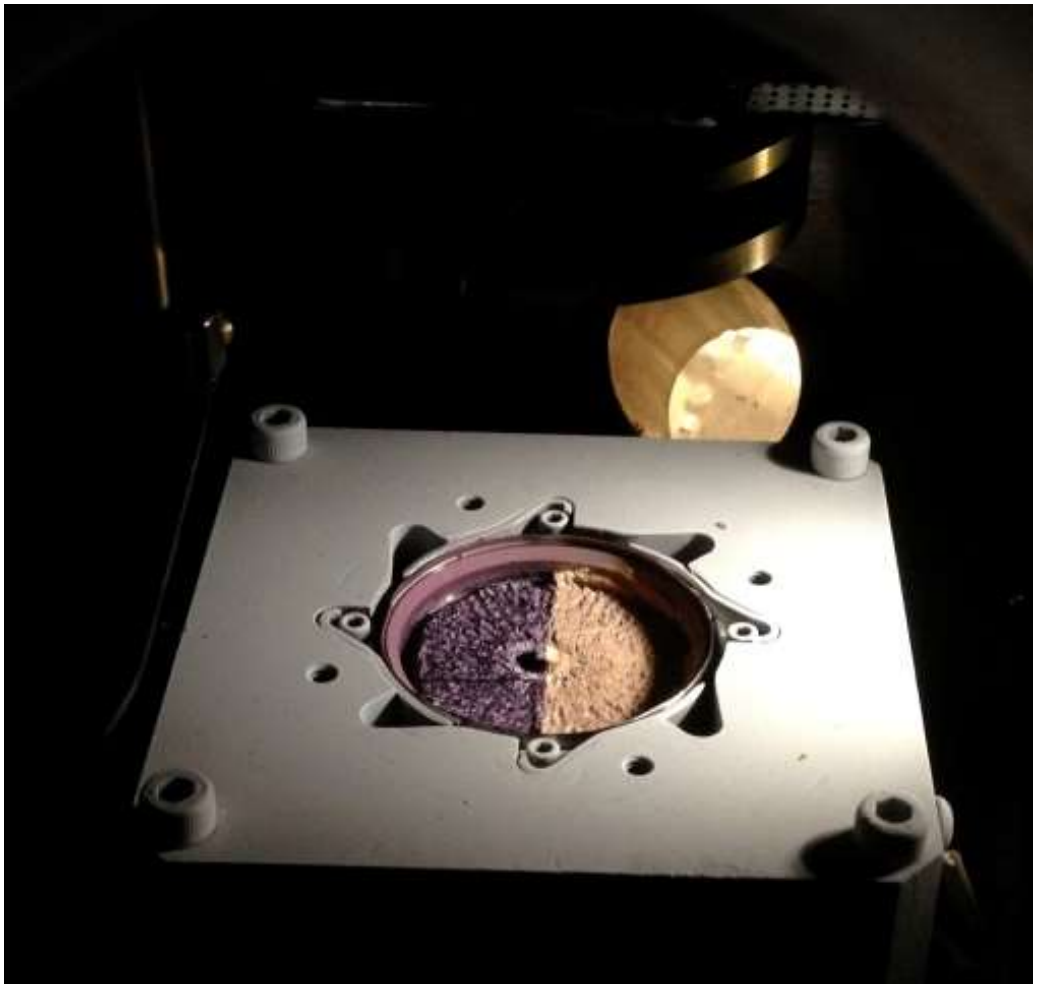
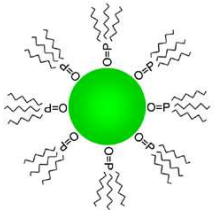
Deposition Modes for Blended Films



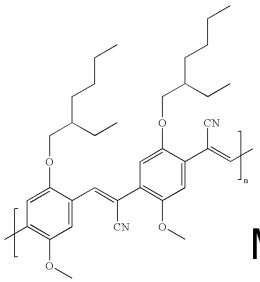


Simultaneous Deposition



TOPO-capped CdSe

Sequential Deposition



MEH-CN-PPV

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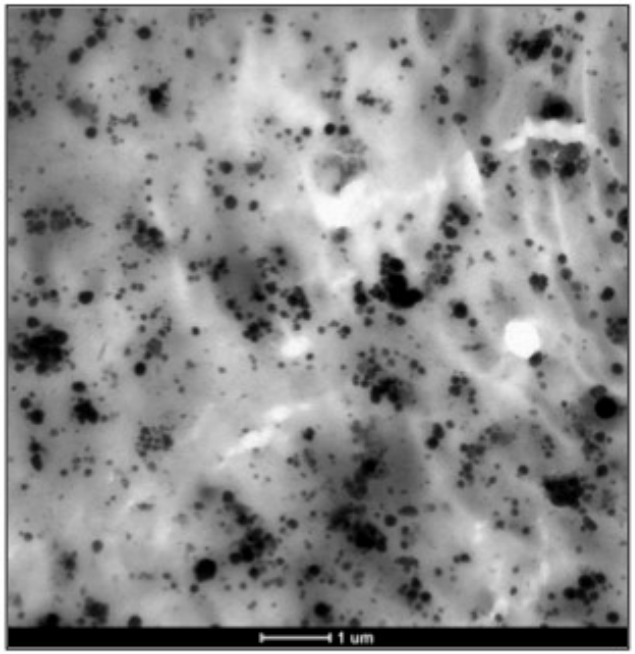
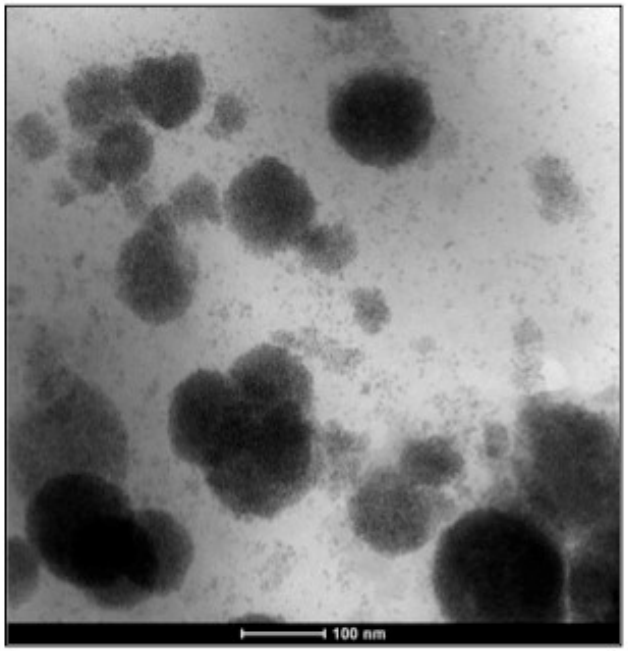
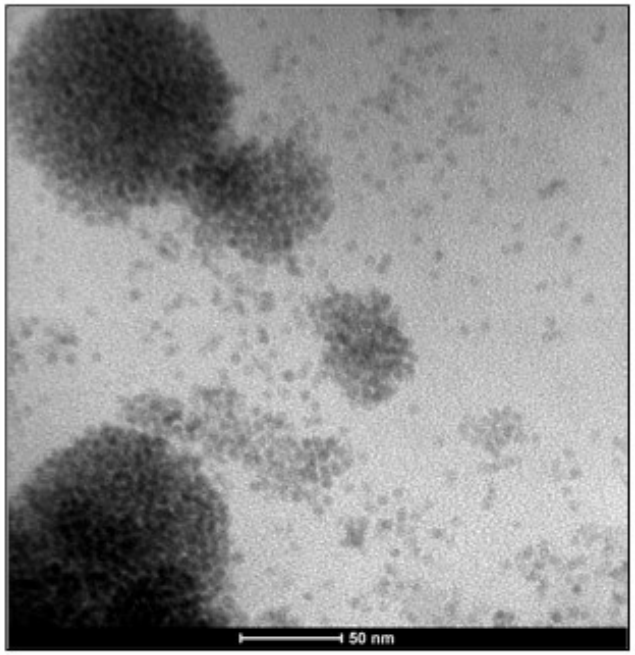
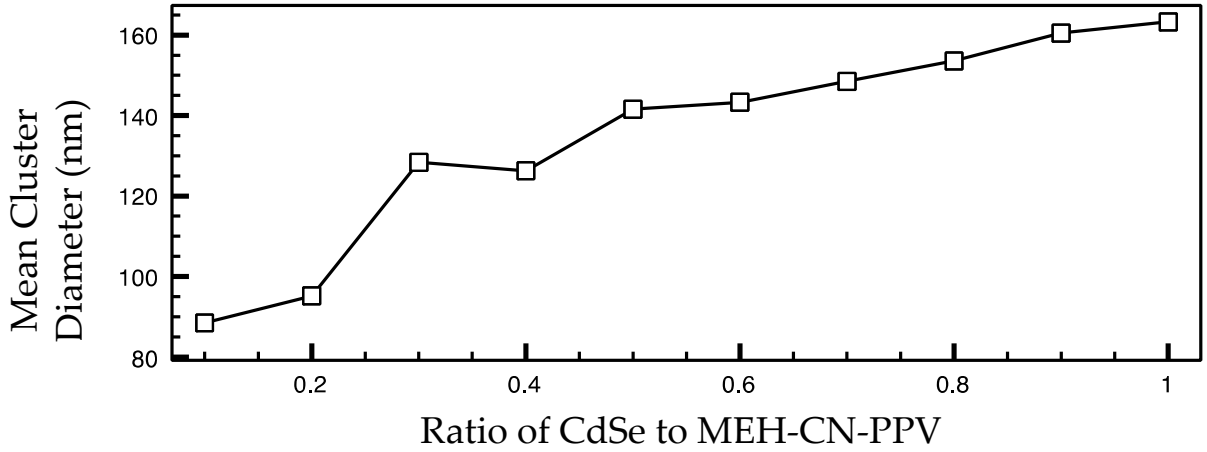
Organic-Inorganic Hybrid Nanocomposites

Simultaneous RIR-MAPLE









R. Pate, K. R. Lantz, and A. D. Stiff-Roberts, *Thin Solid Films*, **517**, 6798 (2009).

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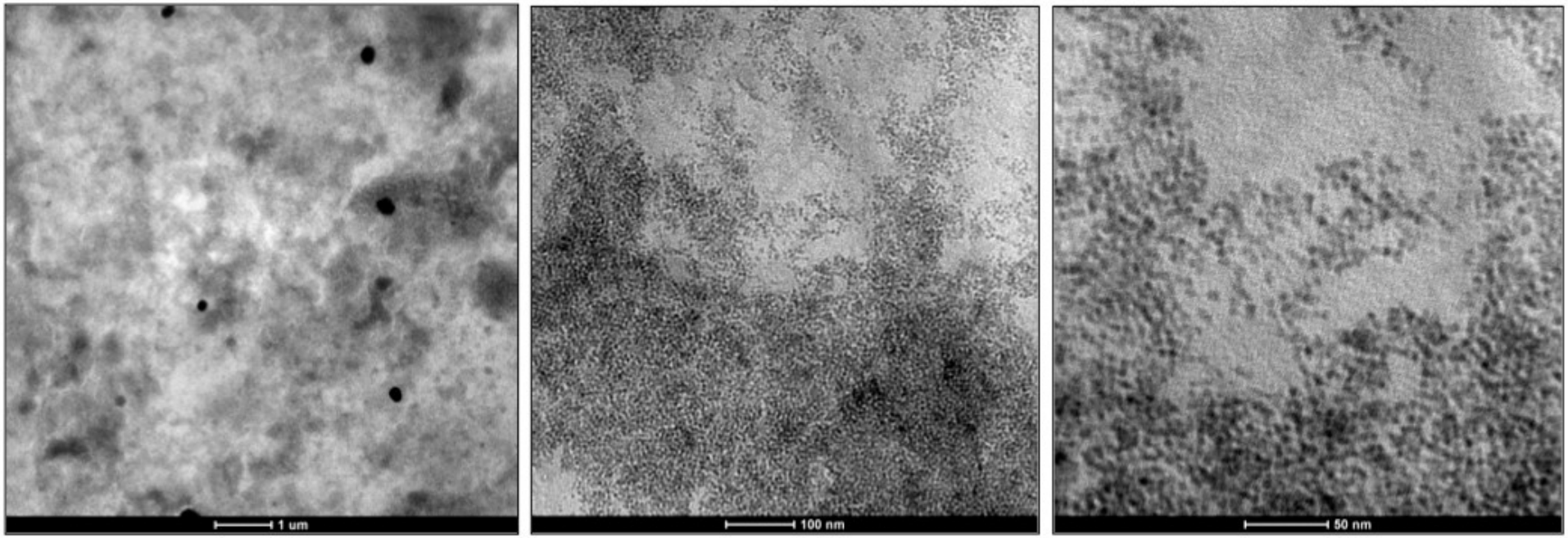
Organic-Inorganic Hybrid Nanocomposites

Sequential RIR-MAPLE



- Near-homogenous distribution of CdSe CQDs in polymer.
- Distribution remains homogenous when the CdSe:MEH-CN-PPV is increased.

R. Pate, K. R. Lantz, and A. D. Stiff-Roberts, *Thin Solid Films*, **517**, 6798 (2009).

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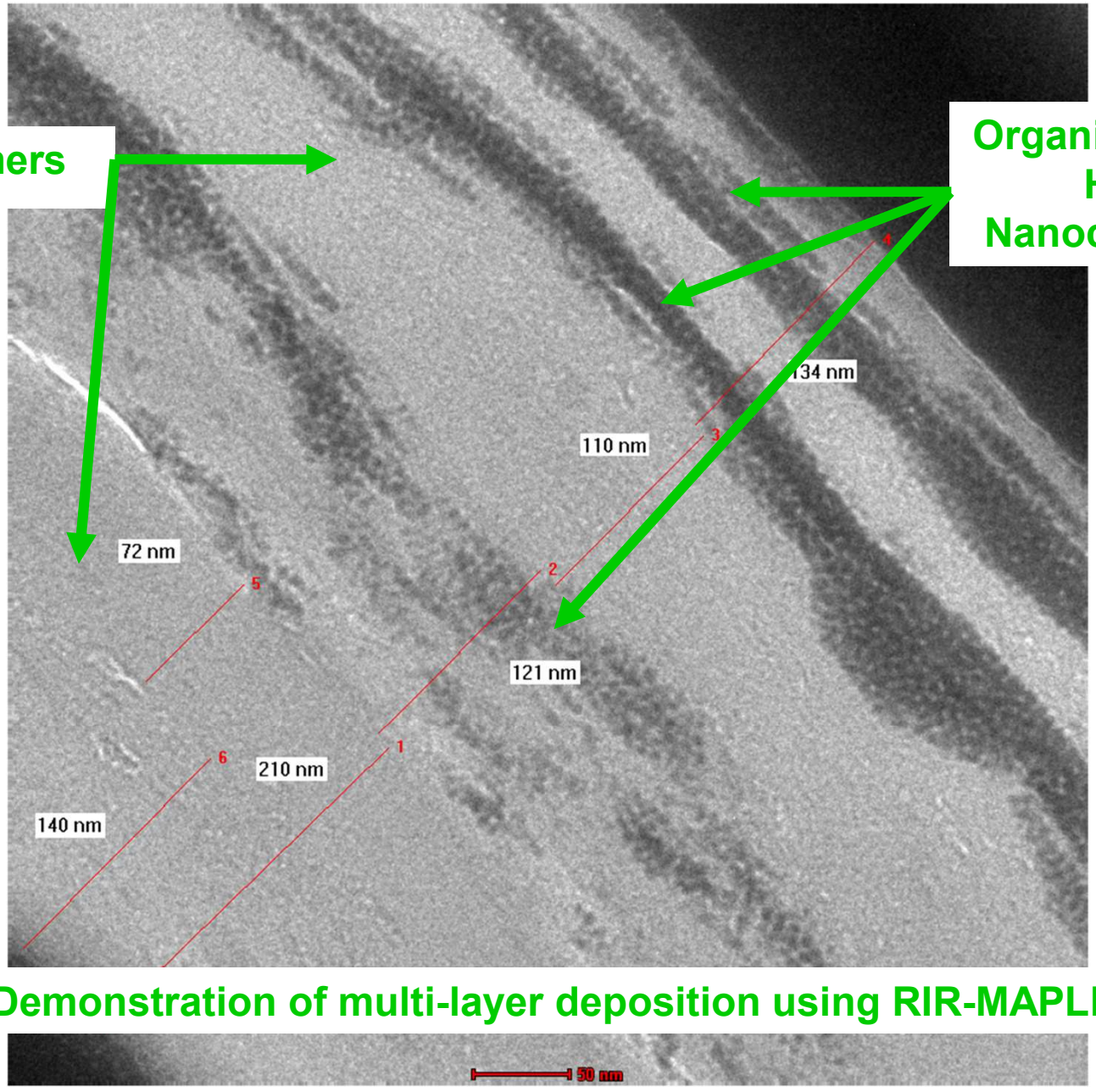
Organic-Inorganic Hybrid Nanocomposites



Demonstration of multi-layer deposition using RIR-MAPLE.

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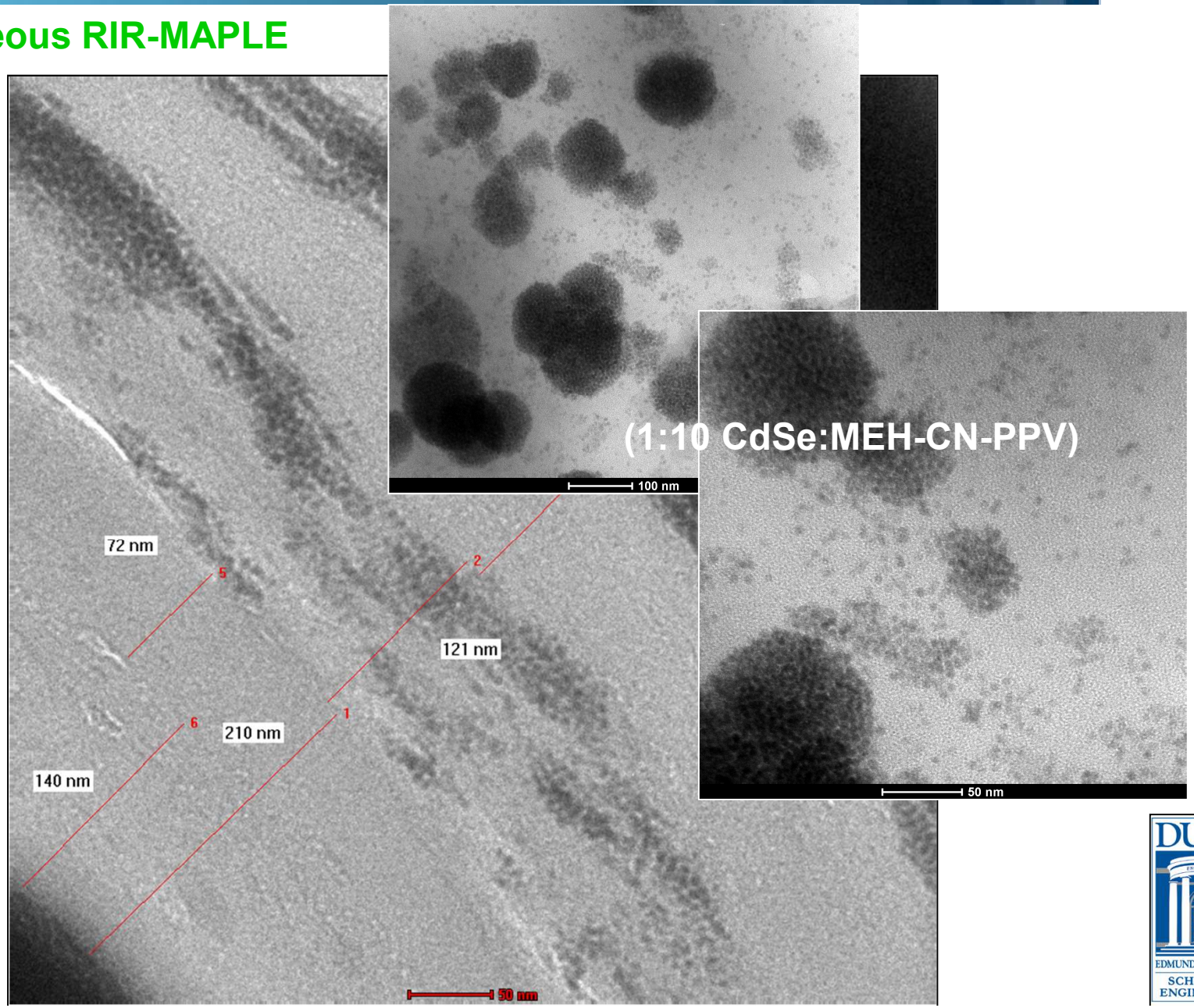
Organic-Inorganic Hybrid Nanocomposites

Simultaneous RIR-MAPLE



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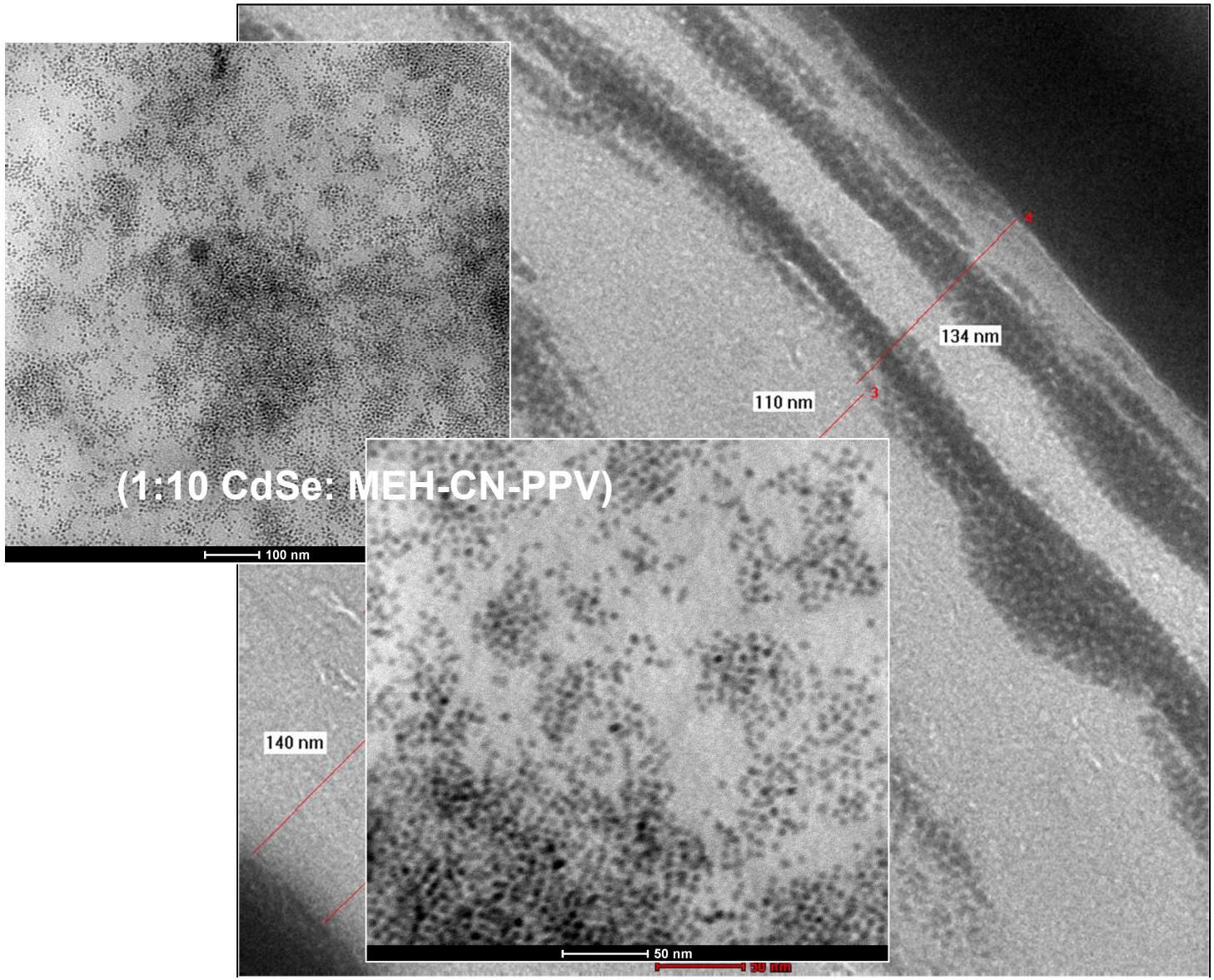
Organic-Inorganic Hybrid Nanocomposites

Sequential RIR-MAPLE



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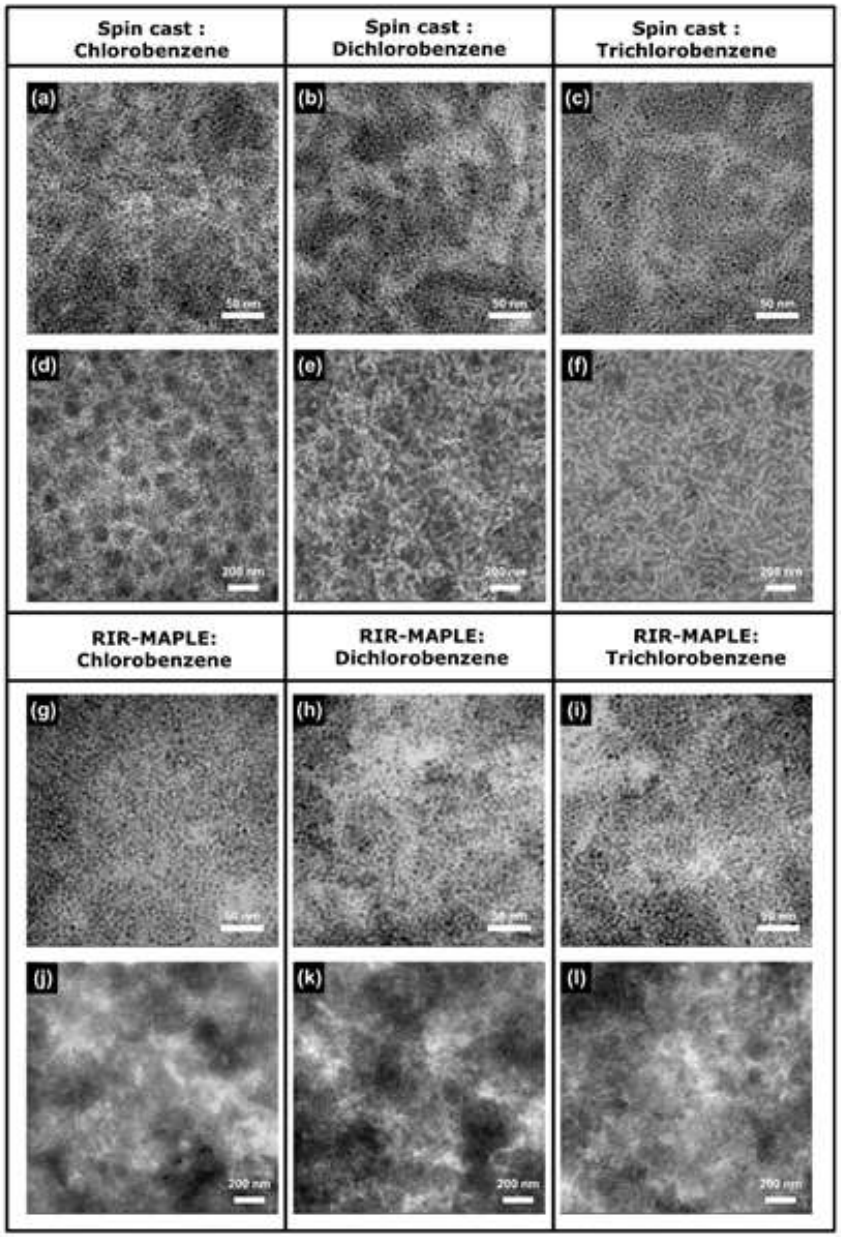
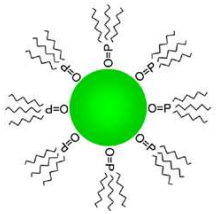
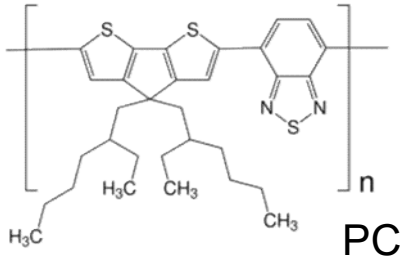
Organic-Inorganic Hybrid Nanocomposites





TOPO-capped CdSe



PCPDTBT

- Hybrid nanocomposites deposited by spin-casting and RIR-MAPLE in the sequential mode have fundamentally different morphologies.
- **The morphology of RIR-MAPLE blended films is independent of the primary solvent used.**

W. Y. Ge, A. Atewologun and A. D. Stiff-Roberts, *Organic Electronics*, vol. 22, pp. 98-107, March 2015.

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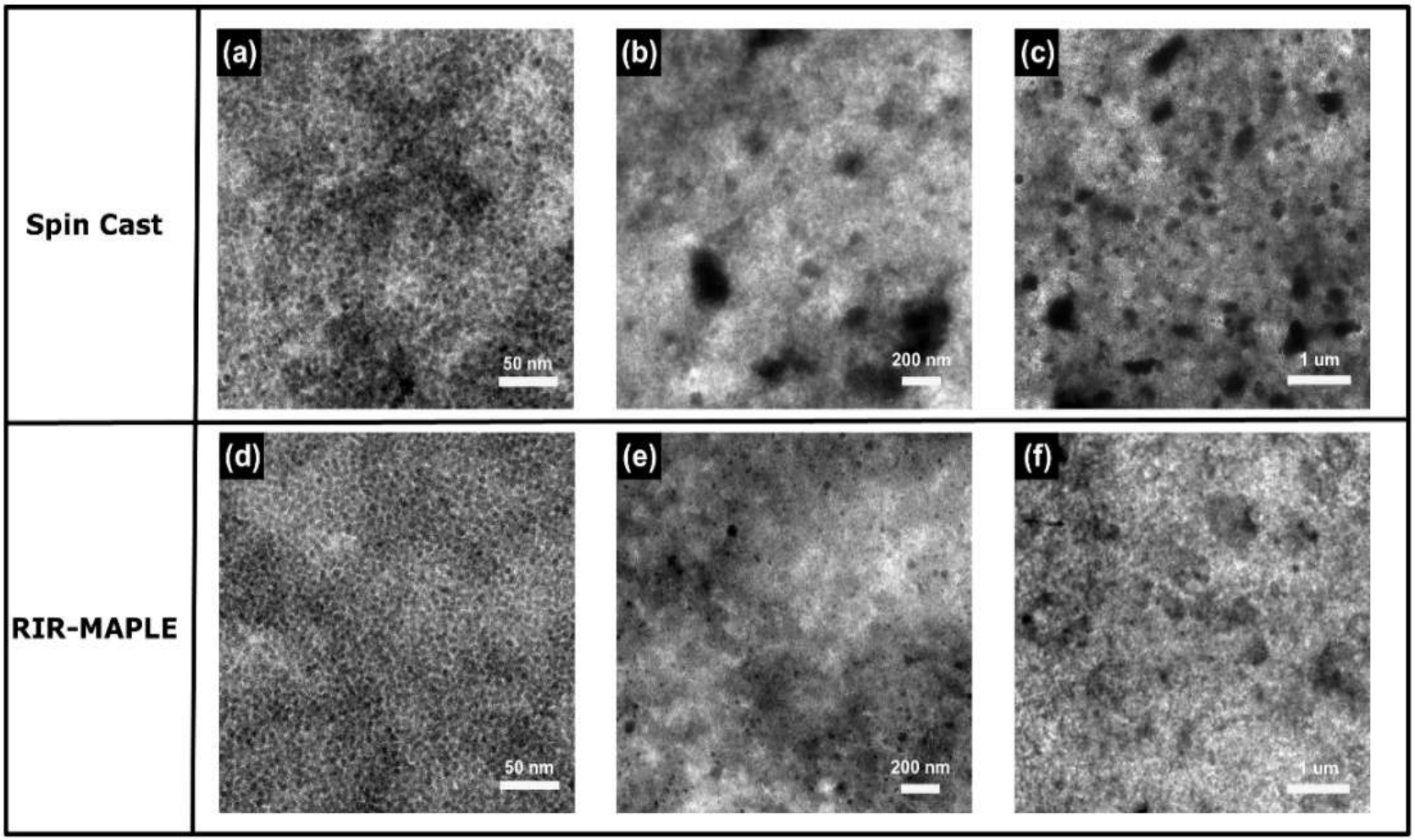
Organic-Inorganic Hybrid Nanocomposites



Hybrid nanocomposites with pyridine-capped CdSe CQDs

W. Y. Ge, A. Atewologun and A. D. Stiff-Roberts, *Organic Electronics*, vol. 22, pp. 98-107, March 2015.

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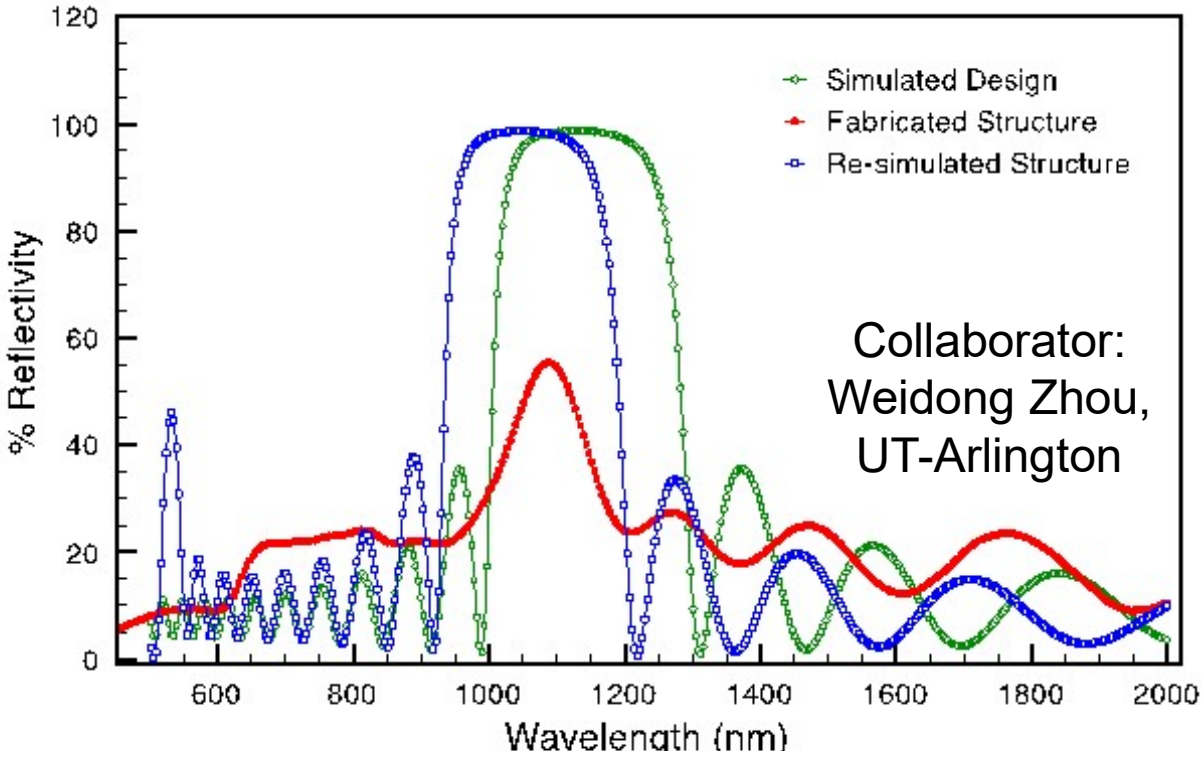
Optical Coatings

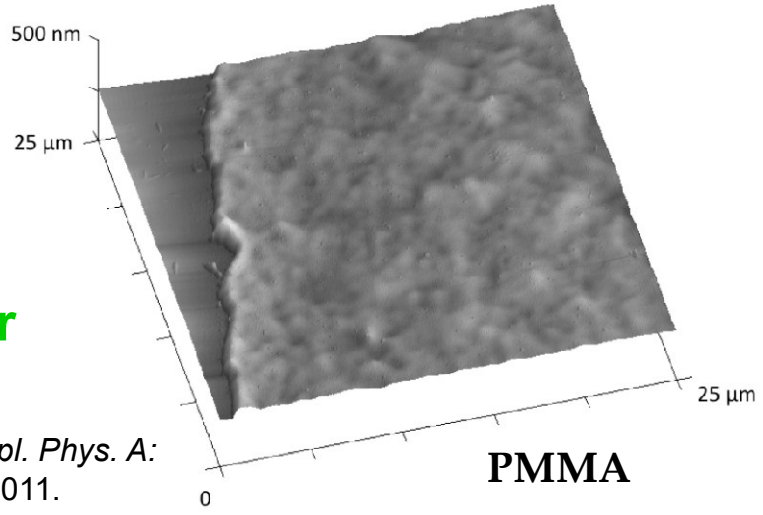
Polymer Distributed Bragg Reflector (DBR)

P3HT: 140.9 nm
PMMA: 189.2 nm
P3HT: 140.9 nm
PMMA: 189.2 nm
P3HT: 140.9 nm
PMMA: 189.2 nm
P3HT: 140.9 nm
PMMA: 189.2 nm
P3HT: 140.9 nm
PMMA: 189.2 nm
P3HT: 140.9 nm
PMMA: 189.2 nm
P3HT: 140.9 nm
PMMA: 189.2 nm
Glass Substrate



Collaborator:
Weidong Zhou,
UT-Arlington

PMMA: 8nm RMS roughness, n=1.49
P3HT: 13nm RMS roughness, n=2.0



16-layer DBR of polymers with similar solubility demonstrated!

R. Pate, R. McCormick, L. Chen, W. Zhou, and A. D. Stiff-Roberts, *Appl. Phys. A: Materials Science and Processing,* vol. 105, pp. 555-563, November 2011.

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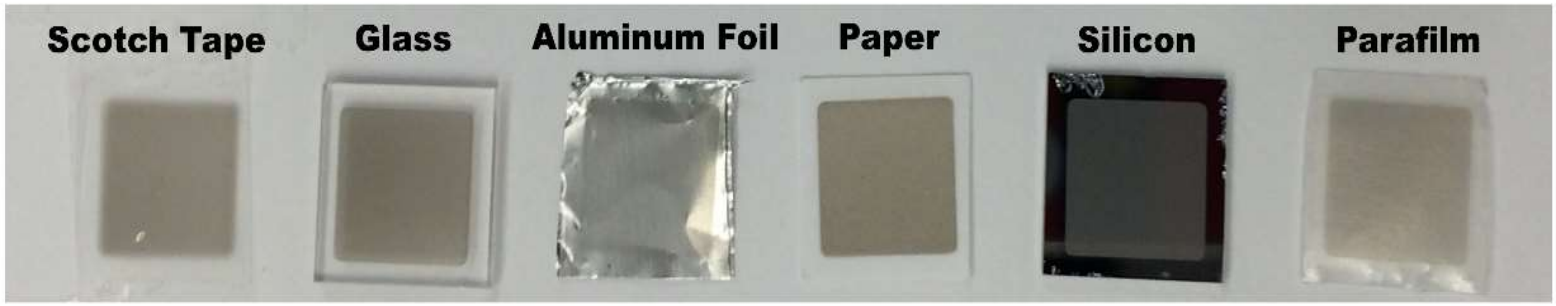
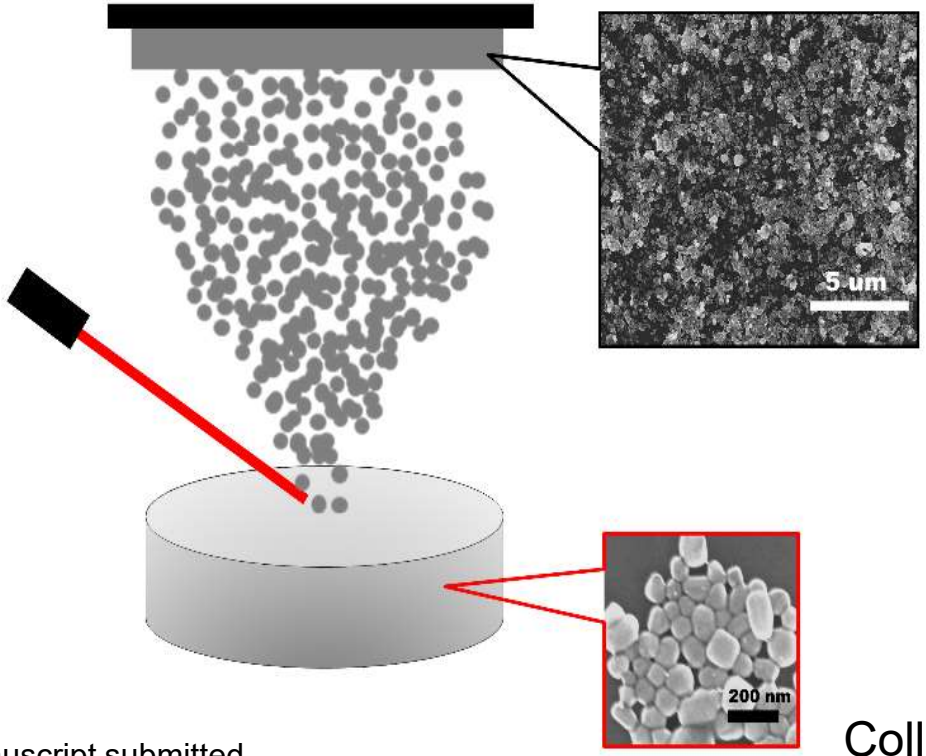
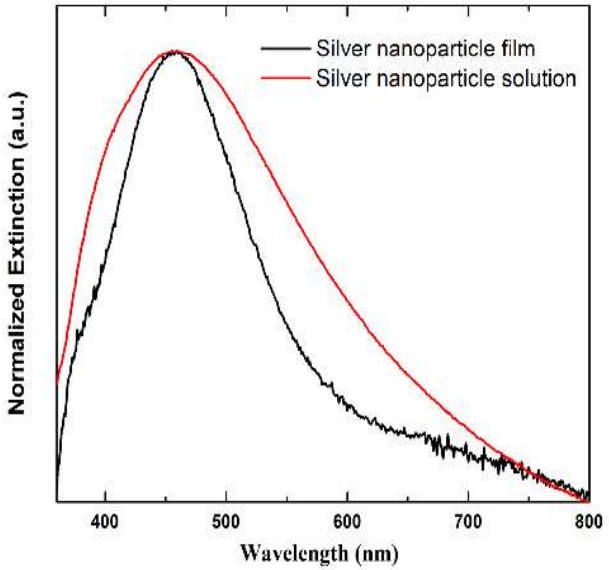
Plasmonic Silver Nanoparticle Deposition



RIR-MAPLE deposition is compatible with a wide range of substrates.





* Manuscript submitted.

Collaborator: Maiken Mikkelsen, Duke

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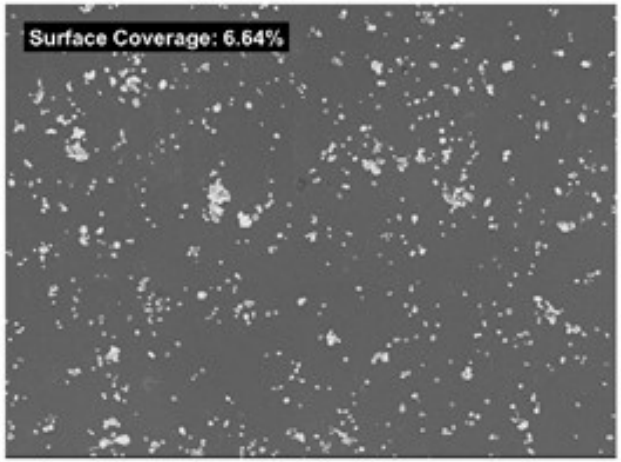
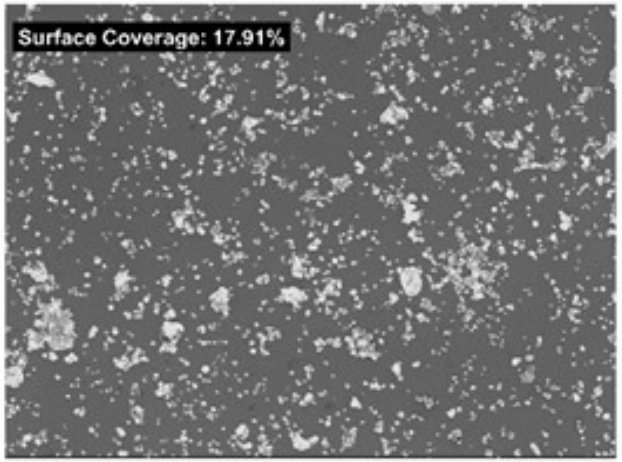
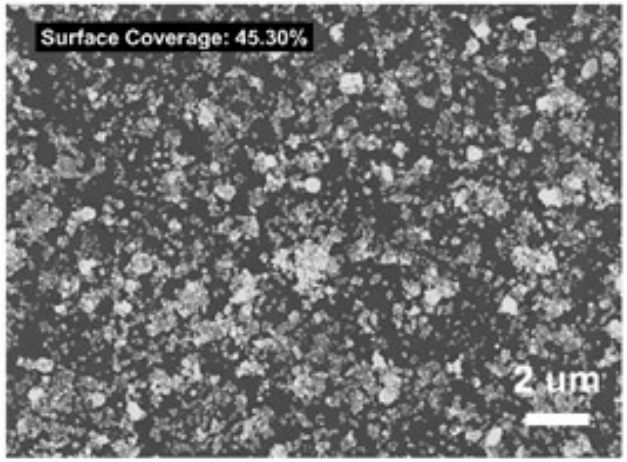
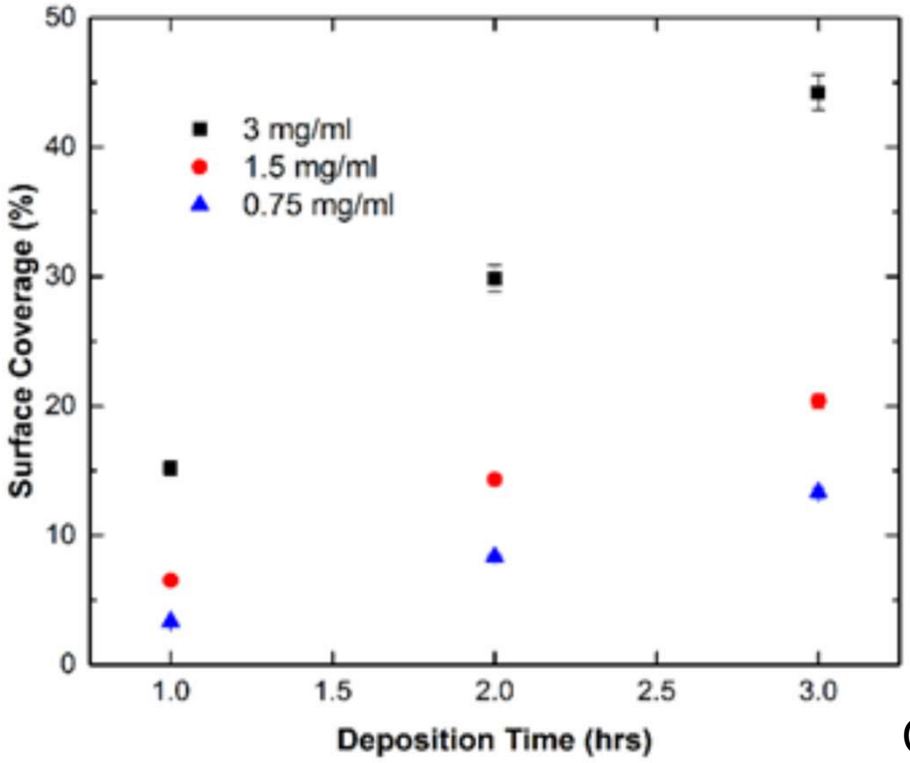
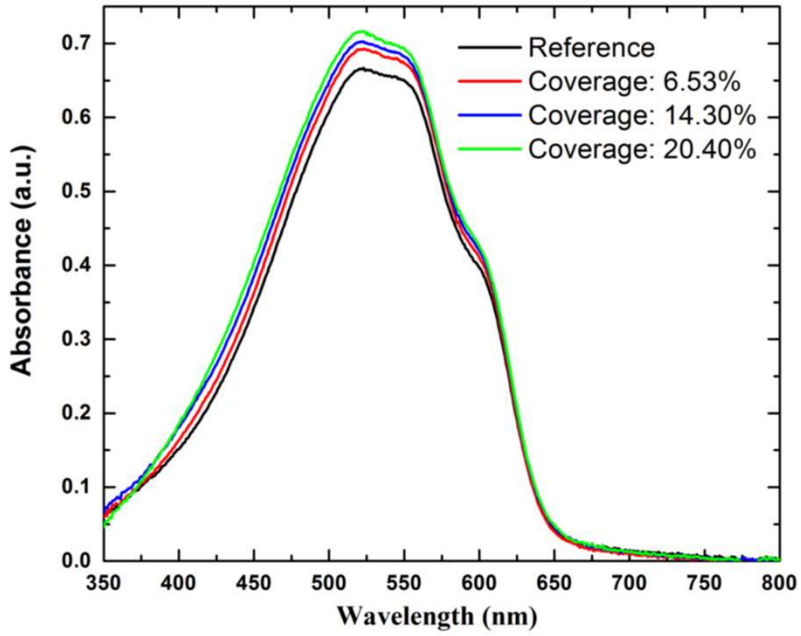
Plasmonic Silver Nanoparticle Deposition











Collaborator: Maiken Mikkelsen, Duke

* Manuscript submitted.

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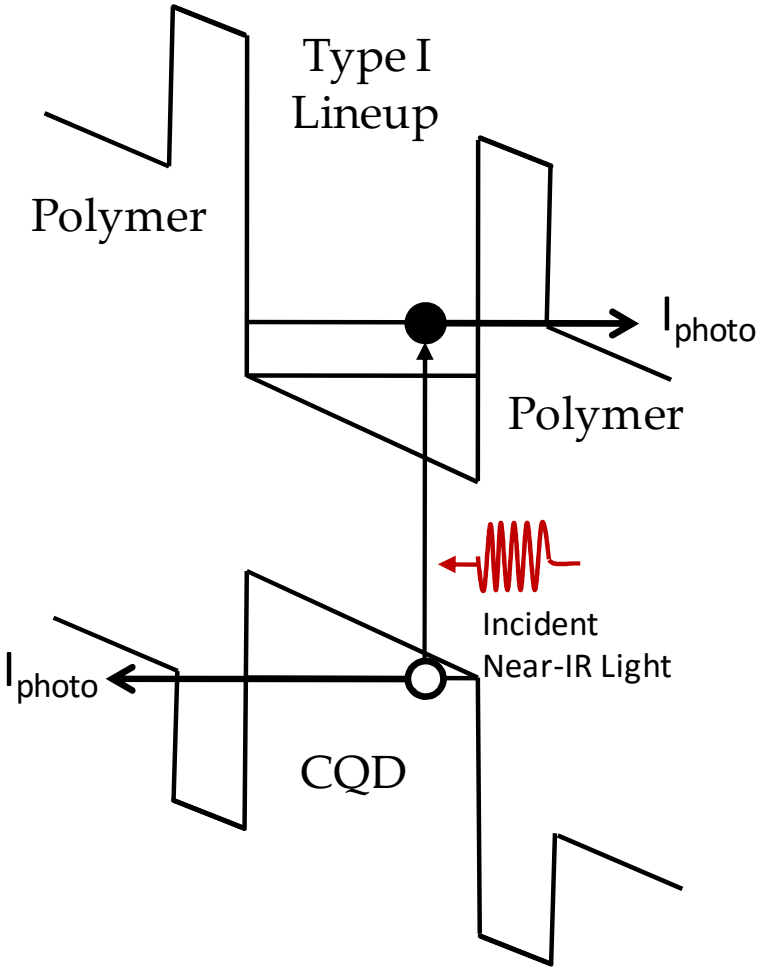
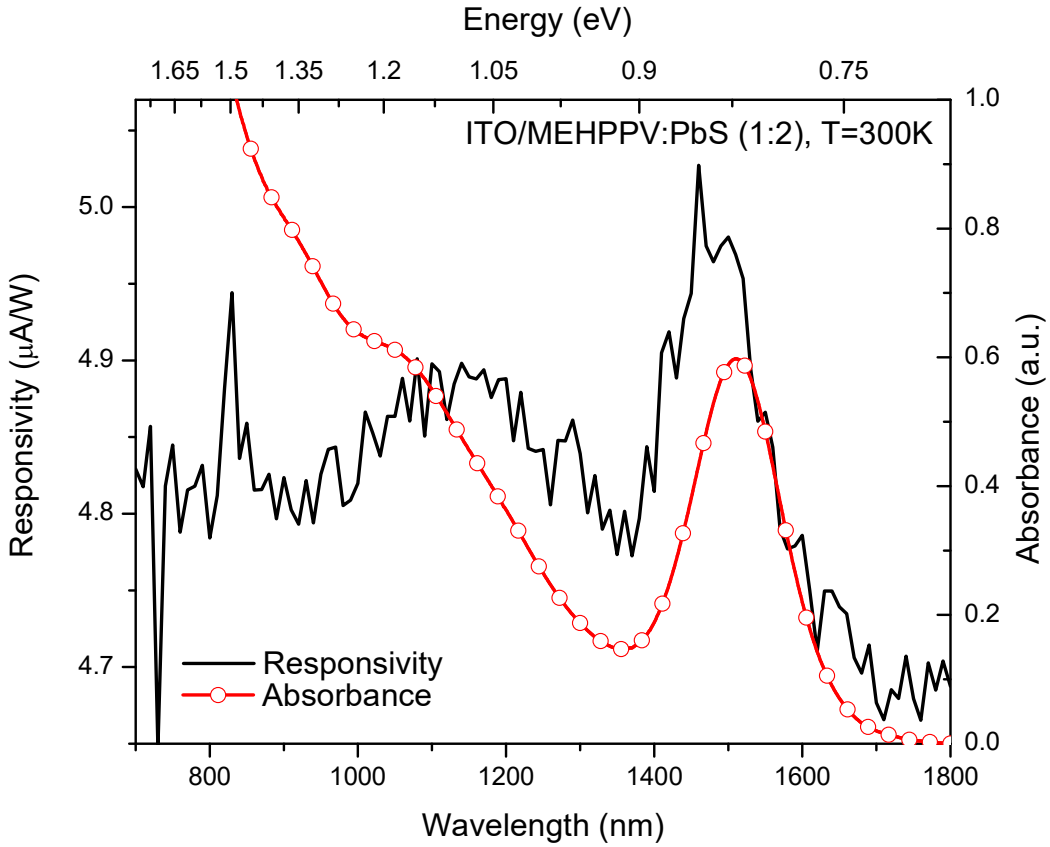
Photodetectors

Hybrid Nanocomposite Photodetectors





Device uses interband bipolar transitions in colloidal quantum dots to generate IR photocurrent.

Measured IR absorbance and spectral responsivity demonstrate good agreement.

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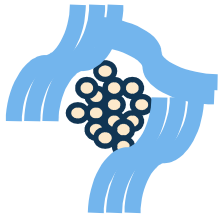
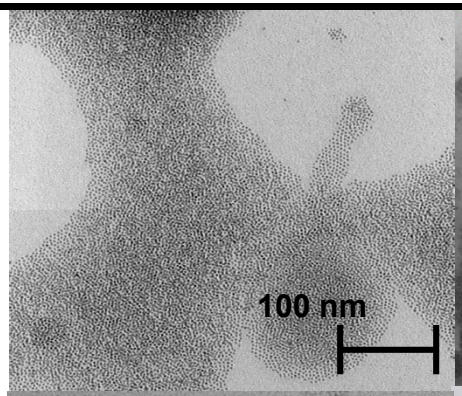
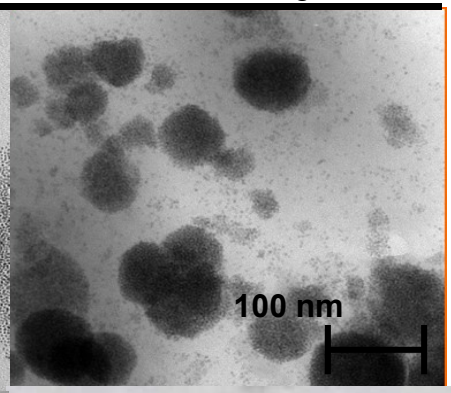
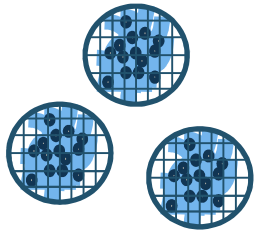
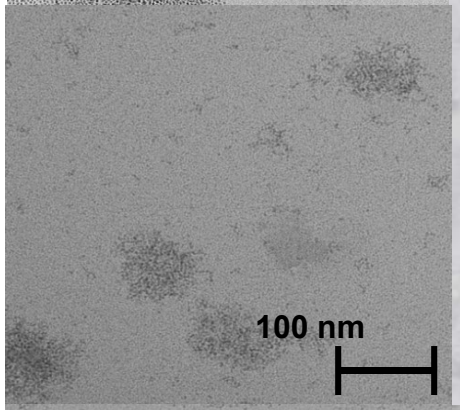
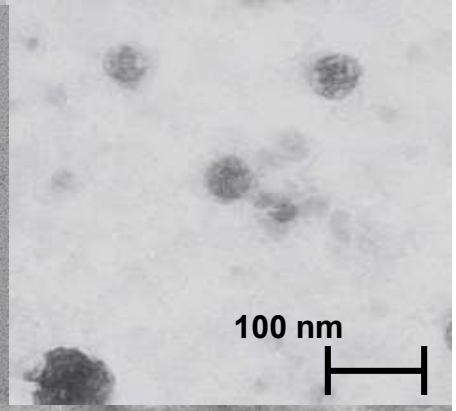
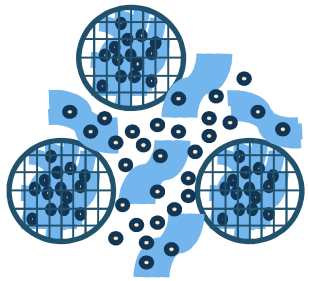
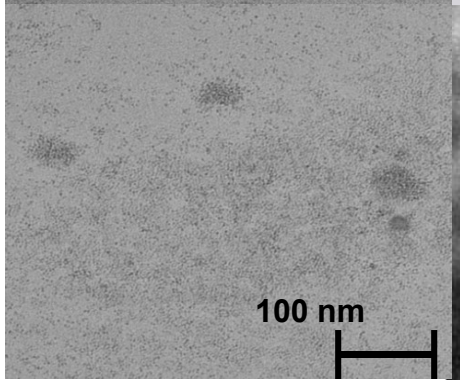
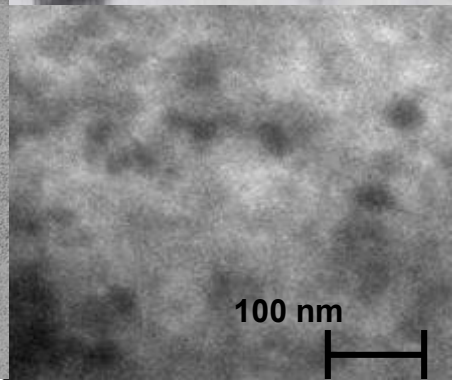
Hybrid Nanocomposite Photodetectors

Samples	Schematic images	Drop cast images	MAPLE images
CdSe CQDs/ MEH-CN-PPV			
CdSe CQDs/ MEH-CN-PPV/ 10% AEM/ P.I./UV			
CdSe CQDs/ MEH-CN-PPV/ 4% AEM/ P.I./UV			

Y. Park, J. Park, M. J. Therien, and A. D. Stiff-Roberts, *Colloid and Polymer Science*, vol. 290, pp. 1501-1509, May 2012.

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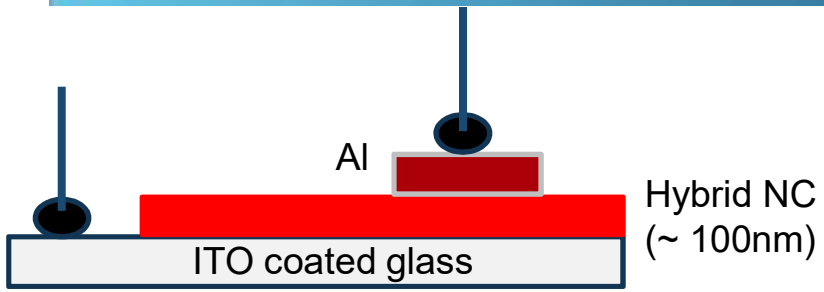
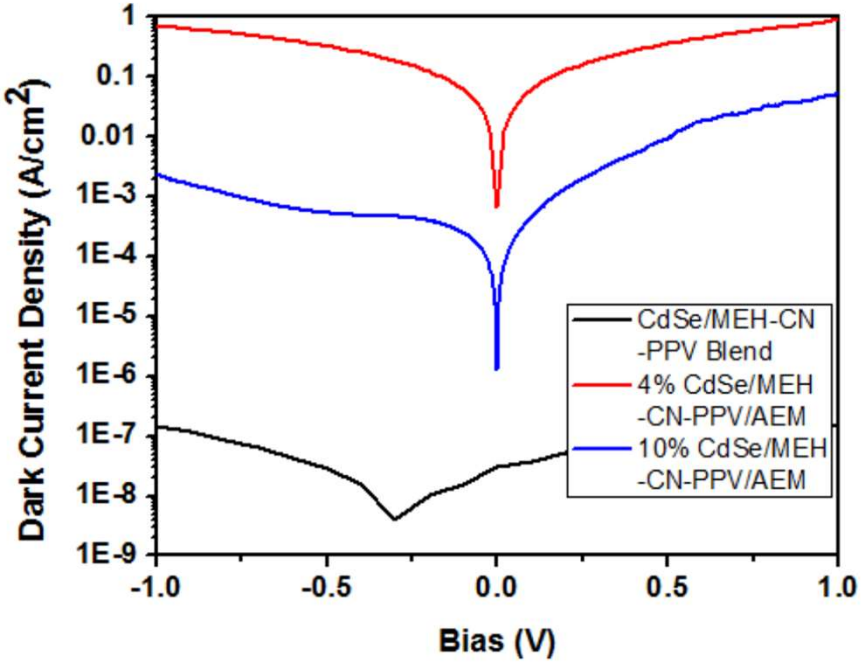
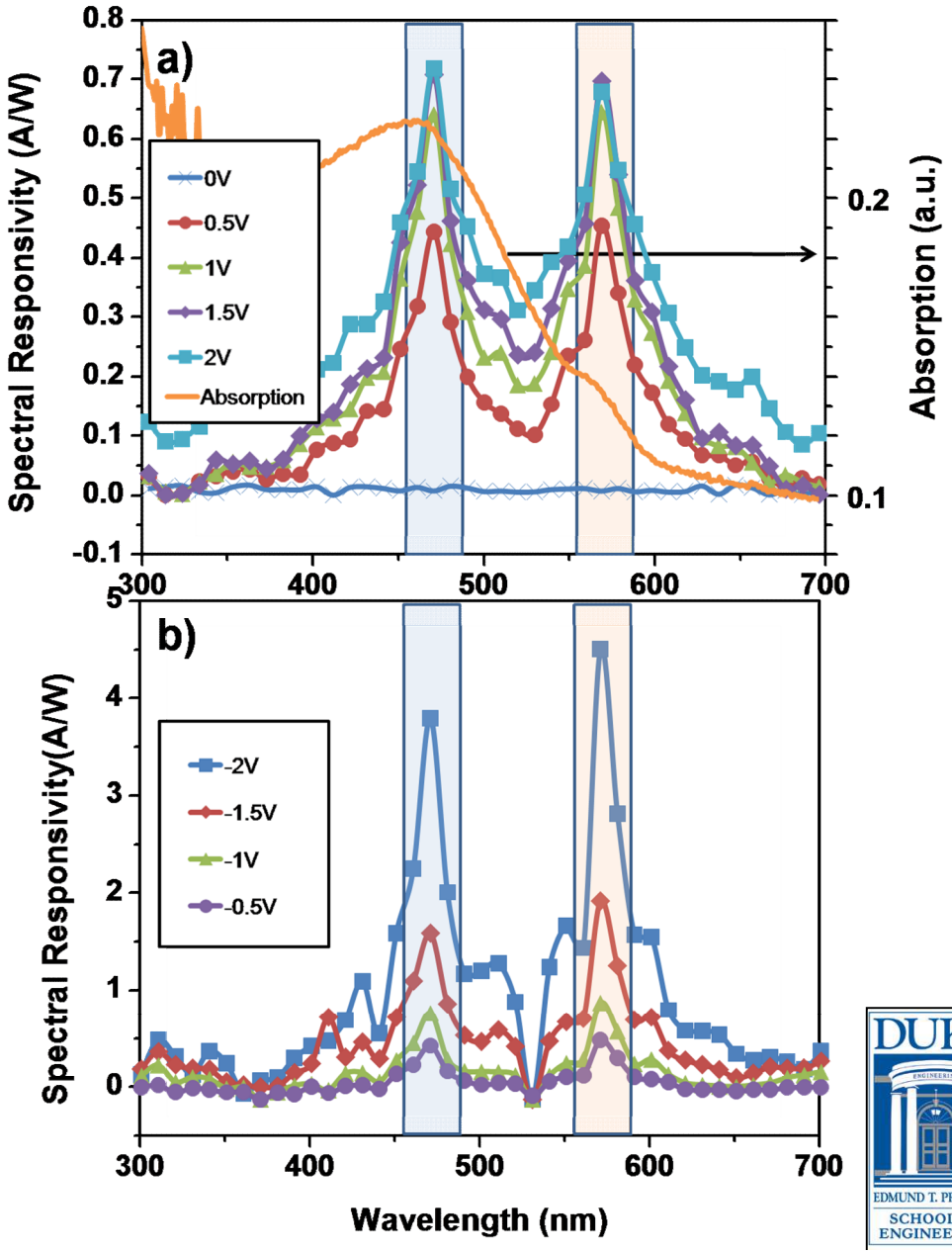
Hybrid Nanocomposite Photodetectors





RIR-MAPLE of dense films of nanocomposite spheres enables high responsivity at low bias!



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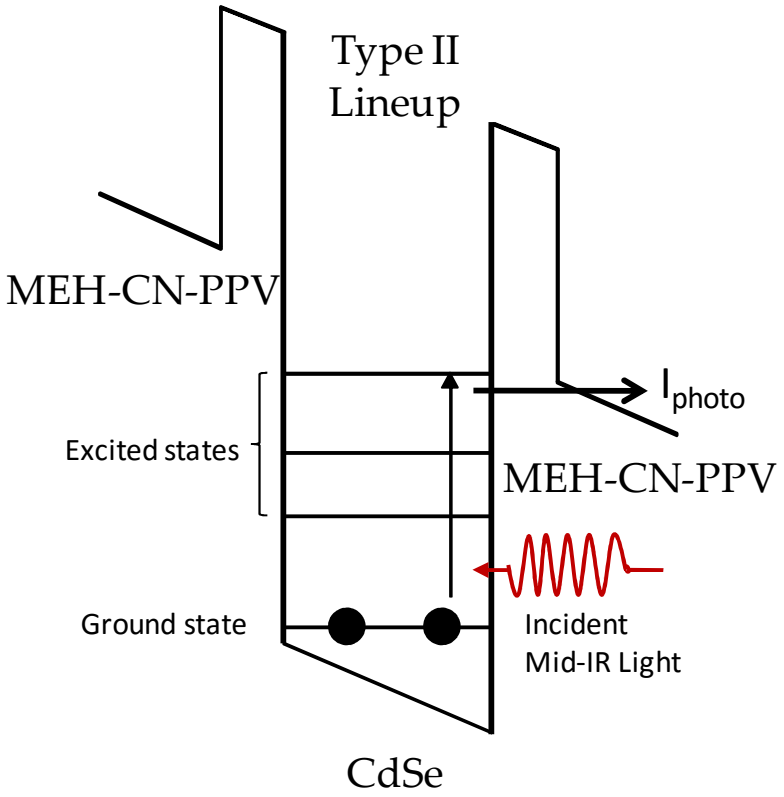
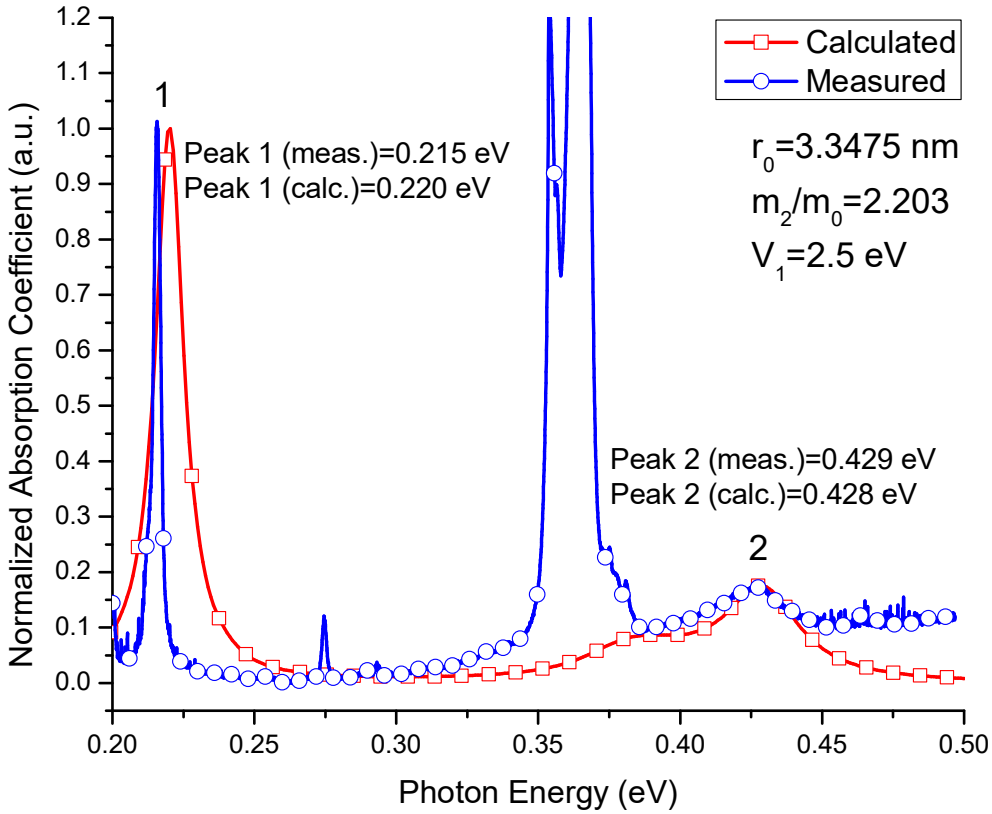
Hybrid Nanocomposite Photodetectors



Device uses intraband electronic transitions in colloidal quantum dots to generate IR photocurrent.



Calculated and measured IR absorption spectra demonstrate good agreement.

A. D. Stiff-Roberts, "Hybrid Nanocomposite Infrared Photodetectors," (INVITED) *11th International Conference on Infrared Optoelectronics: Materials and Devices (MIOMD-XI)*, Evanston, IL, September 2012.

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Hybrid Nanocomposite Photodetectors

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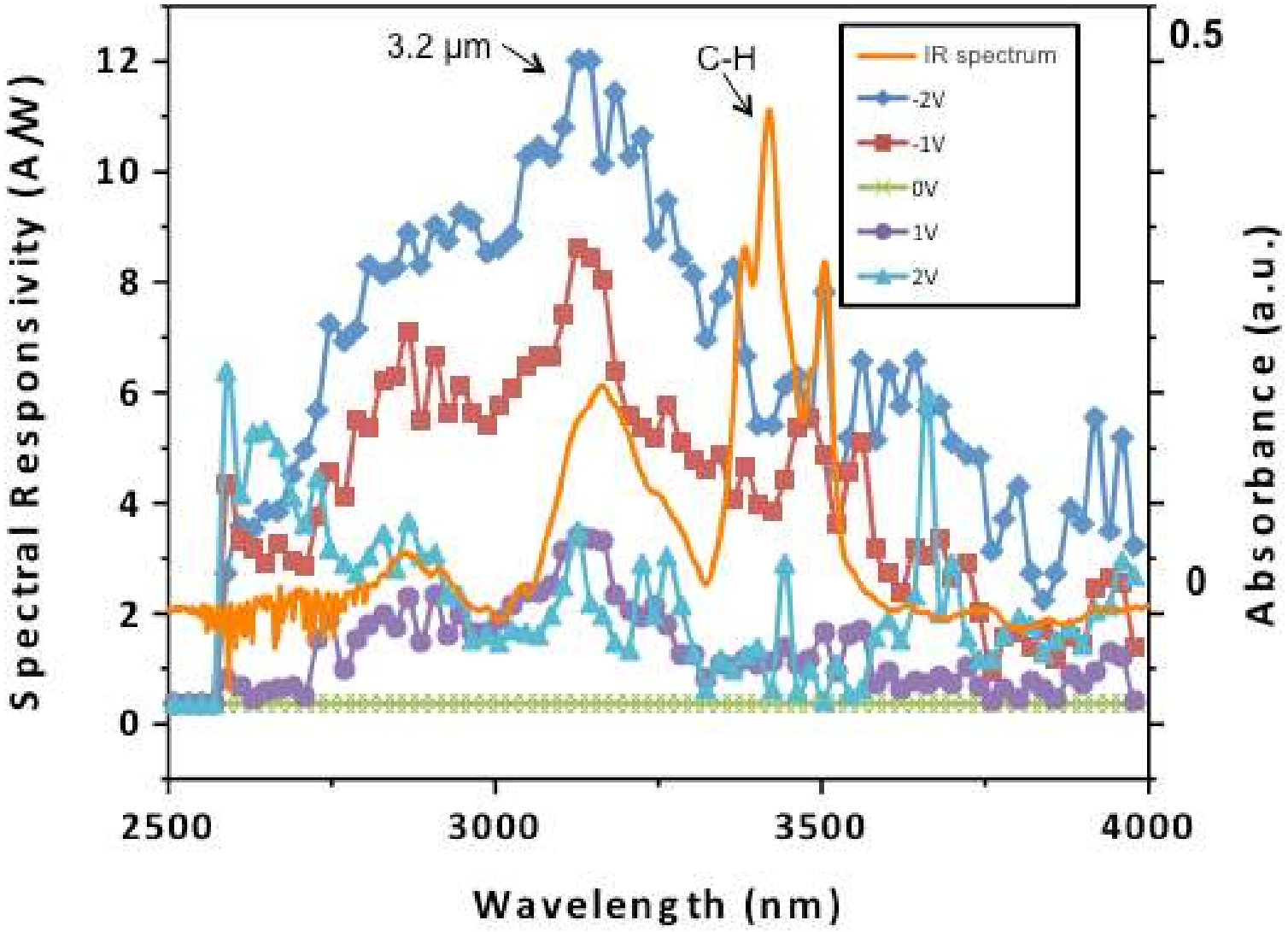

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Hybrid Nanocomposite Photodetectors

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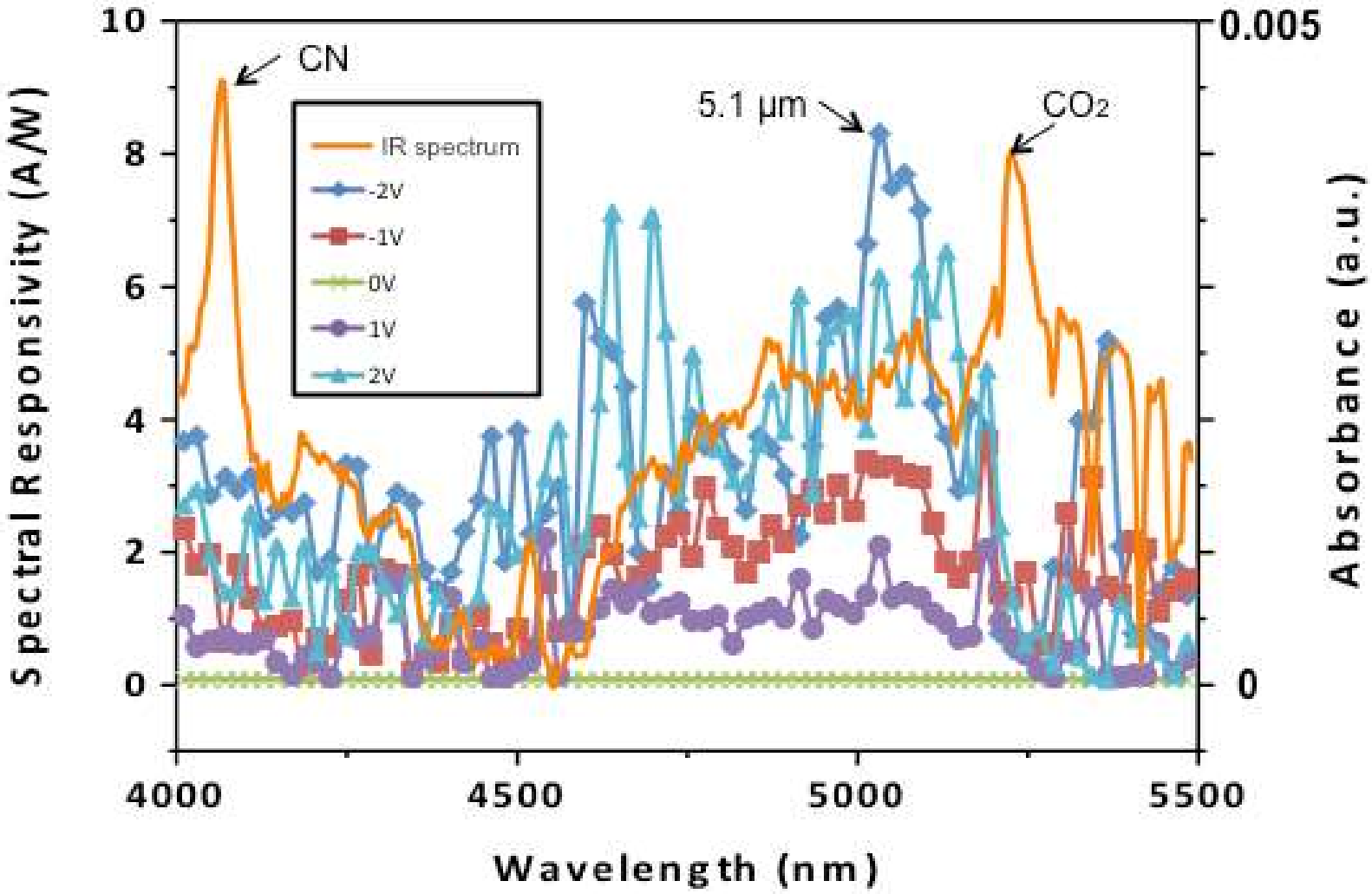

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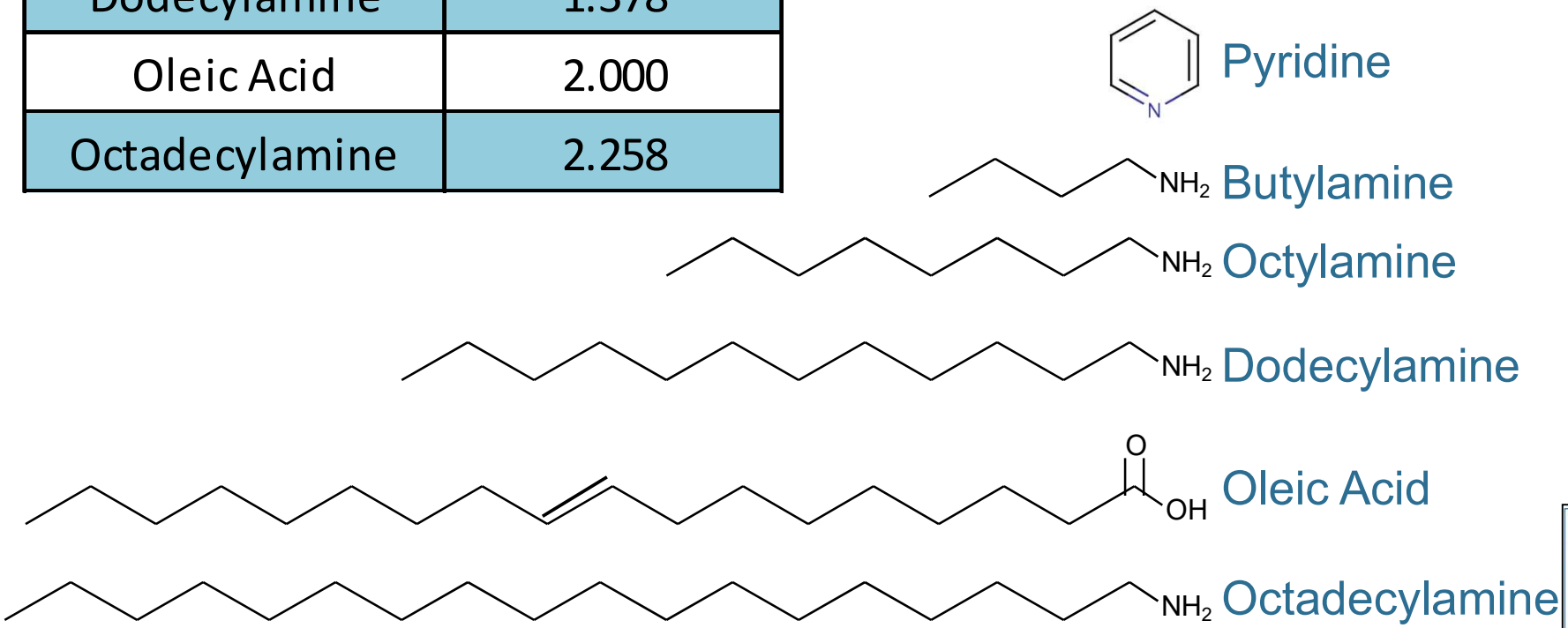
Tuning IR Response by Surface Ligand

Ligand Material	Length (nm)
Pyridine	0.308
Butylamine	0.497
Octylamine	1.000
Dodecylamine	1.378
Oleic Acid	2.000
Octadecylamine	2.258

Bond Lengths

C-C = 1.54Å C=C = 1.34Å

C-N = 1.47Å C-O = 1.43Å



K. R. Lantz and A. D. Stiff-Roberts, *IEEE Journal of Quantum Electronics*, vol. 47, pp. 1420-1427, November 2011.

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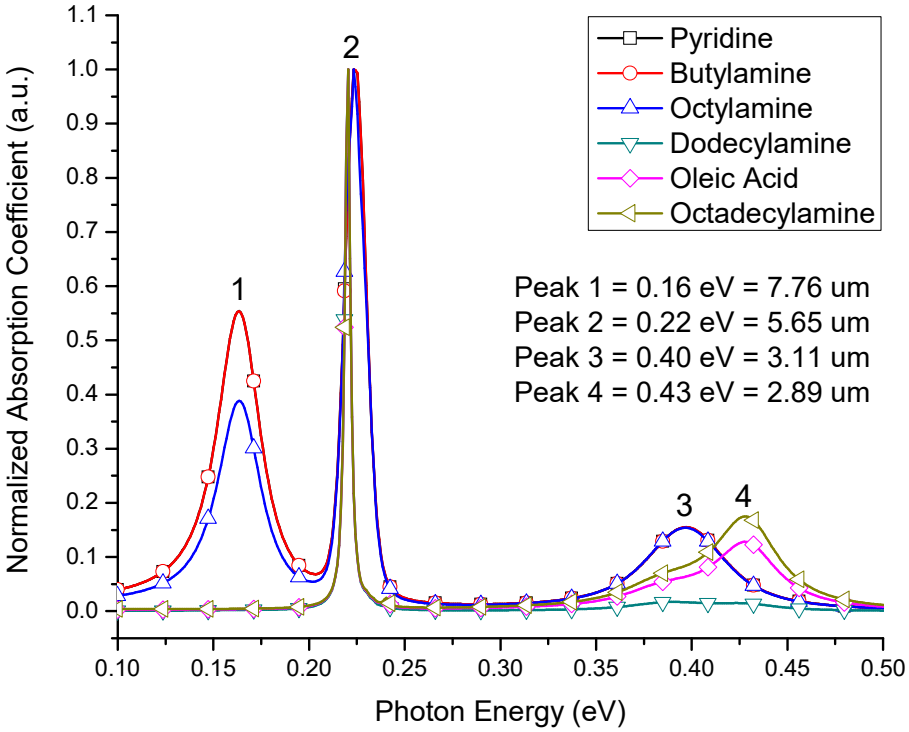
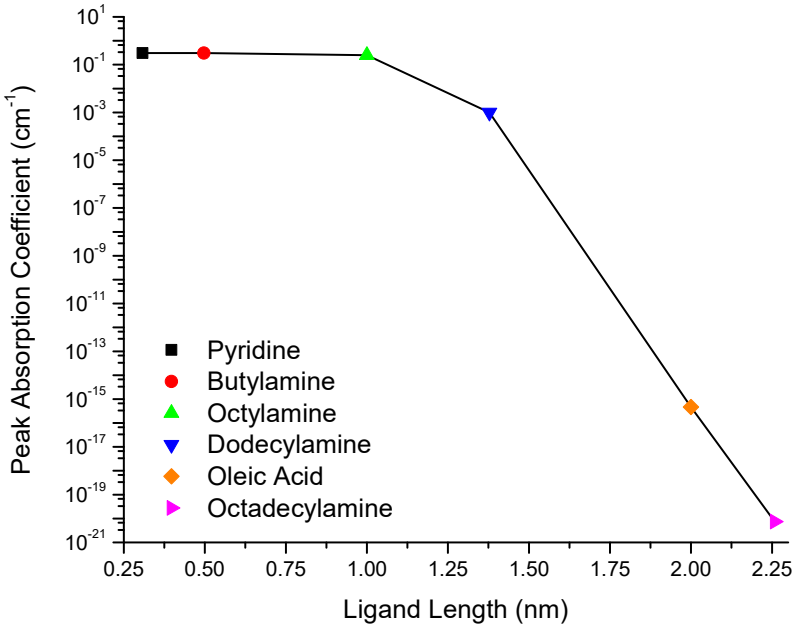
Tuning IR Response by Surface Ligand



IR absorption spectrum depends on surface ligand length and spans mid- to long-wave IR wavelengths.



Shorter surface ligands yield larger absorption coefficients and motivate ligand exchange for as-synthesized colloidal quantum dots.

K. R. Lantz and A. D. Stiff-Roberts, *IEEE Journal of Quantum Electronics*, vol. 47, pp. 1420-1427, November 2011.

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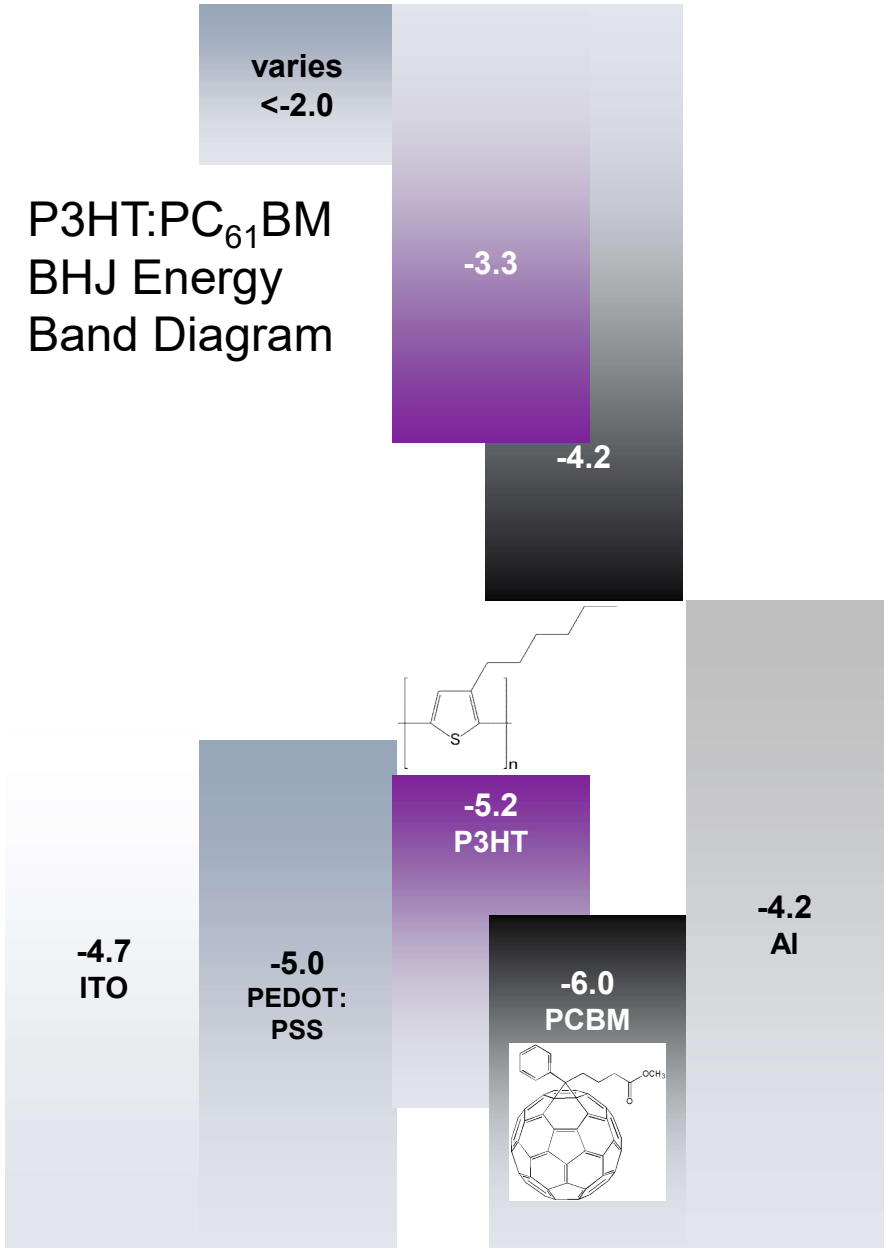
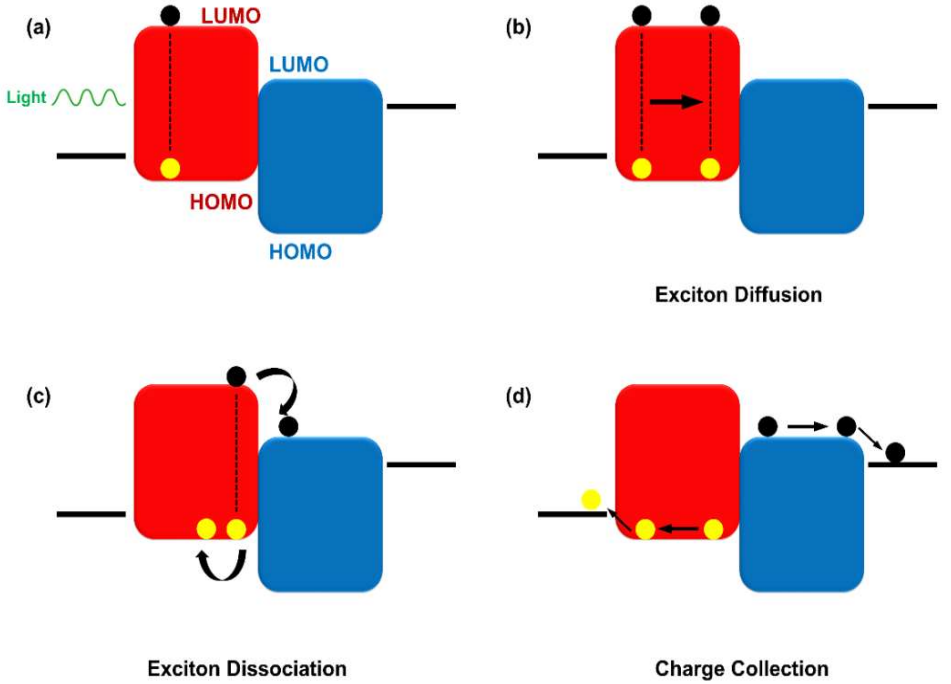
Solar Cells

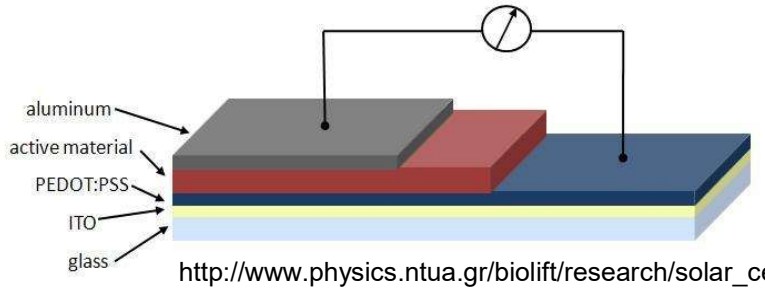
Bulk Heterojunction (BHJ) Active Regions

P3HT:$PC_{61}BM$ BHJ Energy Band Diagram





http://today.slac.stanford.edu/images/2011/ssrl-hl-solar-anneal.jpg



http://www.physics.ntua.gr/biolift/research/solar_cells.html

Trade-off between increasing interfacial area to improve exciton dissociation and increasing continuous domains to improve transport of separated charges.

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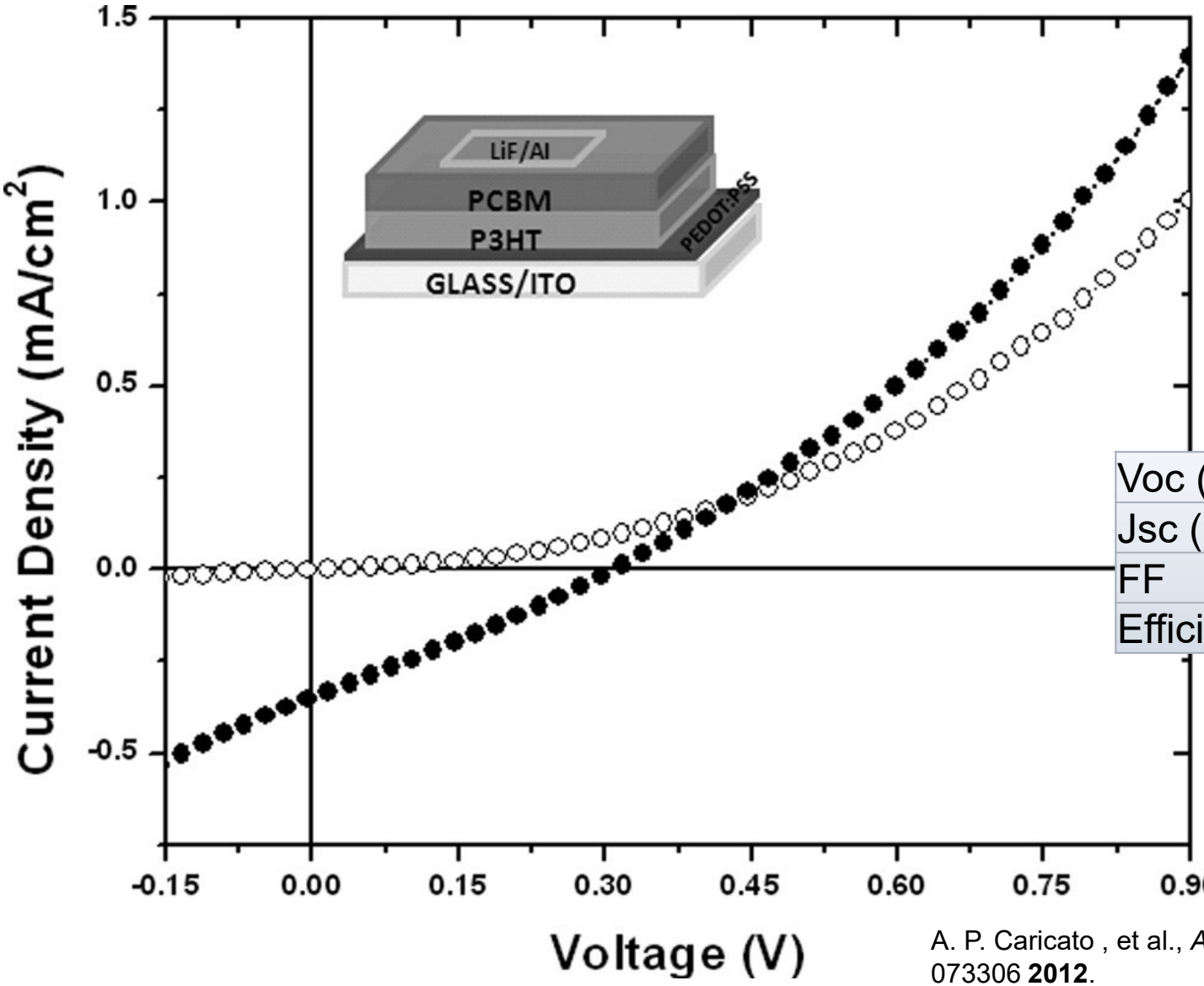
First Organic Solar Cell by MAPLE

Bi-layer Active Region using UV-MAPLE Deposition



Voc (V)	0.32
Jsc (mA/cm^2)	0.33
FF	0. 28
Efficiency	0.03%

A. P. Caricato , et al., *Appl.Phys. Lett.*, **100**, 073306 **2012**.

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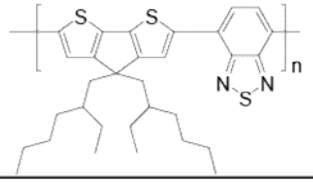
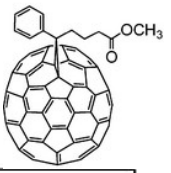
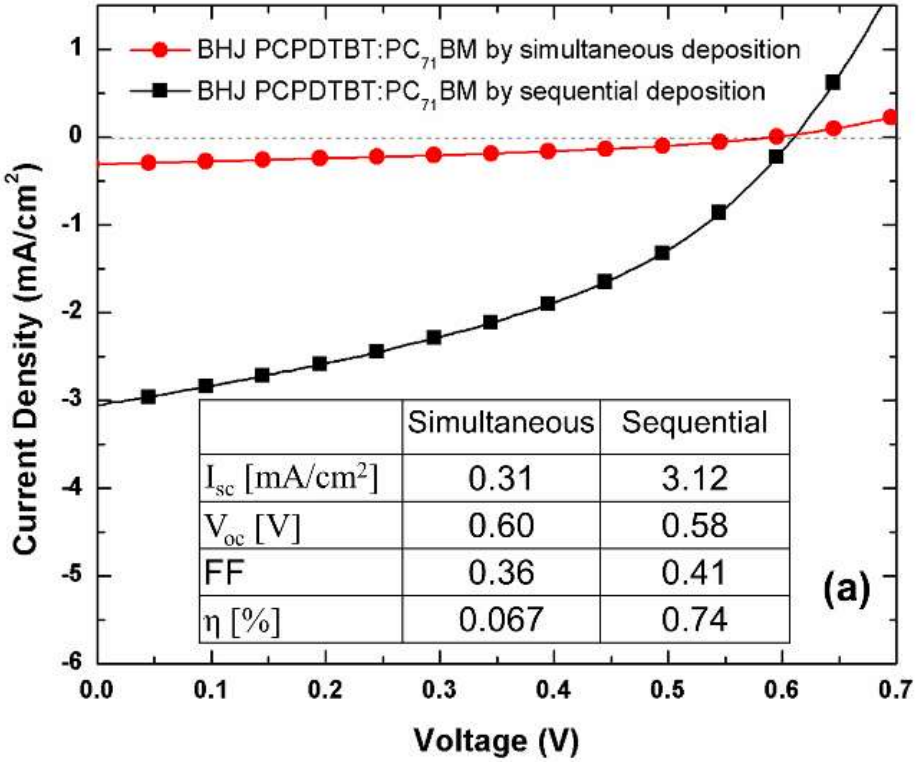
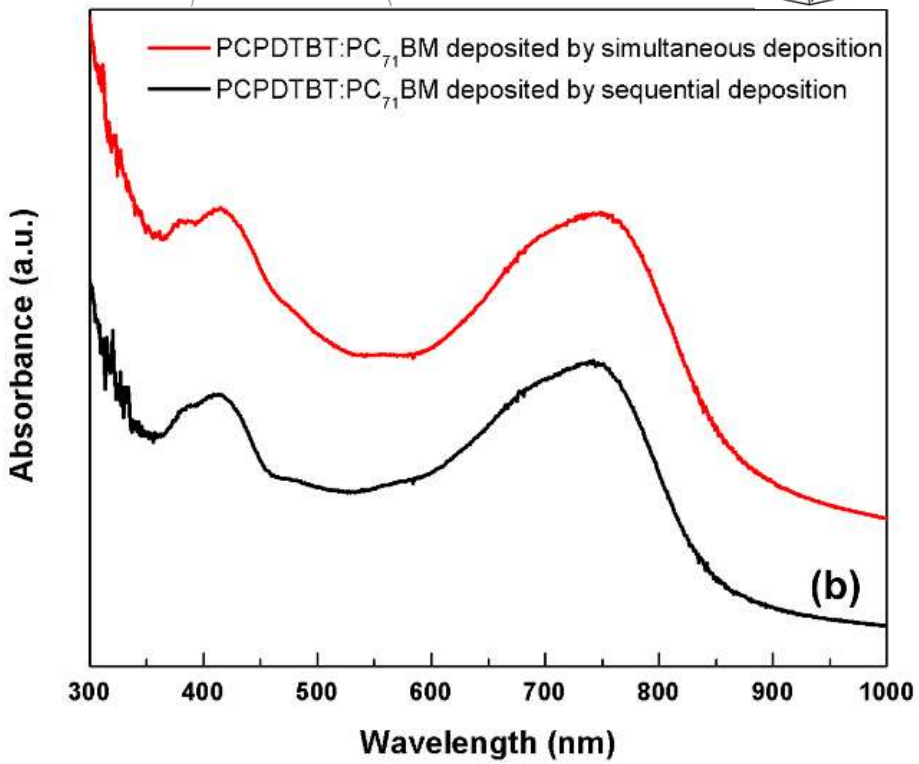
Effect of Deposition Mode

ITO/PEDOT:PSS/PCPDTBT:PC71BM/Al

PCPDTBT  PC71BM 



	Simultaneous	Sequential
I_{sc} [mA/cm²]	0.31	3.12
V_{oc} [V]	0.60	0.58
FF	0.36	0.41
η [%]	0.067	0.74



- **Devices fabricated using the sequential deposition mode have an order of magnitude improvement in PCE compared to simultaneous deposition.**
- **The absorbance data indicates that the different in performance is due to the film morphology, as opposed to different film composition.**

Wangyao Ge, RD McCormick, G Nyikayaramba, and Adrienne D. Stiff-Roberts, Appl Phys Lett **104** , 223901 (2014).

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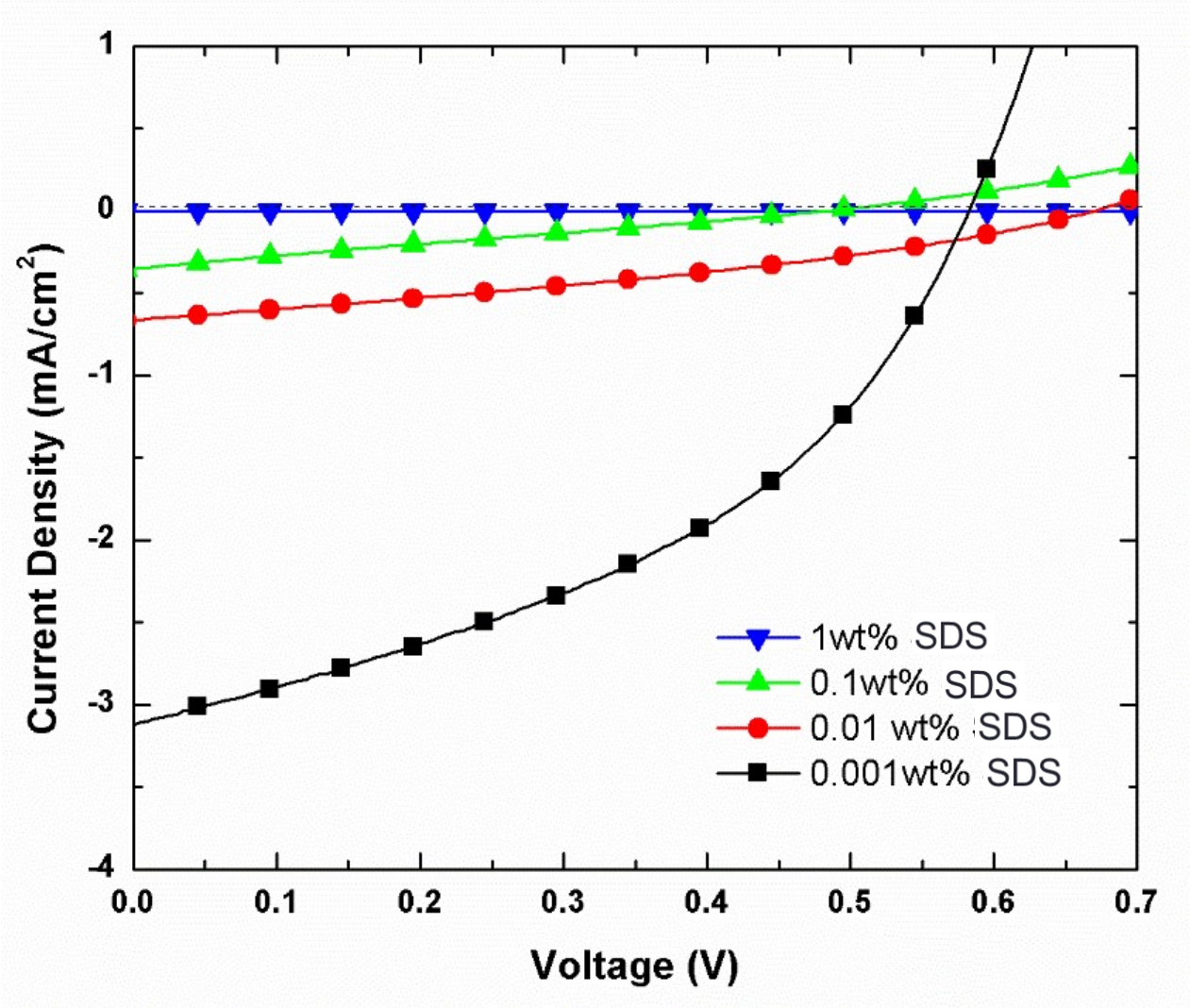
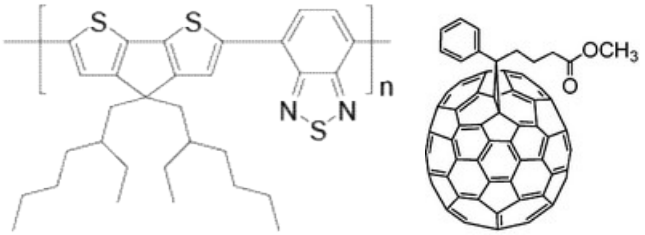
Effect of Surfactant





PCPDTBT **PC71BM**

Deposition recipe:

PCPDTBT:
1(CB):0.25(Phenol):3(DI water)
PC71BM:
1(CB):0.25(Phenol):3(DI water)

PCPDTBT:PC71BM=1:1

Short circuit current reduces as the concentration of SDS in water increases.

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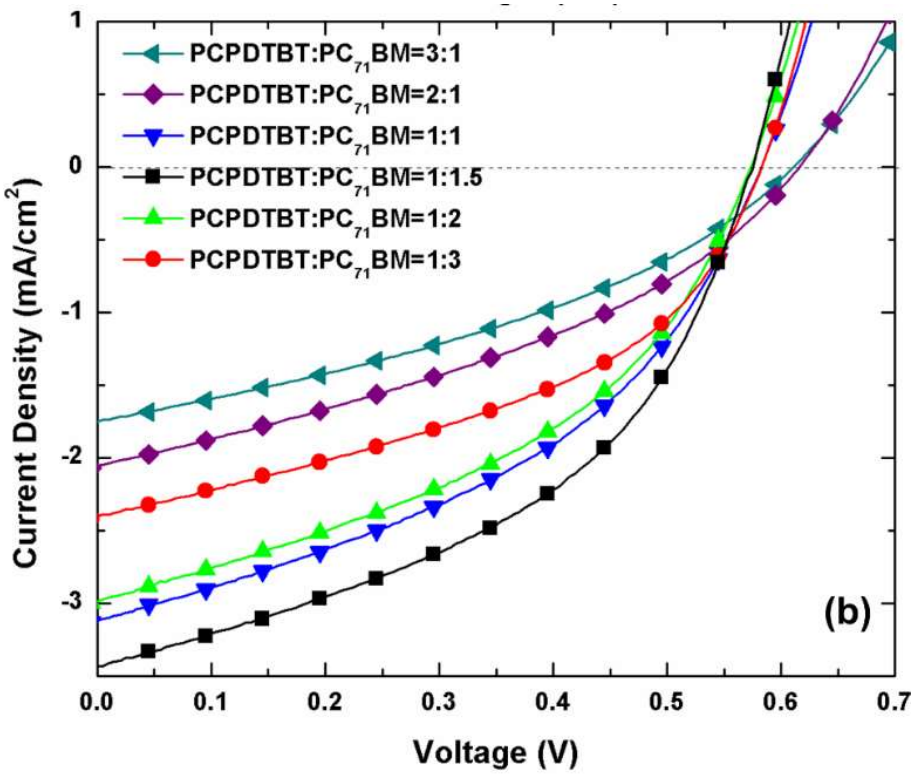
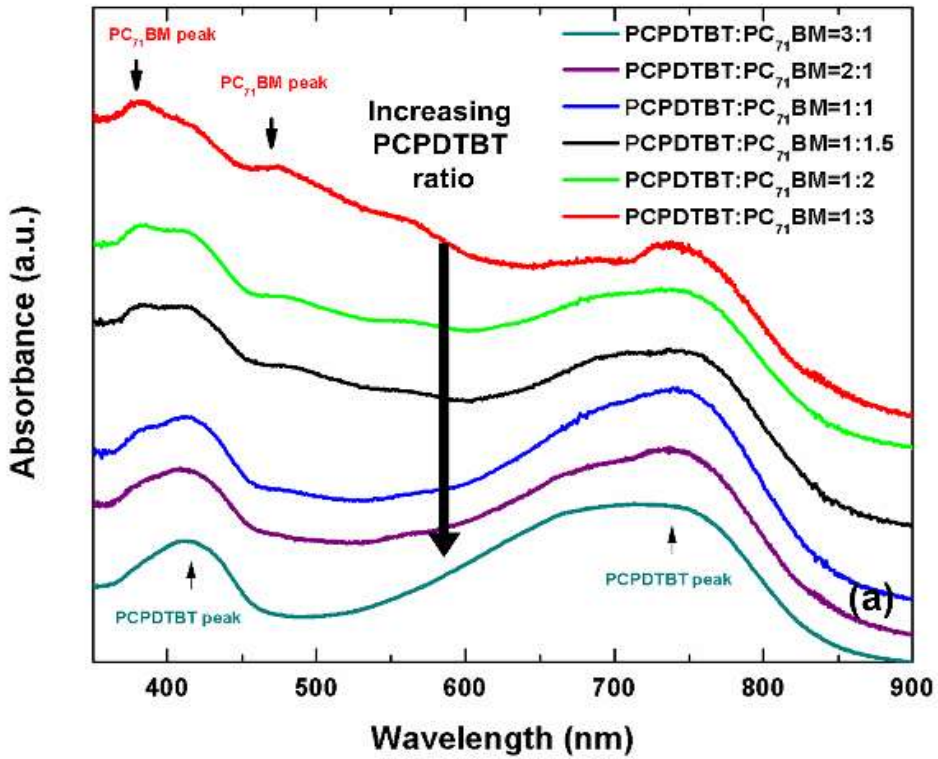
Effect of BHJ Ratio





Deposition Modes	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	η [%]
Sequential (3:1)	1.76	0.61	0.36	0.39
Sequential (2:1)	2.05	0.62	0.36	0.46
Sequential (1:1)	3.12	0.58	0.41	0.74
Sequential (1:1.5)	3.43	0.56	0.45	0.86
Sequential (1:2)	2.99	0.57	0.42	0.72
Sequential (1:3)	2.40	0.58	0.43	0.60

Deposition recipe:
PCPDTBT:
1(CB):0.25(Phenol):3 (DI water)
PC71BM:
1(CB):0.5(Phenol):3 (DI water)

Wangyao Ge, RD McCormick, G Nyikayaramba, and Adrienne D. Stiff-Roberts, Appl Phys Lett **104** , 223901 (2014).

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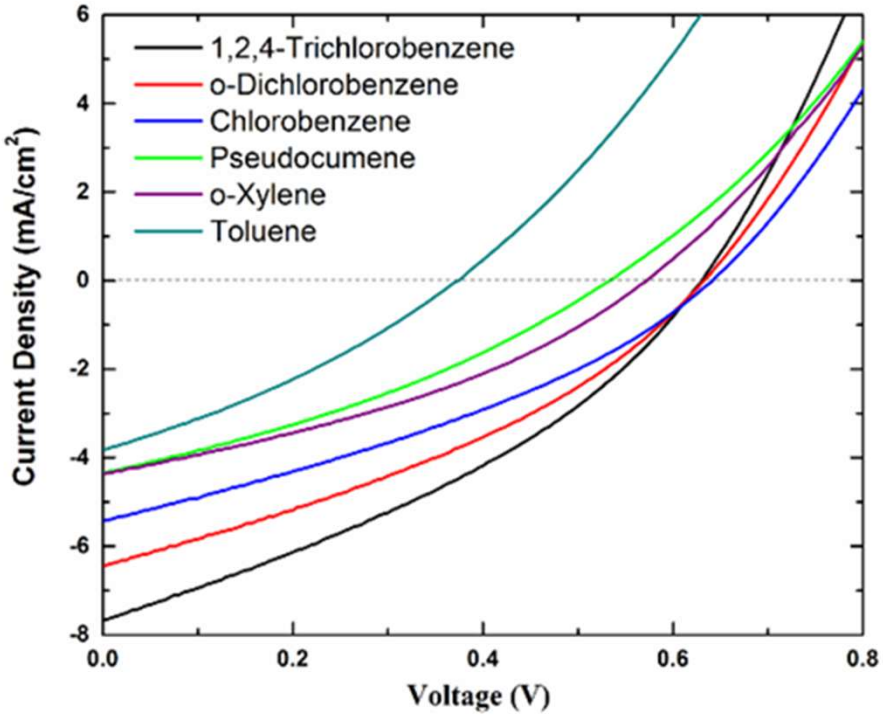
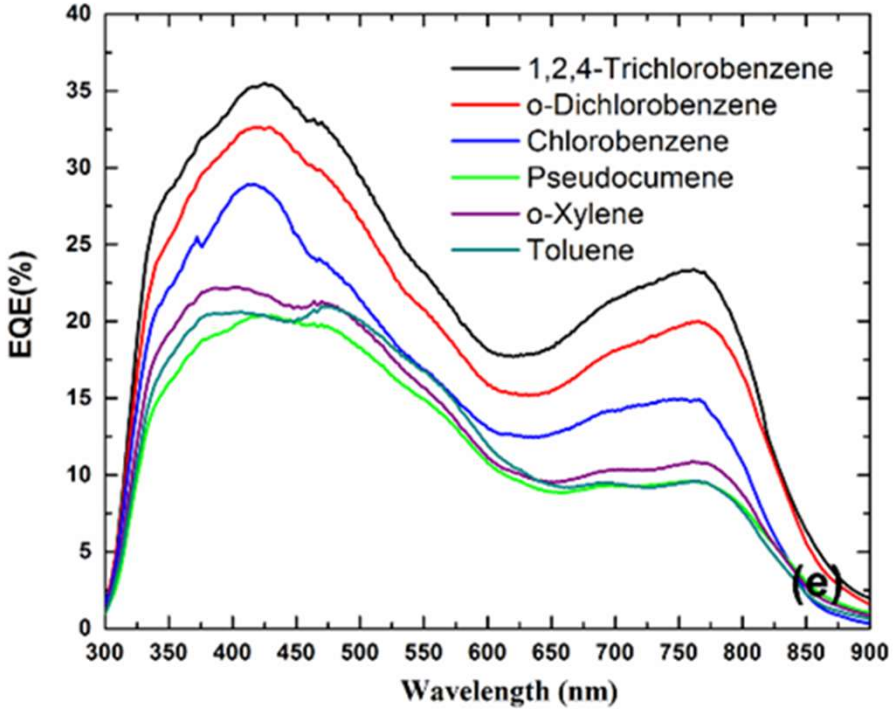
Effect of Primary Solvent

ITO/PEDOT:PSS/PCPDTBT:$PC_{71}BM$/TiOx NPs/Al





Primary Solvents	Voc (mV)	Jsc (mA/cm²)	FF (%)	PCE (%)	Rs (Ohm*cm²)	Rsh (Ohm*cm²)
Toluene	400±18	4.03±0.18	32.2±0.68	0.52±0.06	22.68	108.52
o-Xylene	560±14	4.16±0.19	34.5±0.94	0.80±0.07	31.20	170.38
Pseudocumene	550±7.0	3.96±0.29	31.8±0.77	0.69±0.04	38.01	139.01
Chlorobenzene	640±1.0	5.20±0.34	33.7±0.47	1.14±0.06	23.63	140.32
o-Dichlorobenzene	630±7.5	6.36±0.20	34.9±0.43	1.39±0.05	15.67	123.17
1,2,4-Trichlorobenzene	640±4.5	7.36±0.29	34.2±0.38	1.60±0.07	16.38	103.50

* Manuscript submitted.

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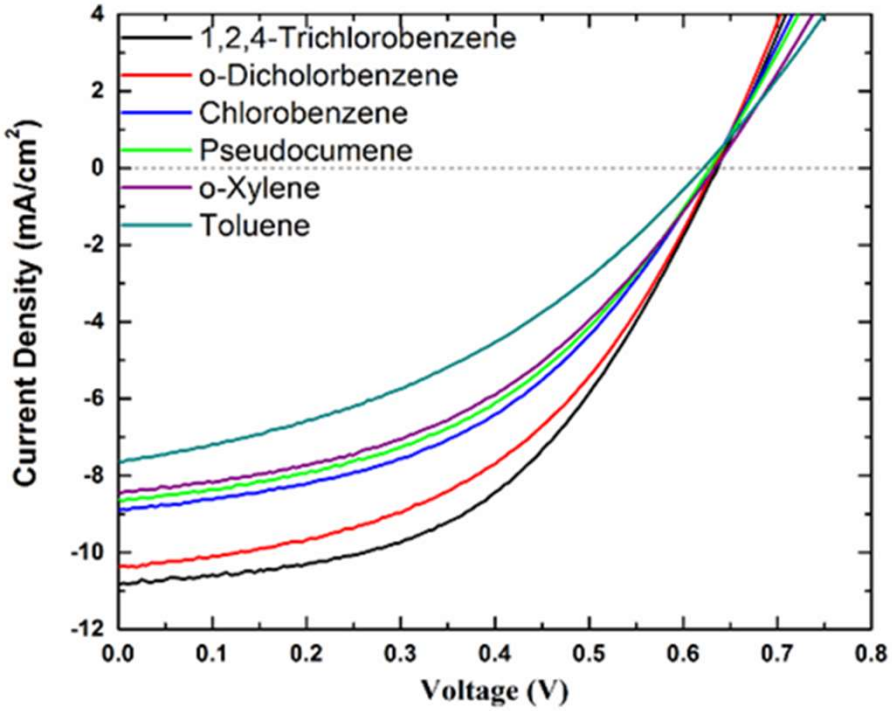
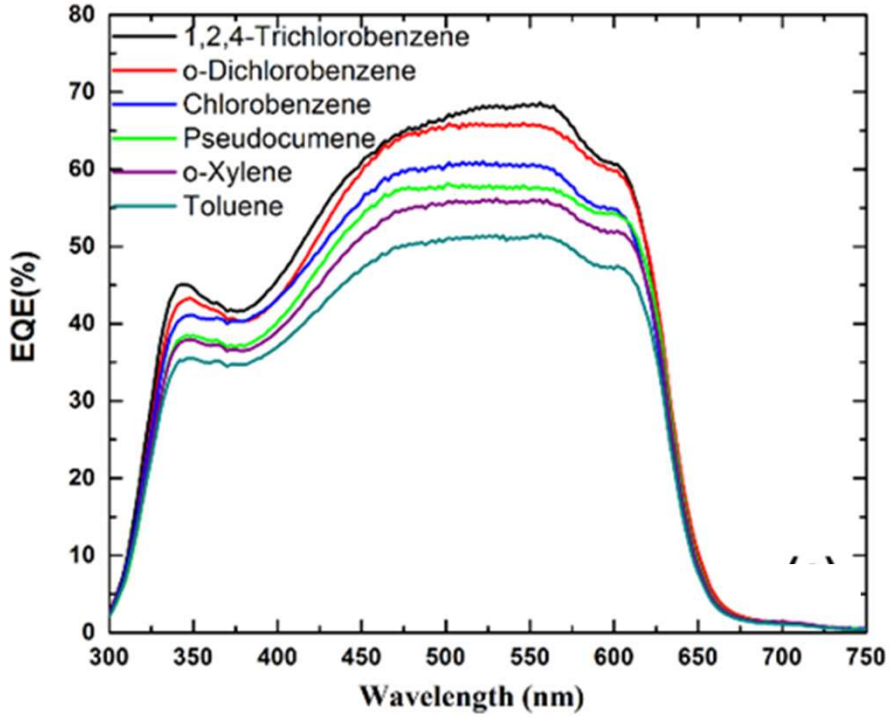
Effect of Primary Solvent

ITO/PEDOT:PSS/P3HT:$PC_{61}BM$/TiOx NPs/Al





Primary Solvents	Voc (mV)	Jsc (mA/cm²)	FF (%)	PCE (%)	Rs (Ohm*cm²)	Rsh (Ohm*cm²)
Toluene	610±9.4	7.79±0.15	38.7±0.6	1.84±0.08	24.52	142.86
o-Xylene	630±3.5	8.33±0.10	39.3±0.6	2.06±0.03	21.92	137.40
Pseudocumene	630±2.5	8.58±0.15	44.5±0.5	2.42±0.04	17.07	215.55
Chlorobenzene	630±3.5	8.85±0.03	45.4±4.3	2.51±0.04	15.84	216.53
o-Dichlorobenzene	630±2.4	10.47±0.10	44.8±1.4	2.99±0.08	12.22	197.05
1,2,4-Trichlorobenzene	630±4.1	10.62±0.27	48.8±1.1	3.27±0.08	14.11	325.26

* Manuscript submitted.

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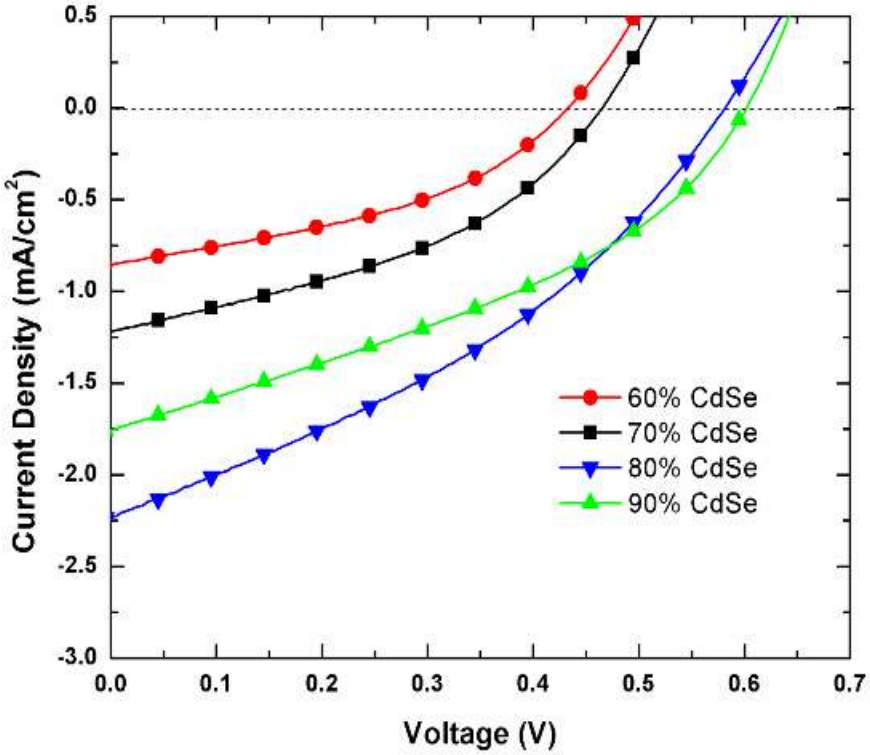
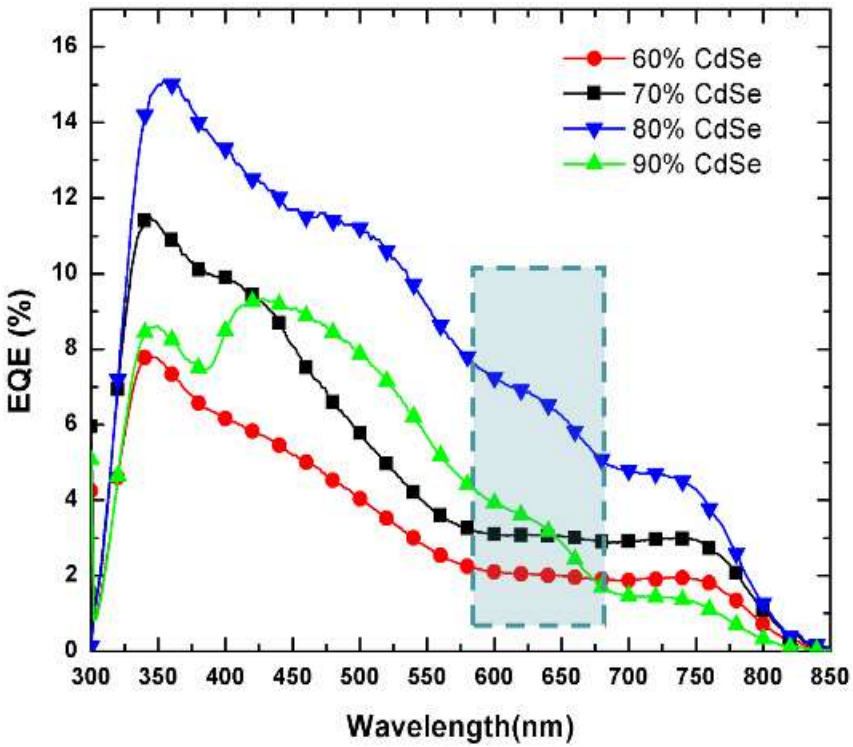
Hybrid Nanocomposite Active Regions





CdSe loading	Short-circuit current I_{sc} [mA/cm²]	Open-circuit voltage V_{oc} [mV]	Fill factor FF [%]	Power conversion efficiency η [%]
60%	0.77±0.06	418.3±21.1	39.7±0.7	0.13±0.02
70%	1.21±0.02	463.3±2.58	39.9±0.2	0.22±0.03
80%	2.04±0.20	567.5±8.80	35.3±0.1	0.41±0.04
90%	1.61±0.14	595.0±5.78	36.6±0.2	0.35±0.03

W. Y. Ge, A. Atewologun and A. D. Stiff-Roberts, *Organic Electronics*, vol. 22, pp. 98-107, March 2015.

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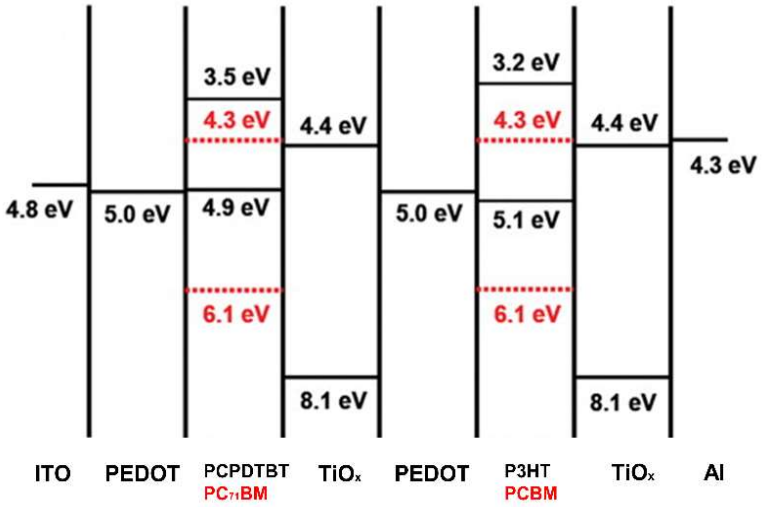
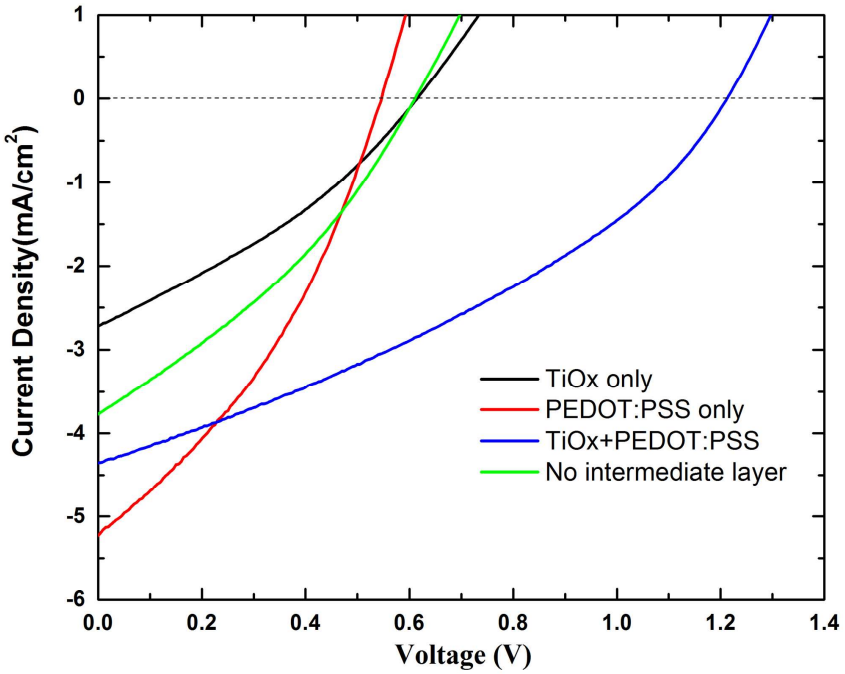
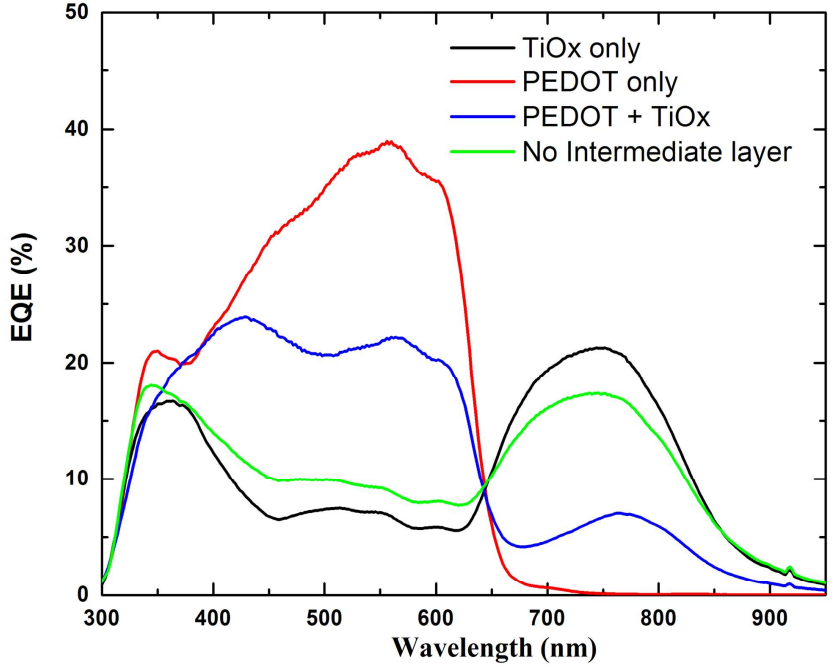
Tandem Solar Cell Active Regions



Tandem Junction Layer	Voc (V)	Jsc (mA/cm2)	FF	Eff (%)
Tandem TiOx only	0.62	3.60	0.348	0.77
Tandem PEDOT only	0.54	5.20	0.353	1.00
With both TiOx and PEDOT	1.21	4.22	0.338	1.73
No Intermediate layer	0.61	3.77	0.331	0.76





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Conclusions

- Emulsion-based RIR-MAPLE is appropriate for a wide range of organic and hybrid material systems.
- The emulsion target recipe has a significant impact on the performance of organic optoelectronic devices.
- Hybrid material systems may benefit most from the unique film properties resulting from emulsion-based RIR-MAPLE.
- The future prospects for emulsion-based RIR-MAPLE include serving as an enabling technology for materials by design (e.g., controlling the crystallinity, orientation, and packing of polymer films or tailoring the nanoscale composition of blended films to achieve desired bulk properties).

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