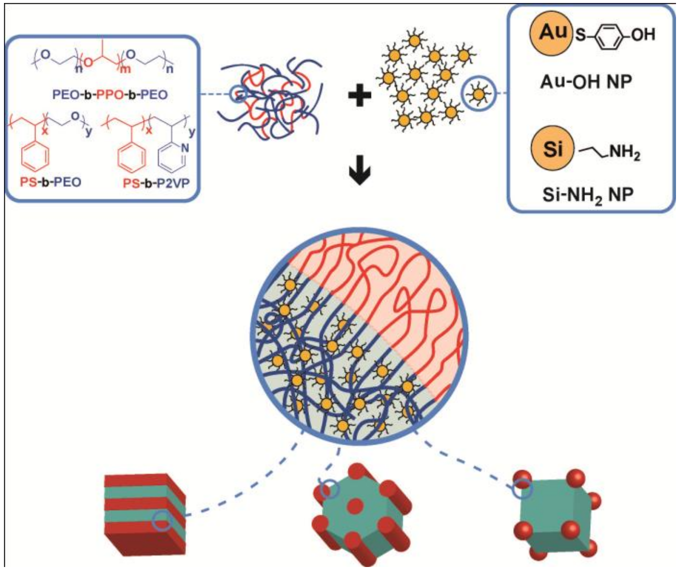
Roll-to-Roll Manufacturing of Nanostructured Materials and Devices

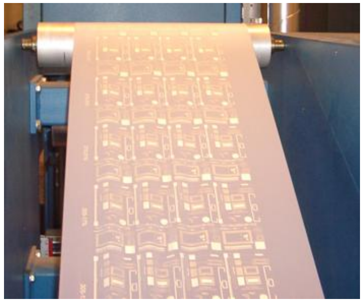


Jim Watkins

Polymer Science and Engineering Department
and Center for Hierarchical Manufacturing – NSF NSEC
University of Massachusetts, Amherst

CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

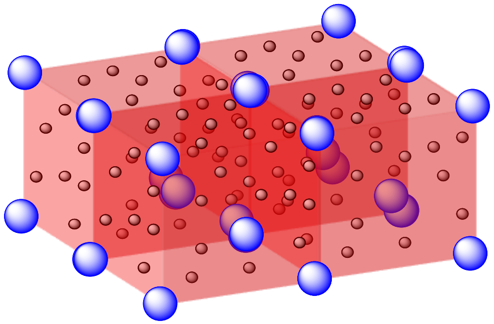
Low Cost Nanodevices by Combining Printed Electronics and Nanostructured Device Layers



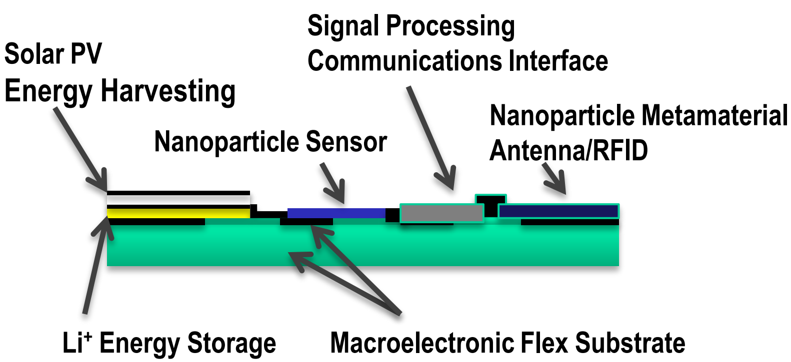
printedelectronicsnews.com

- **Start with Printed Macroelectronic Substrate**
  - low cost, low performance
  - simple devices
  - micron ++ length scales

- **Add Nanostructured Device Layers via Low Cost Processing**
  - low cost, large area
  - enabled or enhanced functionality due to nanostructure
  - length scales less than 50 nm
  - may sit on top of printed macroelectronic substrate
  - PVs, energy storage, magnetic metamaterials, sensors



- **Produce Low Cost, High Performance Nanotech-enabled Devices**
  - single purpose first
  - PV, battery, sensor, antenna
  - integrated devices



CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

Top Down Meets Bottom Up ….. on a Web

National Nanomanufacturing Network

CHM Center for Hierarchical Manufacturing University of Massachusetts Amherst

NIST National Institute of Standards and Technology U.S. Department of Commerce

Nanofabrication Technologies for Roll-to-Roll Processing

An Academic-Industry Workshop on Technologies for American Manufacturing Competitiveness

Seaport Convention Center, Boston, MA

Tuesday September 27, 2011
Atrium-Seaport Convention

5:00-6:15 pm Reception/Poster Session for Nanomanufacturing Summit 2011
6:30pm Workshop Dinner-**Constitution Room, Seaport Hotel**
6:40 pm Introductory Remarks and Workshop Objectives - J. Morse-NNN
6:45 pm Flexible Substrate Nanoanufacturing Roadmap – Dan Gamota, INEMI
7:30 pm Nanofabrication for Roll to Roll Processing – James Watkins, CHM/UMass
8:00 pm High Temperature Roll to Roll Processes – Amit Goyal, Oak Ridge National Lab

Wednesday September 28, 2011
Skyline Room, Seaport Convention Center

7:30-8:30 am Breakfast
8:30 Ken Carter-CHM/UMass Amherst
8:55 Nikolaos Kehagias, Catalan Institute of Nanotechnology
9:20 Jay Guo-University of Michigan
9:45 Jennifer Ernst -ThinFilm, Inc.
10:10 Robert Praino-Chasm Technologies

1030 Break

10:50 Rick Daniels-Carestream
Nanometer Functionality Delivered by the Meter
11:15 Dennis Slafer-Microcontinuum
11:40 William Jarvis-Flexcon
12:05 Michael Hunter-Liquidia Technologies

12:30 Lunch and Group Discussions
1:00 Dan Gamota, INEMI, Standards Initiatives
1:15 Ganesh Sundaram, Cambridge Nanotech, inc.
1:40 Hong-Yee Low-AStar/IMRE
2:05 Mark Poliks-CAMM
2:30 S.V. Sreenivasan-University of Texas Austin/Molecular Imprints
2:55 Trevor Niblock-Magzor, Inc.

3:20 Break

3:40 Joe Petrzelka, MIT
Scaleup of Soft Lithography to R2R Technology: Modeling and Control of the Contact Region
4:05
4:30 Discussions and Readout of Key Challenges, Issues
5:00 Adjourn

- Tues. Evening through Wed.
- International Workshop
- 20 + Talks
- See Jeff Morse if Interested

Challenges for R2R Manufacturing of Nanostructured Materials and Devices

- **Materials and Process Costs**

- **Planarization and Base / Barrier Layers**
  - includes transparent conducting films, coat-able dielectrics

- **Creation of Ordered Nanoscale Hybrid Materials as Active Layers**
  - directed and/or additive driven self-assembly

- **Continuous Device Level Patterning**
  - roll-to-roll nanoimprint lithography

- **Availability of Collaborative Demonstration Facilities / POC Projects**
  - UMass CHM R2R Tool Platforms
  - PVs, Flexible Memory as Example Devices

Challenges for R2R Manufacturing of Nanostructured Materials and Devices

- **Materials and Process Costs**

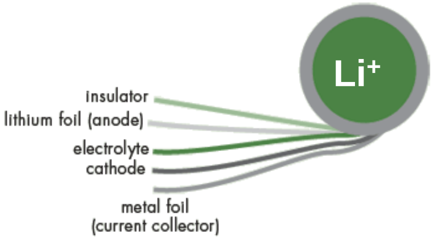
- **Planarization and Base / Barrier Layers**
  - includes transparent conducting films, coat-able dielectrics

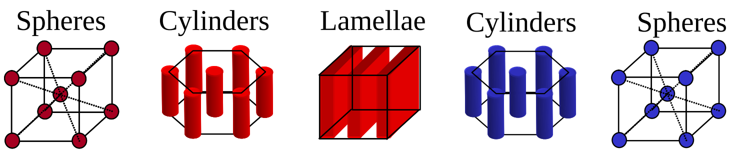
- **Creation of Ordered Nanoscale Hybrid Materials as Active Layers**
  - directed and/or additive driven self-assembly

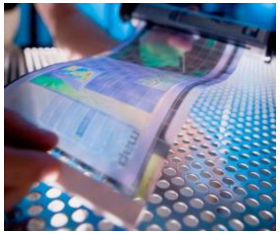
- **Continuous Device Level Patterning**
  - roll-to-roll nanoimprint lithography

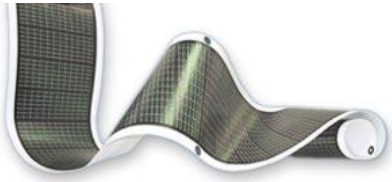
- **Availability of Collaborative Demonstration Facilities / POC Projects**
  - UMass CHM R2R Tool Platforms
  - PVs, Flexible Memory as Example Devices

Nanotechnology Is Enabling but Many Important Applications are Cost Sensitive
Energy, Water, and Flexible Electronics
Nanomanufacturing Must Adapt to Serve Low Cost Per Area Devices









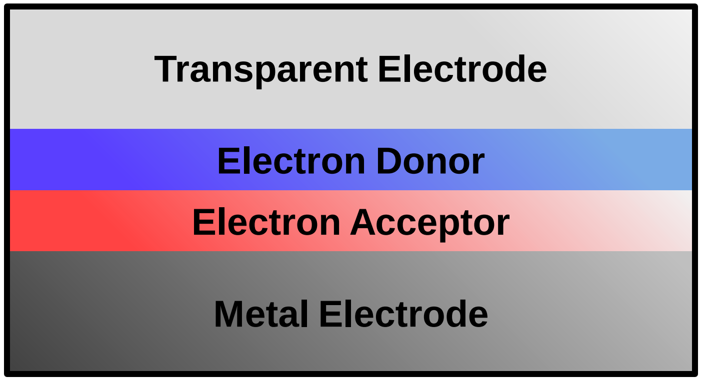
- Morphology is key to performance
- BCP template yields periodic structures
  (5 – 45 nm domains)
- Hybrid materials for functionality
  - co-assembly required
- Roll-to-Roll manufacturing
- Integration with top down processes

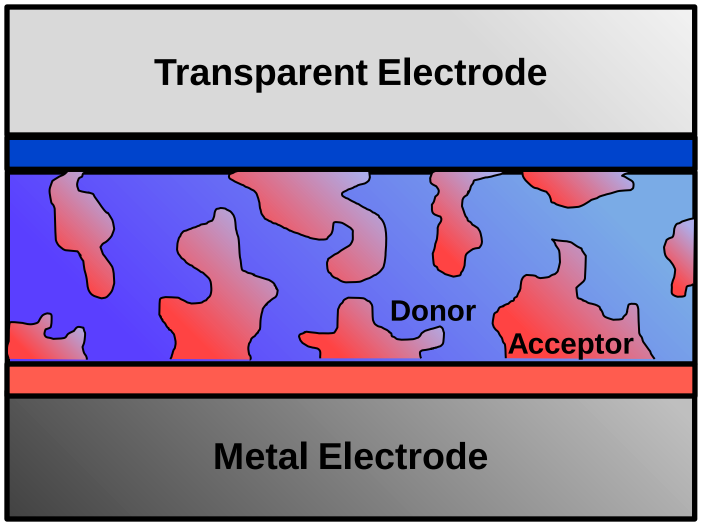
Target ~ $25/m^2$

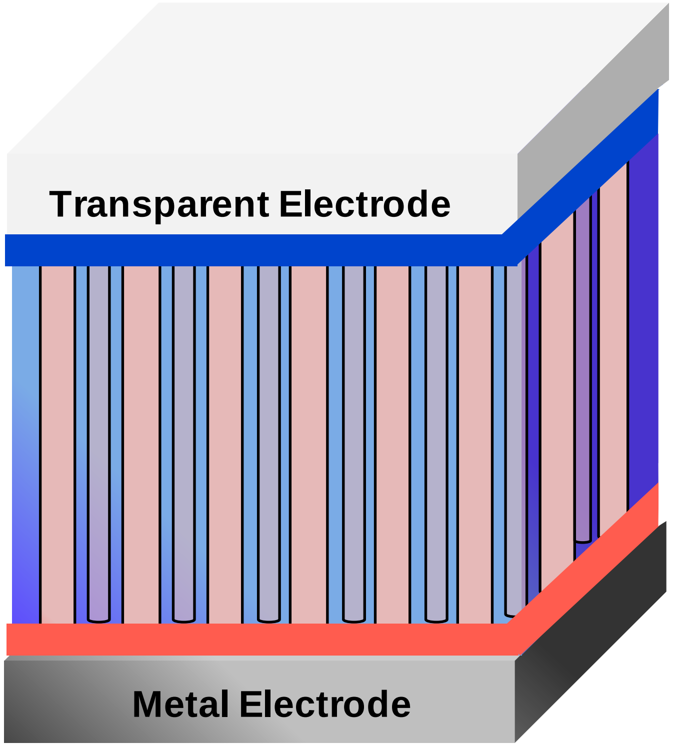
CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

Controlling Morphology at the Nanoscale Can Be Critical to Device Performance

Heterojunctions in PVs – Length Scale and Morphology



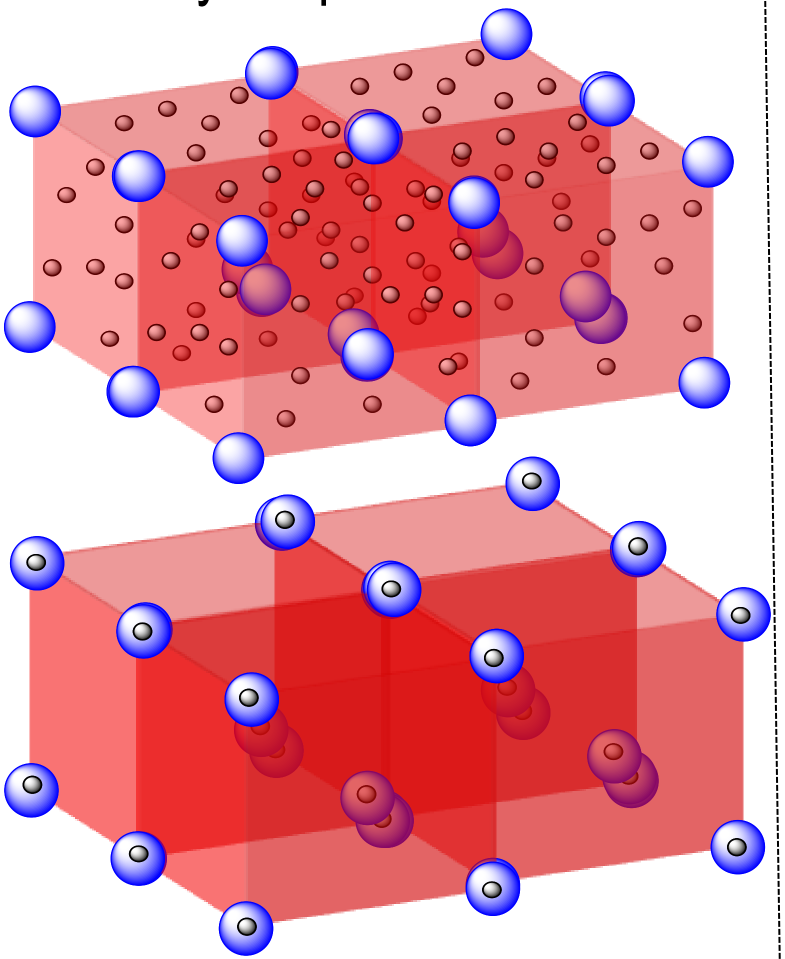




10 nm domain size straight channels

Controlling Morphology at the Nanoscale Can Be Critical to Device Performance

Modify Properties with NPs

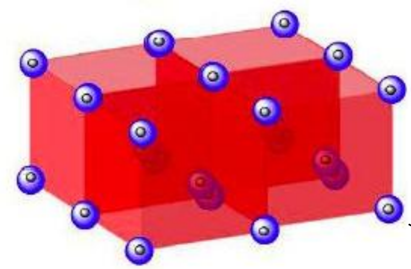


NPs = ●

High Magnetic Permeability Metamaterials

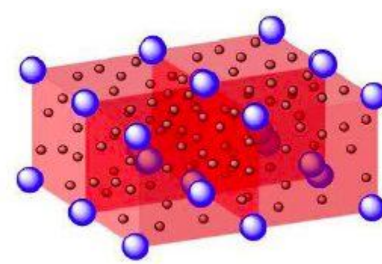
miniaturization

$$L \sim 1/\sqrt{\mu}$$



impedance matching

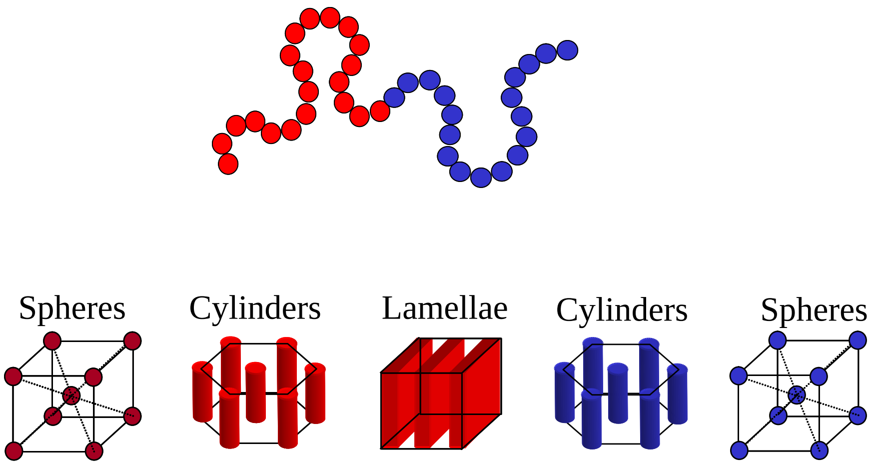
$$Z = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}}$$



Miniature, low loss, high band width antennas

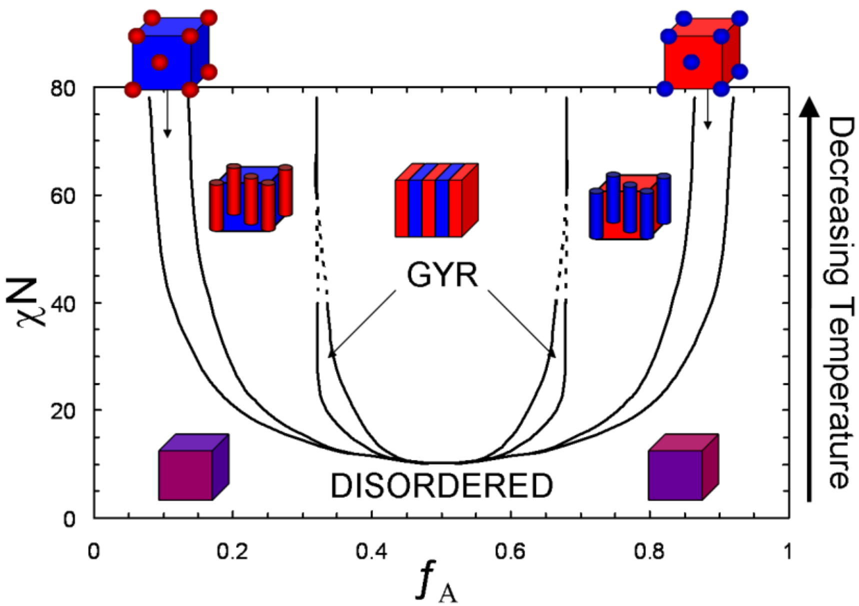
Block Copolymer Templates:
Spontaneous Assembly upon Spin Coating, Complete Control of Morphology

Di-block Copolymer



Increasing f

BCP Phase Diagram



(Adapted from Bates, 1994; Matsen, 1996)

Key Parameters: block volume fraction, f → controls morphology
Flory Parameter, χ → χN controls segregation
degree of polymerization, N → controls domain size

Small N requires large χ for strong segregation

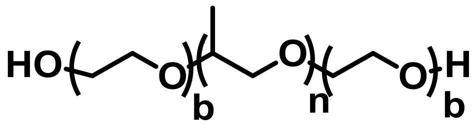
Extension of Self-Assembly for High Volume Fabrication of Nanostructured Materials and Devices

Key Issues and Strategies:

- Commodity scale availability for low cost/high volume systems
- Creation of technologically useful materials: functionalize to realize electronic, mechanical, optical properties
- Create well-ordered nanoparticle/BCP systems with prescriptive placement of NPs and high NP loadings
- Develop robust R2R manufacturing platform
    - scalability, process models, manufacturability, metrology, QA, process control

Commodity Block Copolymers: Pluronic™ Surfactants

• PEO_m-PPO_n-PEO_m (Mw/Mn ~ 1.2)



•Inexpensive and readily available with various f_{PEO} and N

• Low $\chi_{PEO\text{-}PPO}$: $\chi(T) = -0.122+66.8/T$[1]

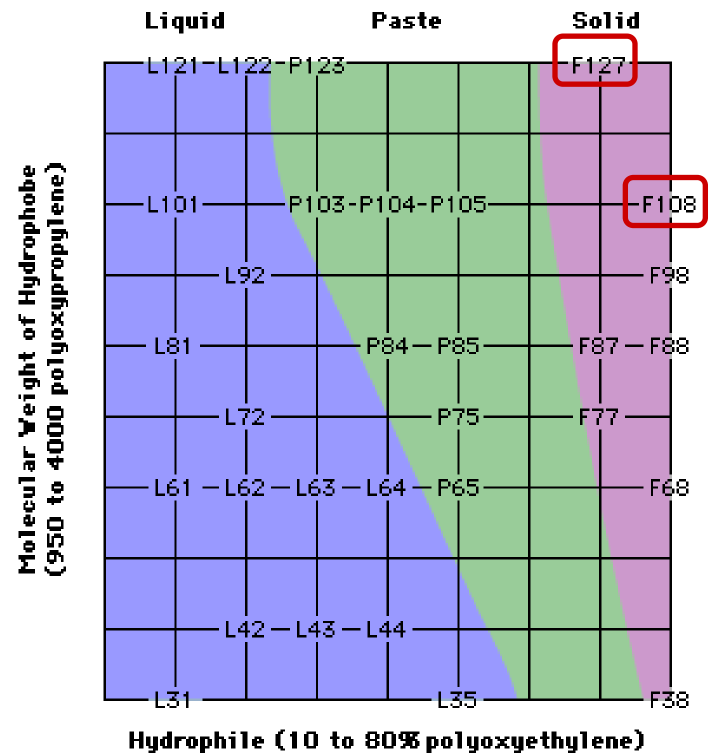
$\chi_{PEO\text{-}PPO}$ @ 80 °C = 0.066-0.068

Segregation strength of Pluronics[2]

Polymer	Total M_W	f_{PEO}	χN* (calc.)	Min. ODT (K)*
F127	12,000	0.7	16.95	256
F108	15,000	0.8	20.29	337.5

At very low Mw, χN is typically too low for phase separation

Pluronics Grid



http://www.basf.com/performancechemical/bcperfpluronic_grid.html

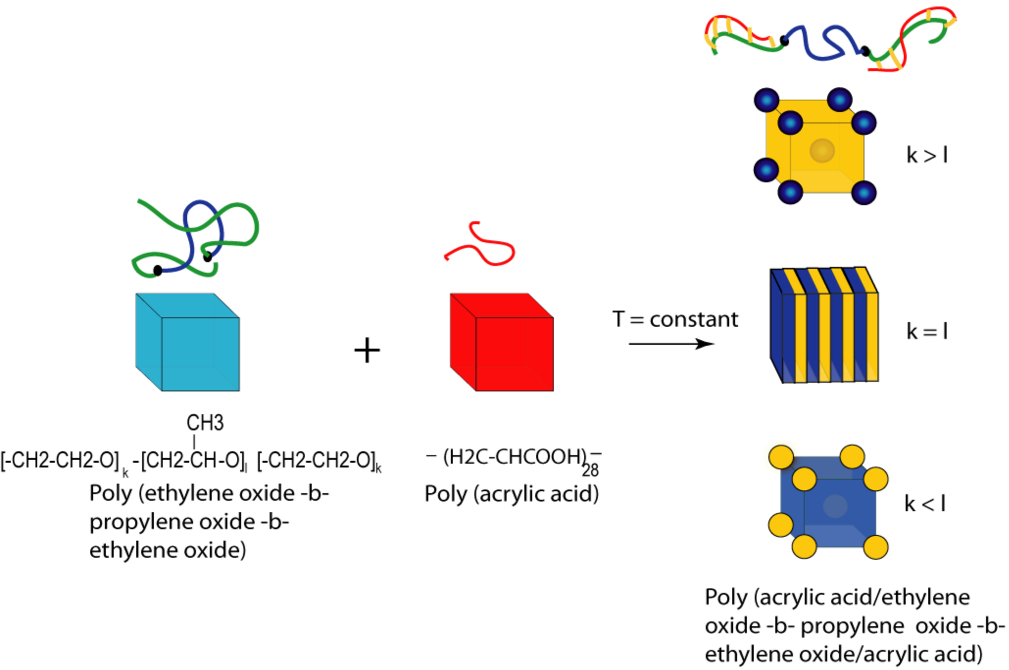
No Microphase Separation at 80°C

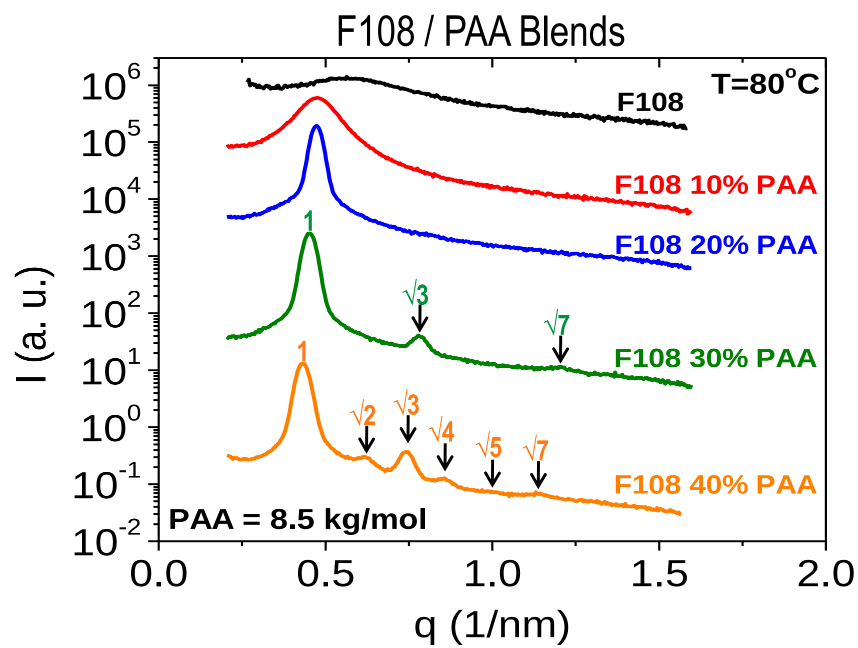
1 Ryan, Booth, and coworkers, *Phys. Chem. Chem. Phys.* ***2000***, *2*, 1503-7

2 Tirumala, V.R.; et al. *Advanced Materials*, ***2008***, *20*, 1603-1608

CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

Strengthening Phase Segregation via Segment Specific Interactions:





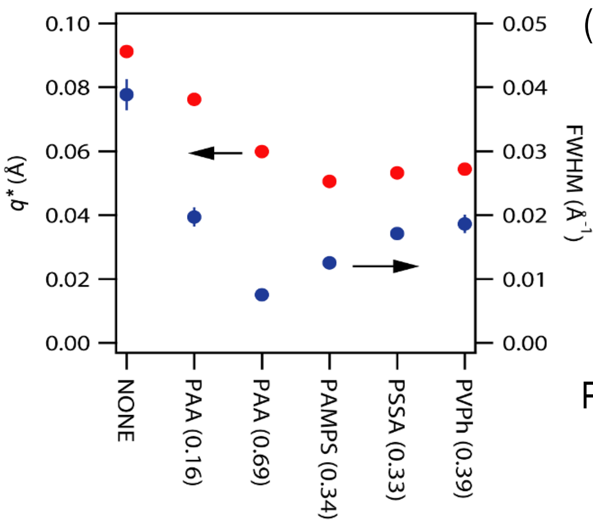
We find blending with homopolymers that H+ bond to the majority PEO block yields exceptionally well-ordered materials by increasing segregation

- Demonstrates the role of strong selective interactions in polymer assembly
- Induce order in compositionally heterogeneous systems with small χ
- Will enable use of BCP templating in low cost applications (roll to roll, extrusion)
- Increases in χN will reduce feature size

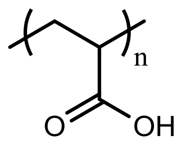
Strengthening Phase Segregation via Segment Specific Interactions: Stable Functional Templates

Broad Class of Behavior

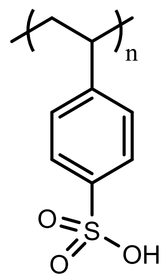
Flexibility in Choice of Homopolymers



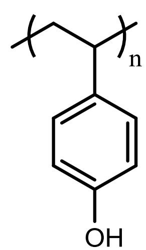
Poly(acrylic acid) (PAA)



Poly(styrene sulfonic acid) (PSSA)

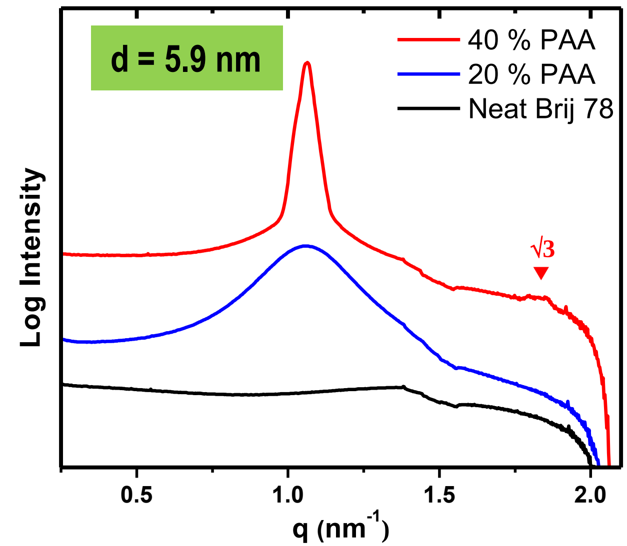


Poly(vinyl phenol) (PVPh)

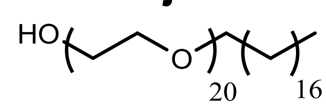


Flexibility in Choice of Surfactant

Brij 78 (PEO_{20}-*b*-$C_{18}H_{27}$) 70 °C



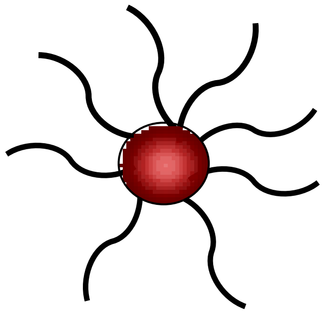
Brij 78

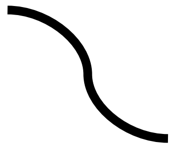


stable, functional, self-assembled templates that can be coated at high rate

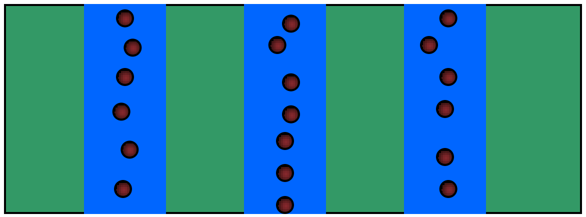
BCPs as Templates for Well-ordered Nanocomposites

ligands can be used to control particle location





= homopolymer of one block



NP distribution in target domain influenced by NP size, chain stretching

---

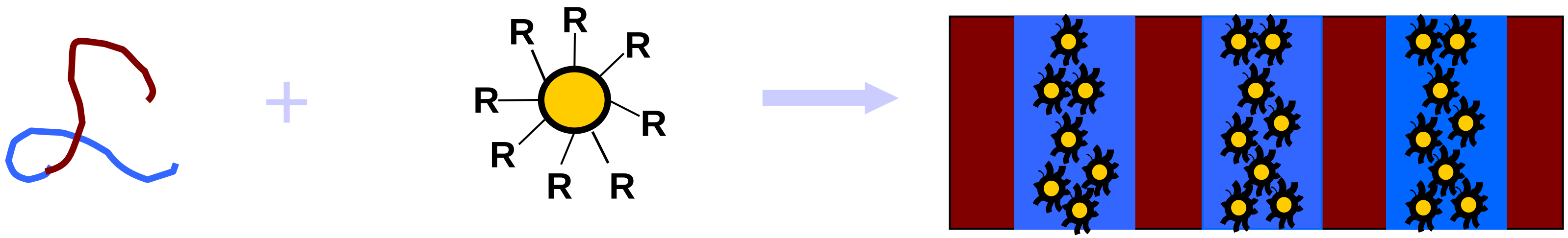
Issue for High Particle Loadings:

- Entropic penalties arise from chain stretching to accommodate NPs
- Entropic penalties push systems towards disorder in systems with neutral (or weak) enthalpic interactions

Thompson et al., Science 2001
Balazs, Emrick, Russell Science 2006
Lo et al., Macromolecules 2007

Addition of NPs with Enthalpically Favorable Interactions Induces BCP Order

Using hydrogen bonding, ligands can be used to drive NP sequestration & segregation at high loadings



 = H-bonding acceptor

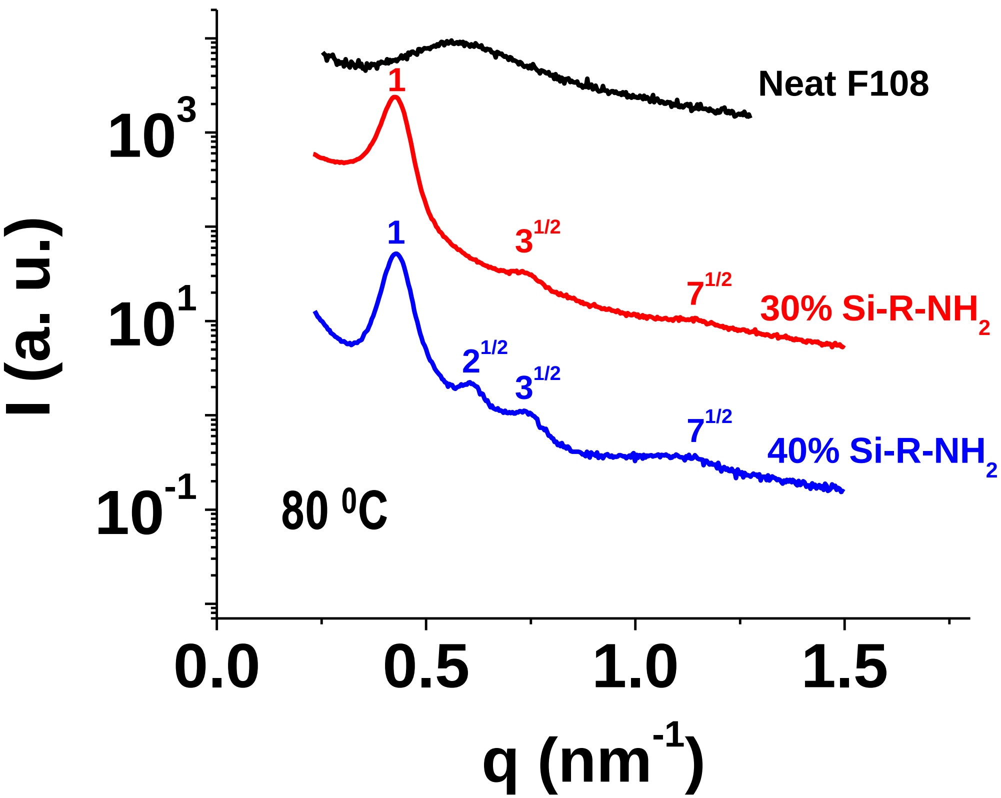
R= H-bonding donor, use "short" ligand

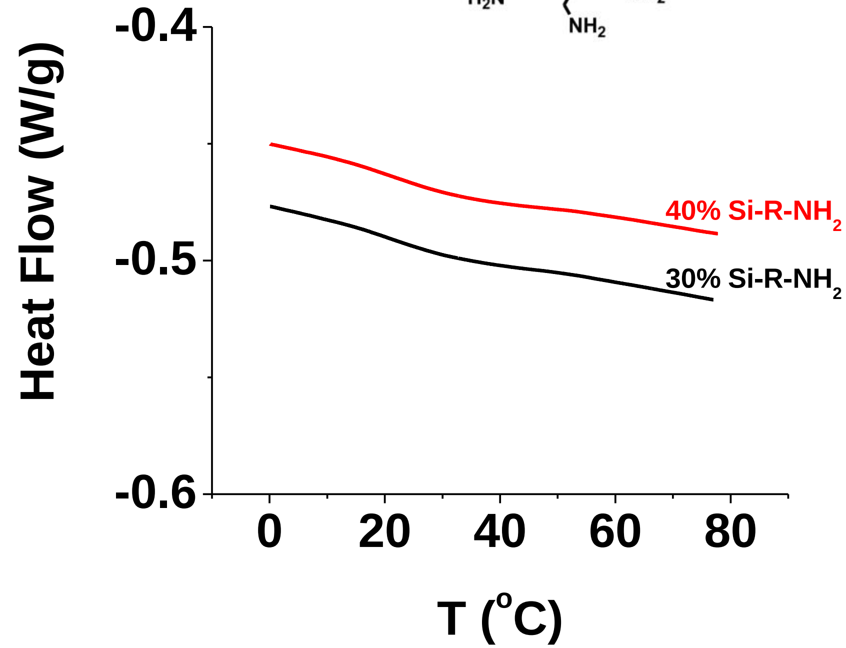
entropic penalty is offset by an enthalpic gain.

Disorder to Order Transition Induced by Si Nanoparticles

Phase Behavior of F108 with Si Quantum Dots (2-4 nm) Functionalized with Ally Amine

F108 = (PEO_{127}-PPO_{48}-PEO_{127}), 14.6 kg/mol





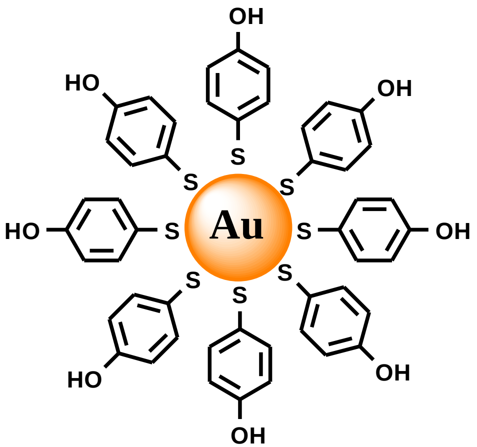
- Disorder → Cylinders→ Spheres

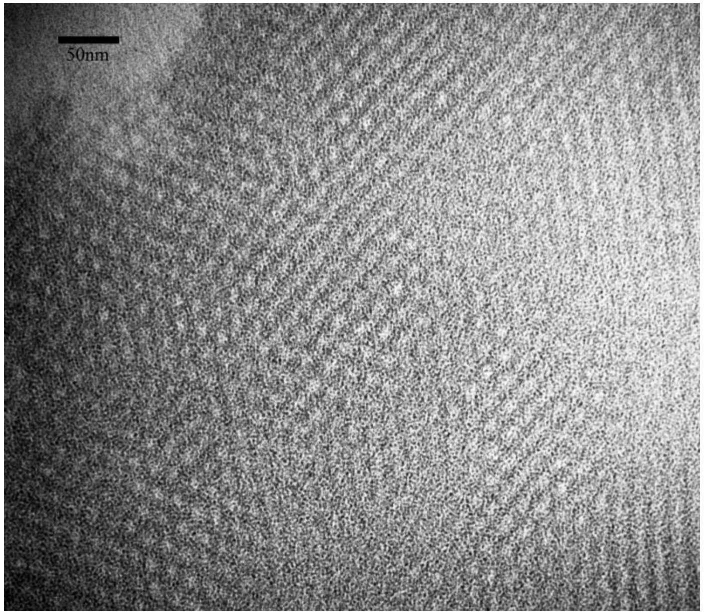
- PEO crystallization suppressed
- T_g at 30% and 40% loading = 20.6 ^{o}C

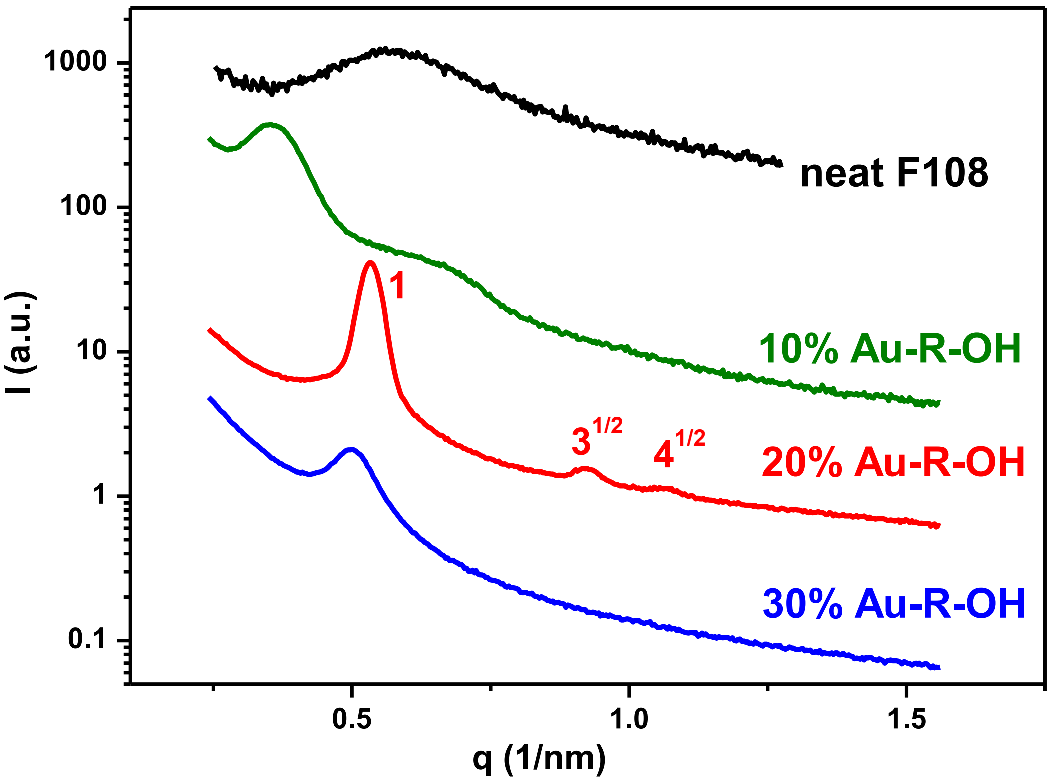
CHM Center for Hierarchical Manufacturing University of Massachusetts Amherst

Y Lin, VK Daga, ER Anderson, SP Gido and JJ Watkins, *J. Am. Chem. Soc.*, **2011**, 133, 6513

Functionalized Gold NPs in F108: SAXS



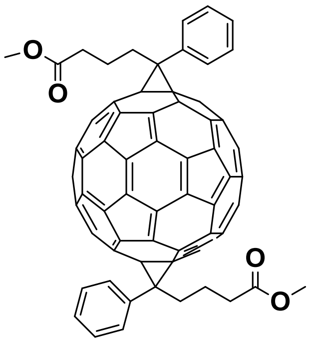




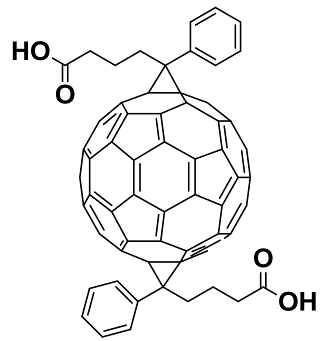
Similar results for high and low molar mass BCP systems, e.g. PS-b-PEO

CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

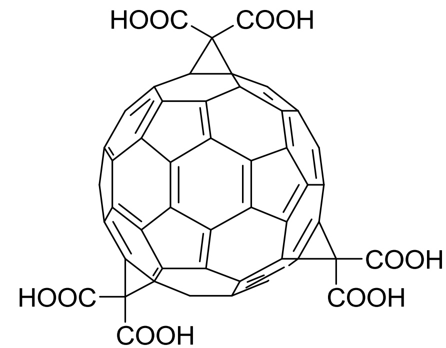
Assembly Using Fullerene Derivatives



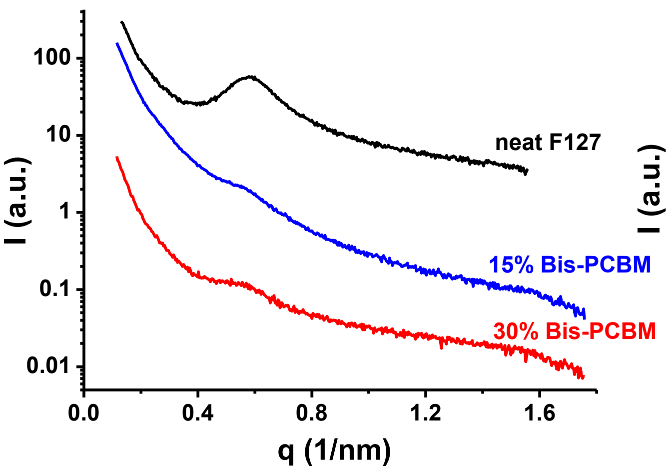
Bis-PCBM

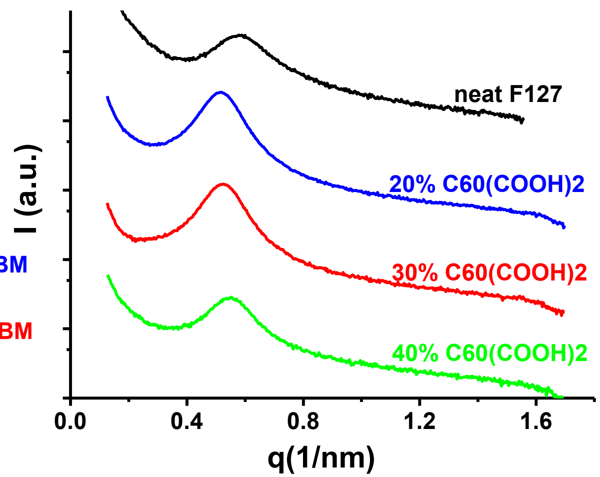


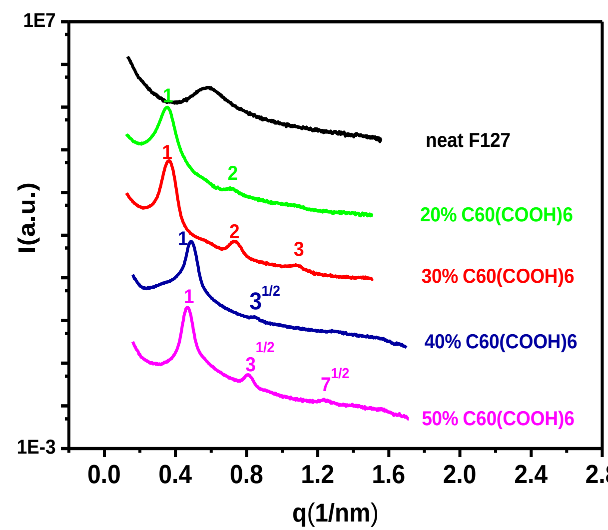
$C60(COOH)_2$



$C60(COOH)_6$



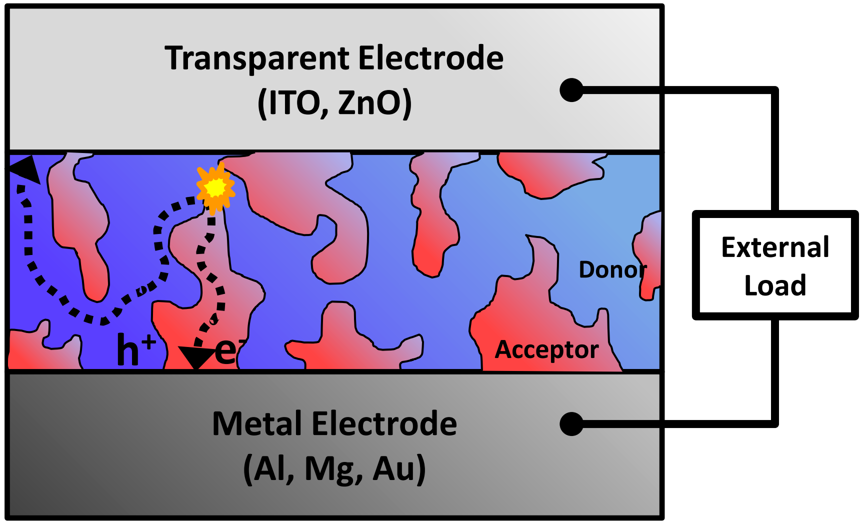




H-bonding exists between PEO and C60-COOH
Higher functionality, more favorable interaction, more order

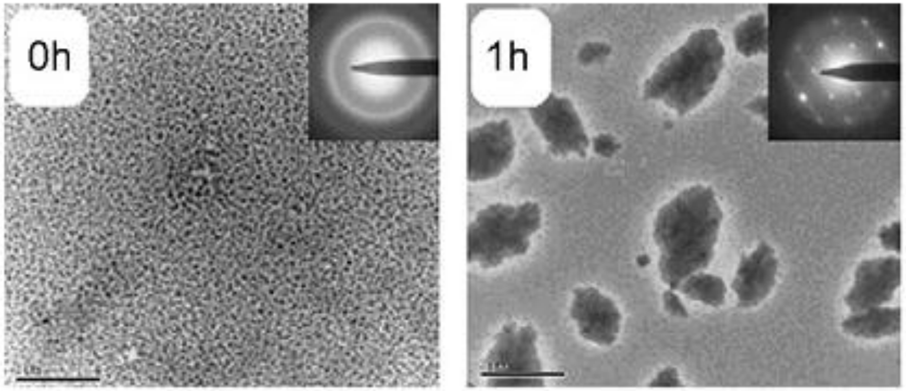
CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

The importance of morphology control in BHJ PV cells



P3HT+ PCBM

P3HT/PCBM 150C annealing for 1h



Bertho, S. Sol. Energy Mater. Sol. Cells 2008, 92, 753.

Advantages:

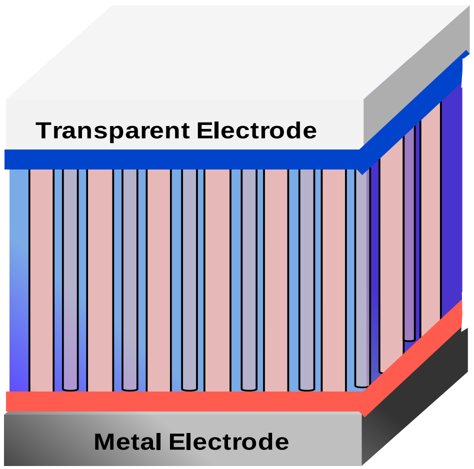
(1) Large interfacial area
(2) Effective charge generation
(3) Extremely fast electron transfer

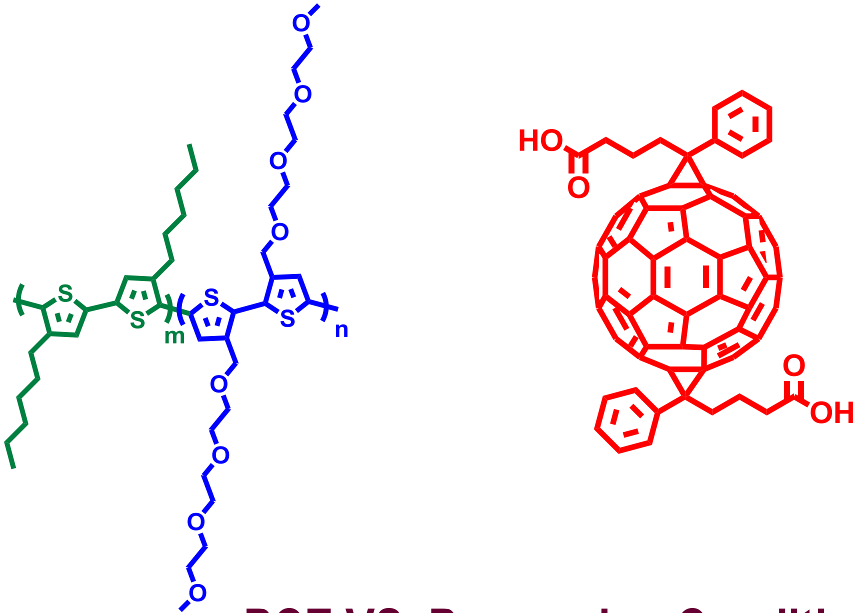
Drawbacks:

(1) Poorly controlled D/A domain size distribution (strongly dependent on processing conditions)
(2) Morphological instability & aging (aggregation of fullerene nanocrystal)

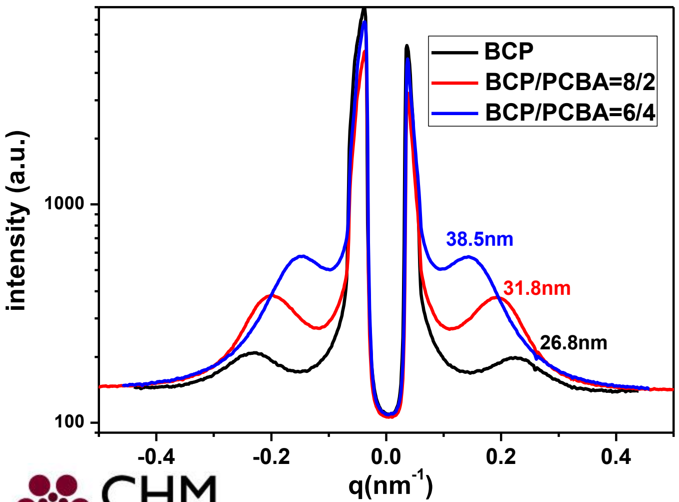
CHM Center for Hierarchical Manufacturing University of Massachusetts Amherst

An Example of a Device Based on Additive Driven Assembly: Block Copolythiophenes/Fullerene Blends for Photovoltaics





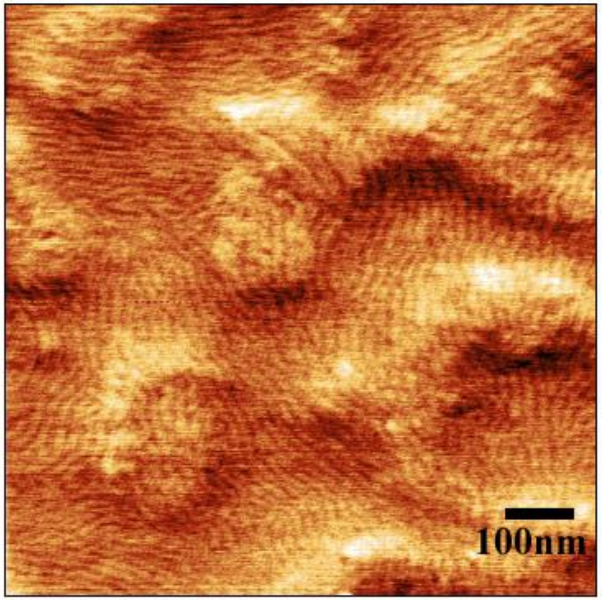
GISAXS – Ordered Structure

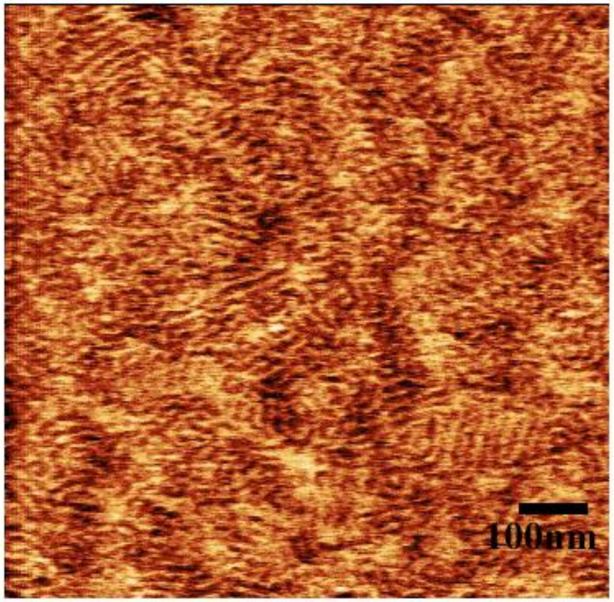


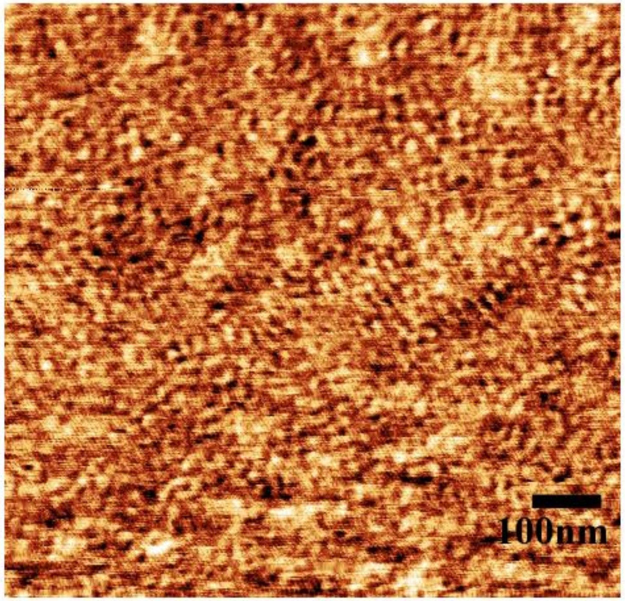
PCE VS. Processing Conditions

	V_{OC} (V)	FF(%)	J_{SC} (mA/cm^2)	PCE (%)
as spun	0.57	53.58	6.23	1.90
pre-annealing 150C 10min	0.60	54.27	6.29	2.04
post-annealing 150C 10min	0.59	52.46	6.37	1.97

AFM phase images







BCP: P3HT-b-P3TEOT

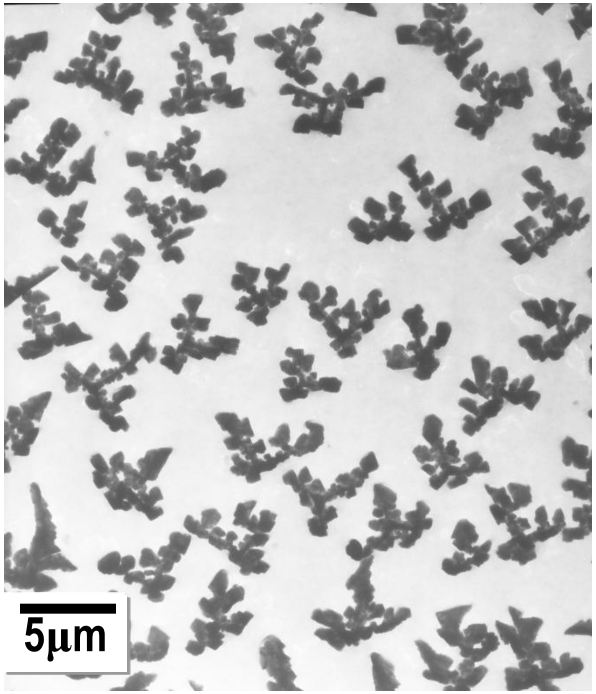
150^{o}C 30min

BCP/bis-PCBA=8/2

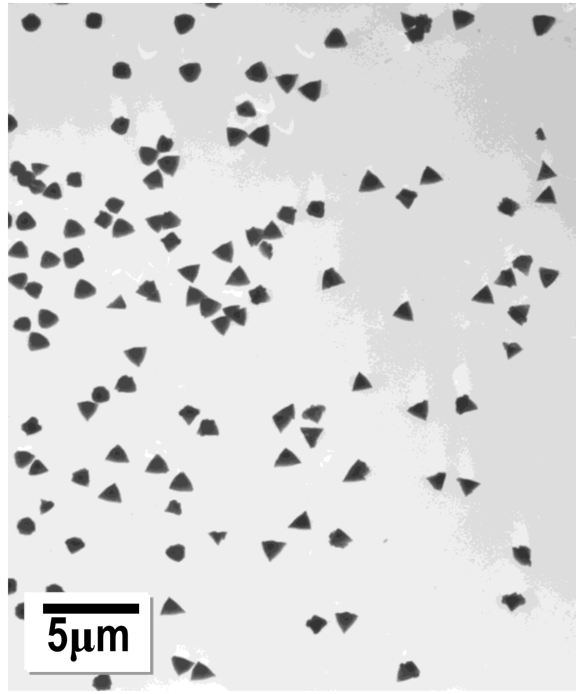
BCP/bis-PCBA =6/4

- **Incompatibility of hydrophobic and hydrophilic side chains induce microphase separation**
- **Microphase separation is maintained at high loadings of C60**

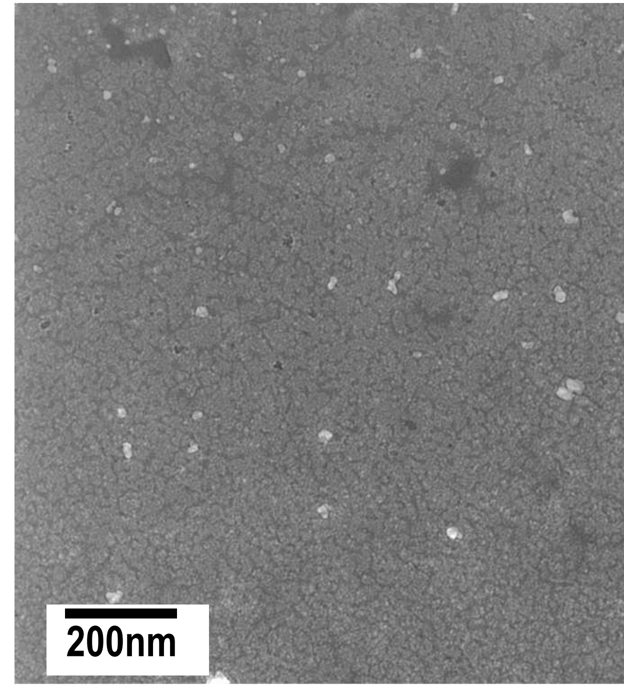
Suppression of C60 Crystallization over Extended Annealing



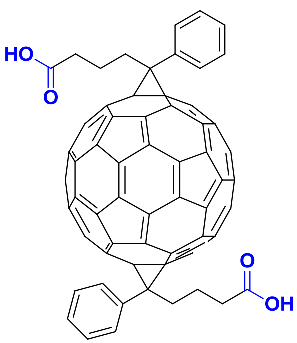
P3HT/bis-PCBA(6/4)



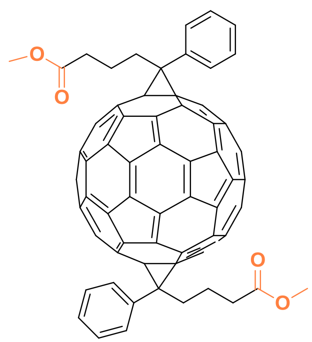
BCP/bis-PCBM(6/4)



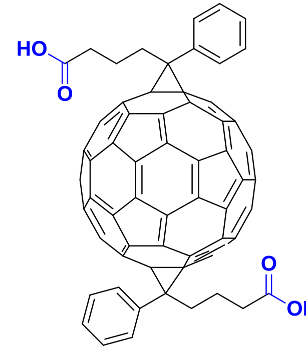
BCP/bis-PCBA(6/4)



Bis-PCBA



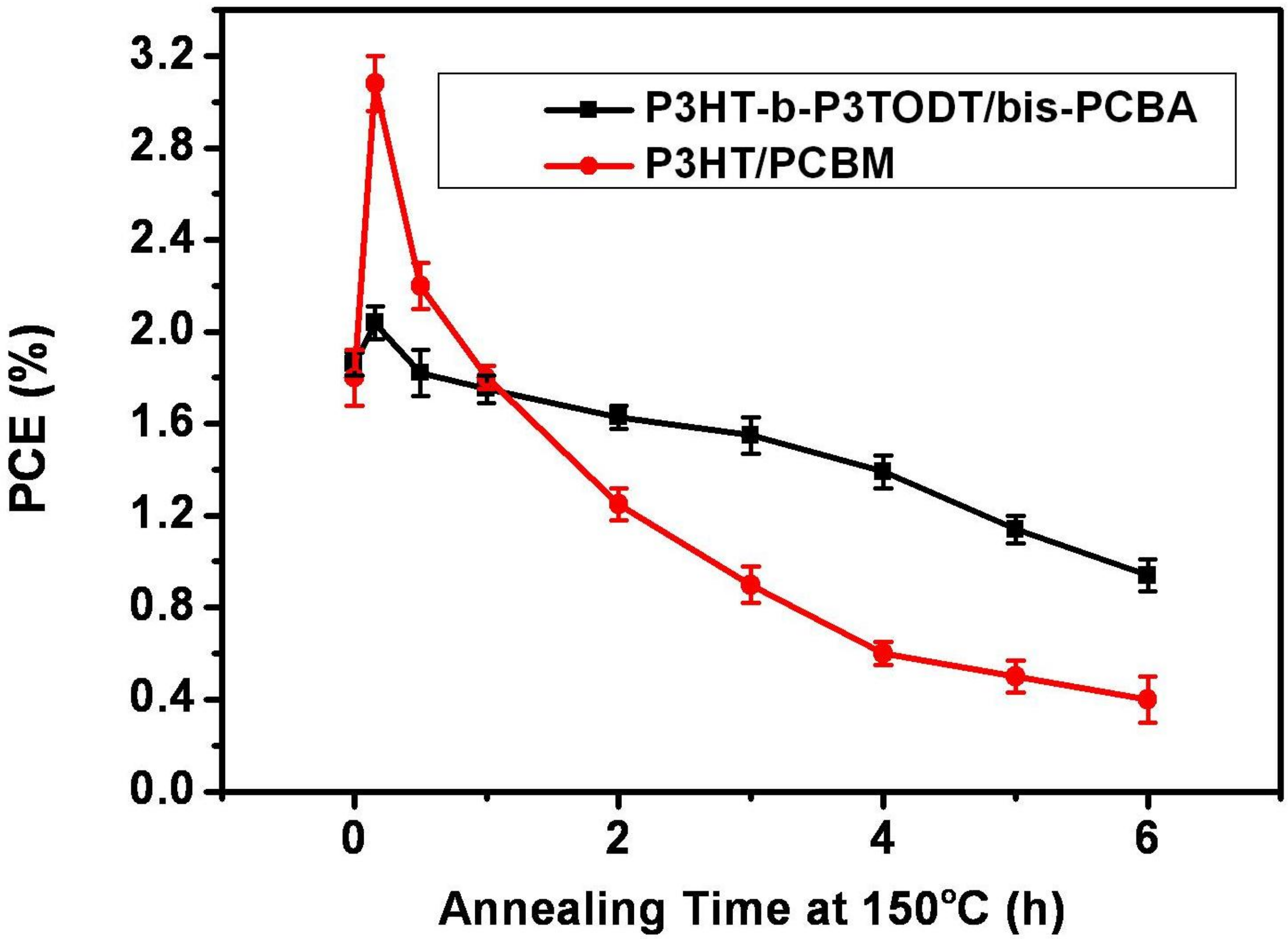
Bis-PCBM



Bis-PCBA

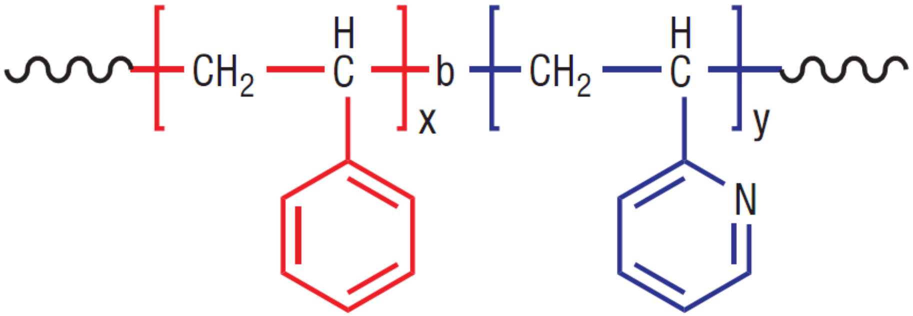
Annealing at 150^{O}C for 12hr

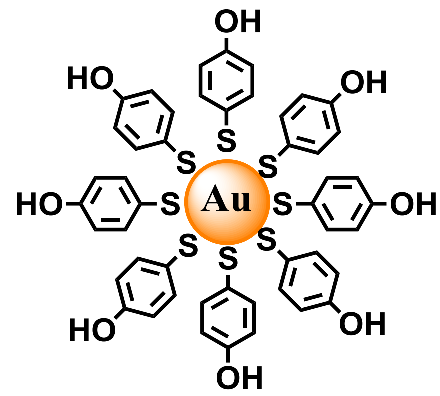
Comparison of P3HT Based Devices: Accelerated Aging

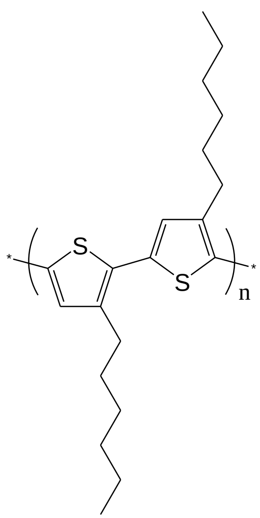


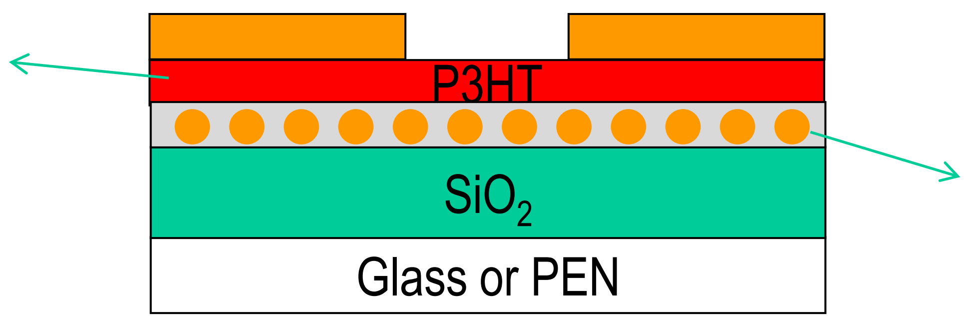
Floating Gate Memory via Self Assembly

PS-*b*-P2VP



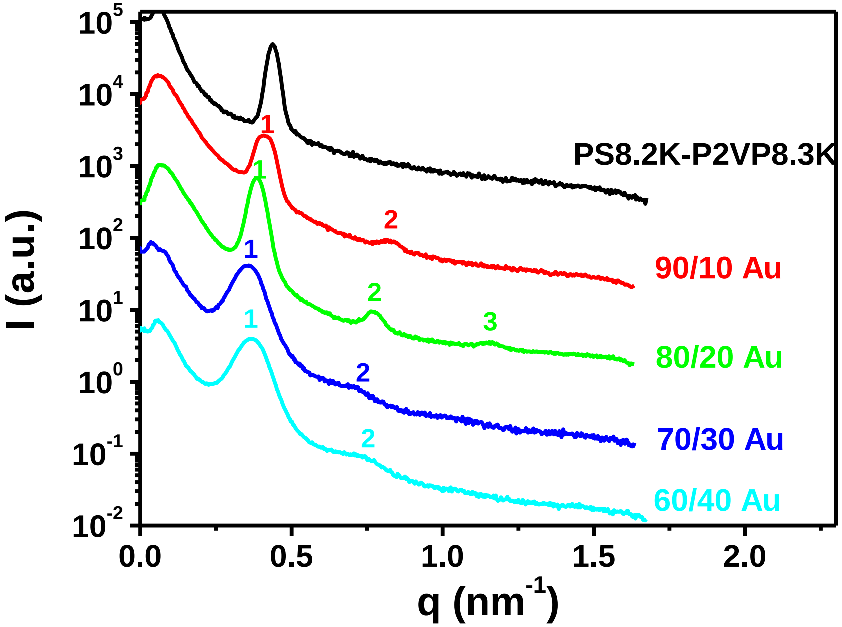


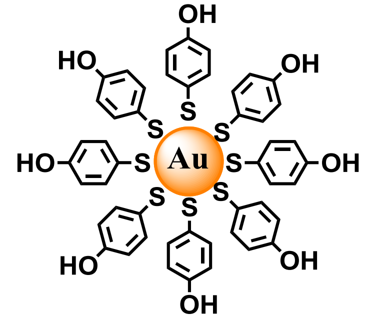




Block-copolymer with Au NPs

SAXS and TEM

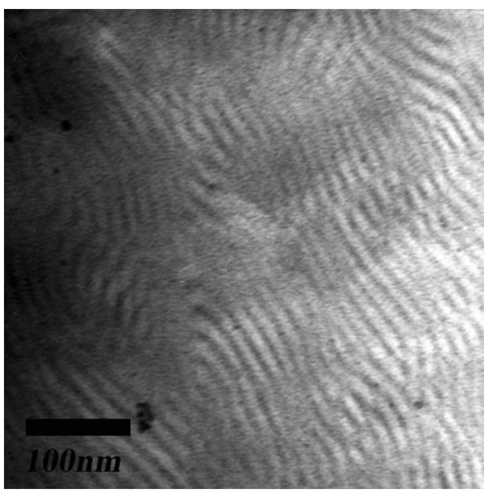




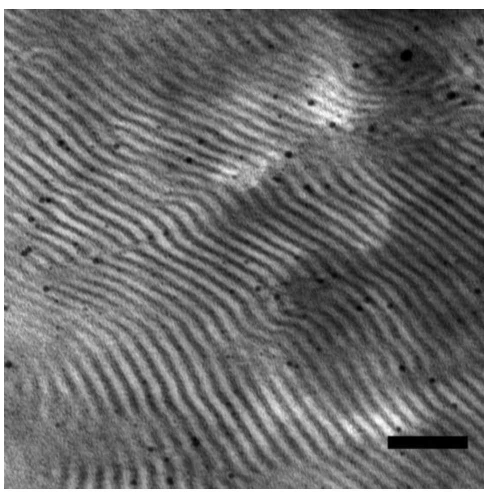
✓Better order occurs with the addition of Au-OH NP.

✓Lamellar morphology remained even at 30% loading.

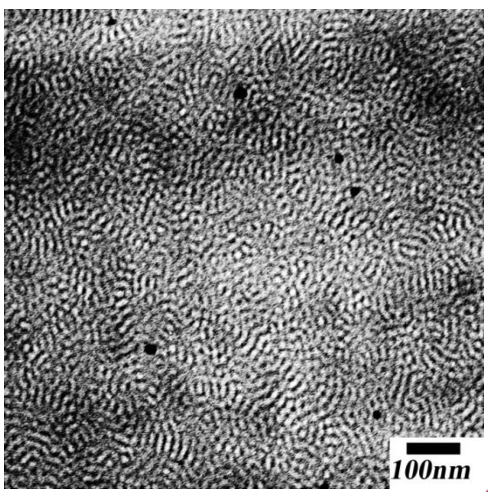
80/20



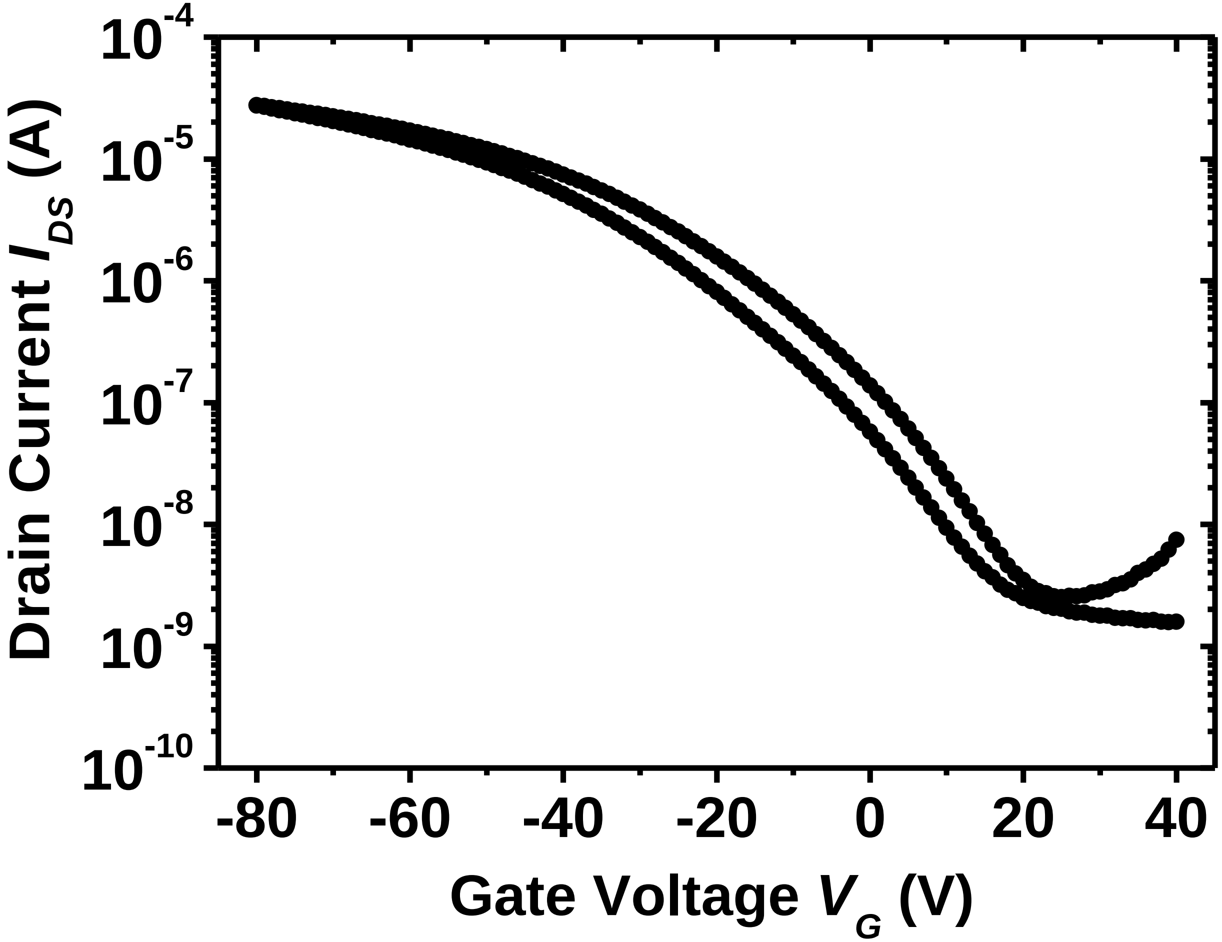
70/30

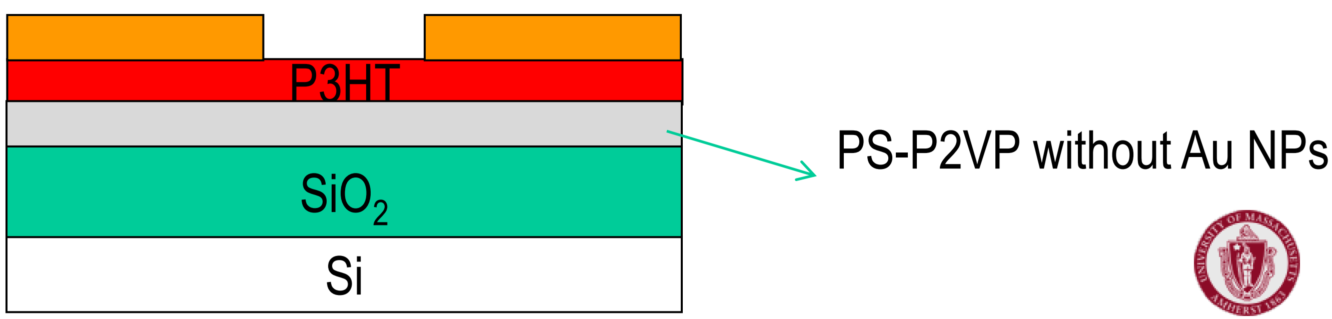


60/40



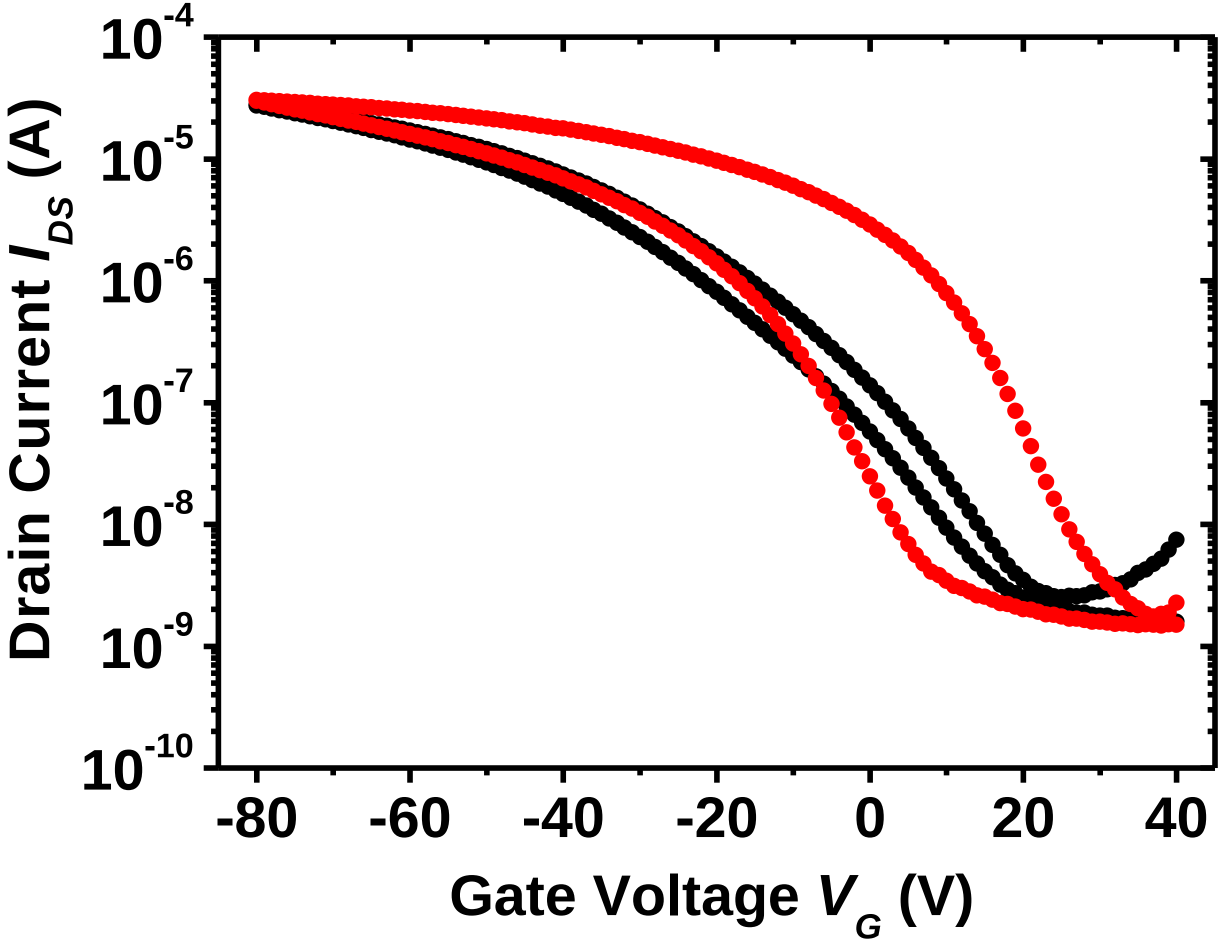
Transfer Characteristics of the Device without Au NPs

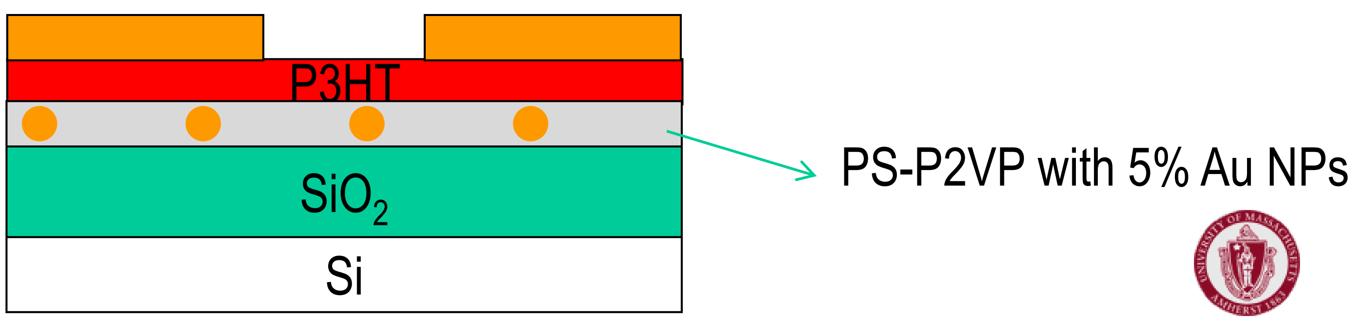




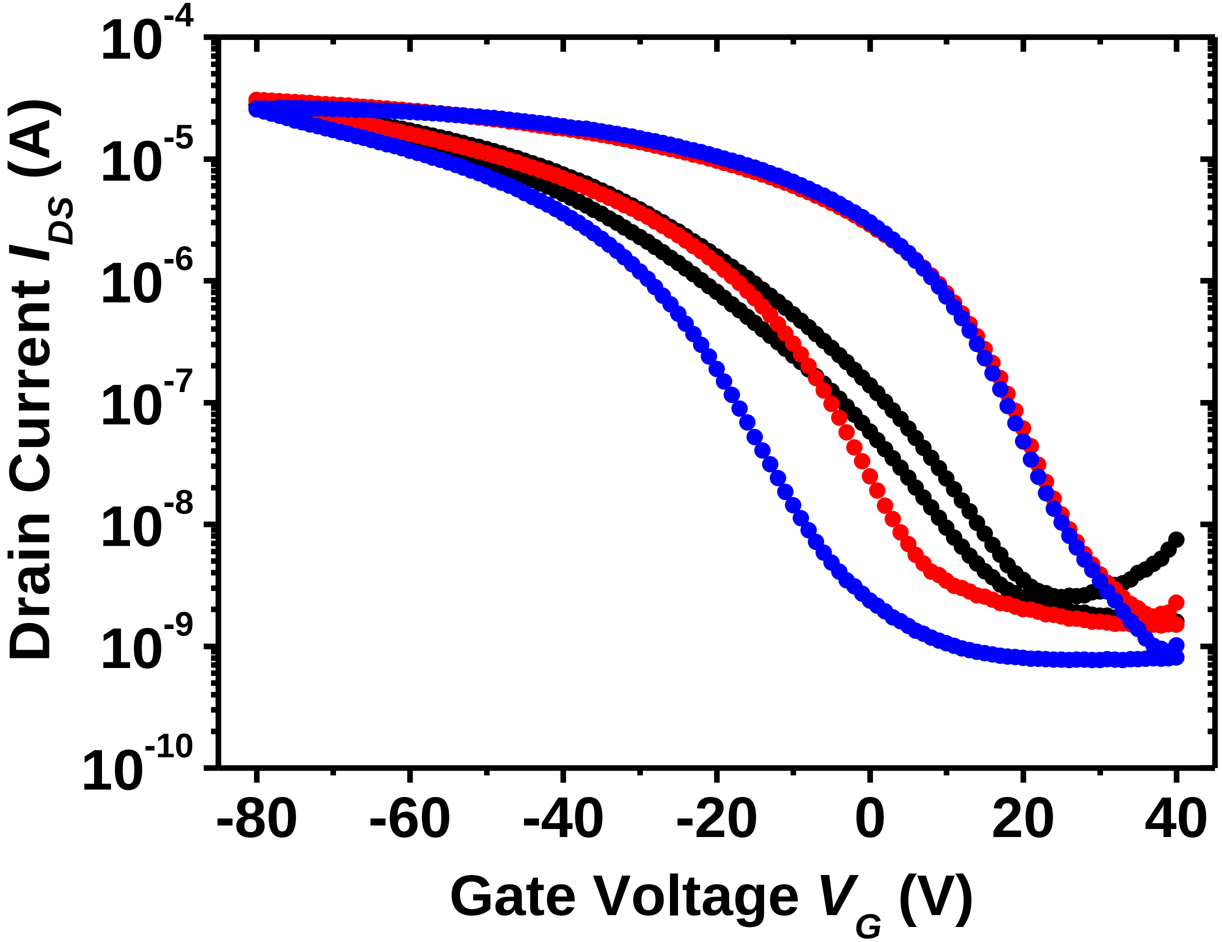
CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

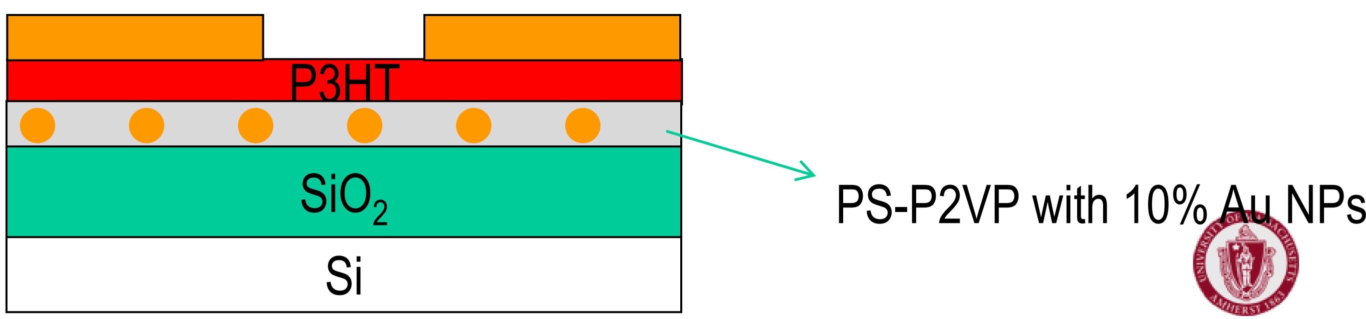
Transfer Characteristics of the Device with/without Au NPs



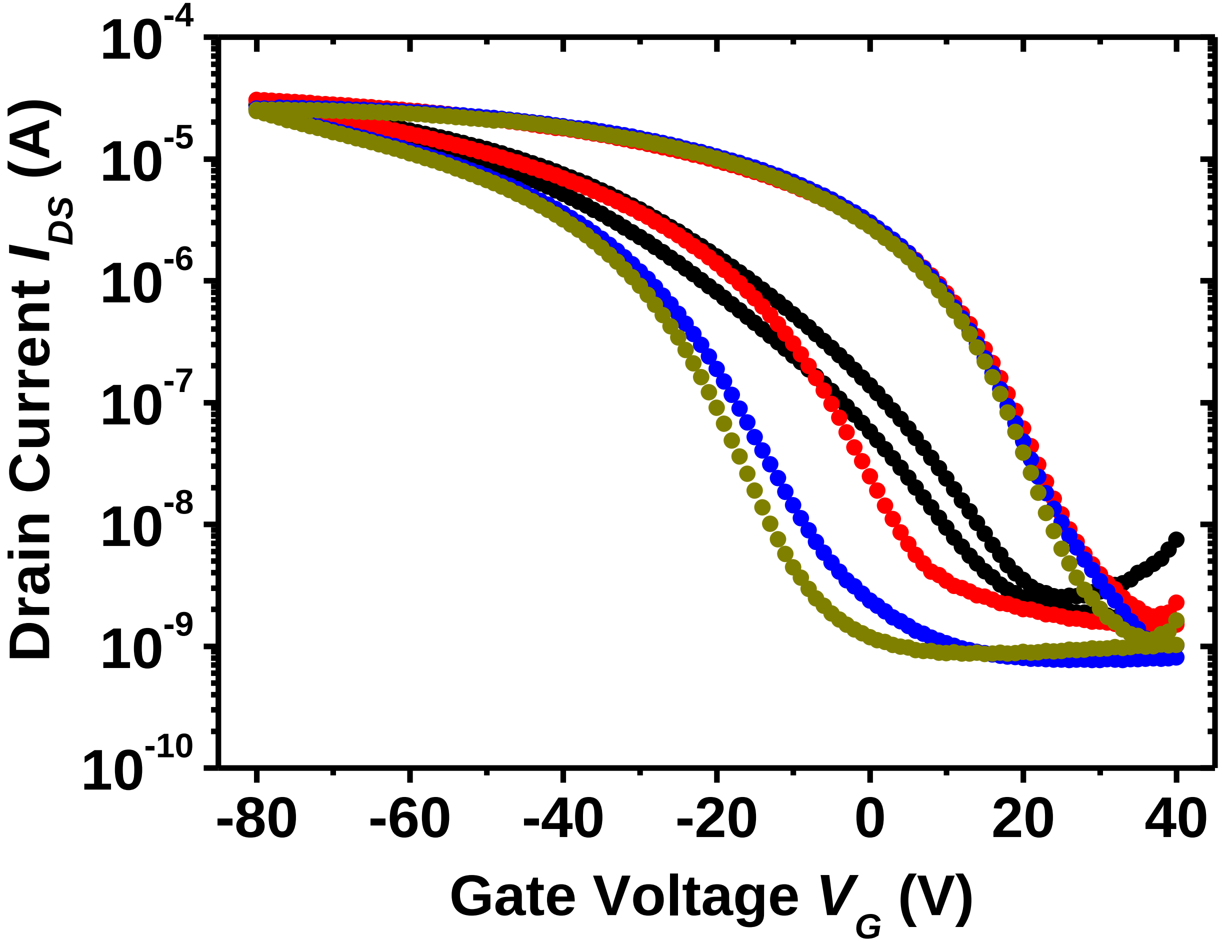


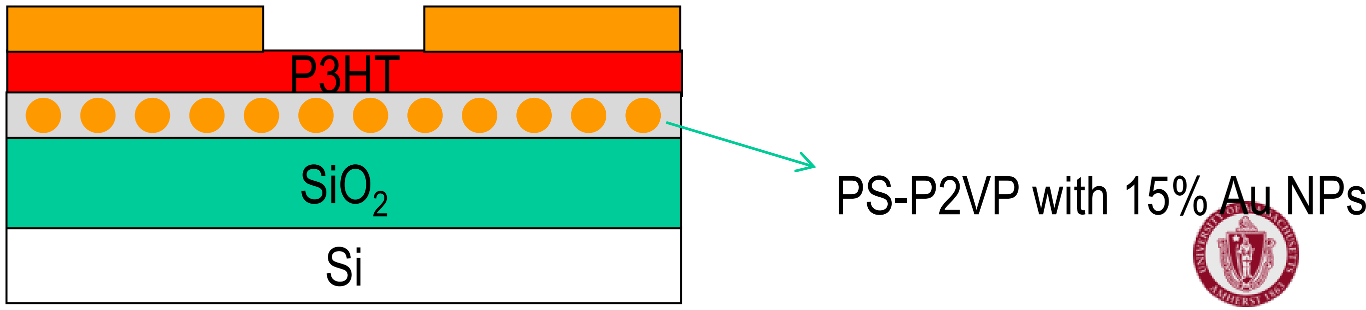
Transfer Characteristics of the Device with/without Au NPs



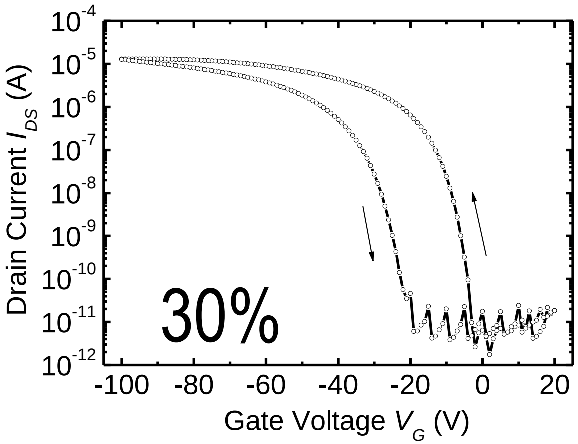


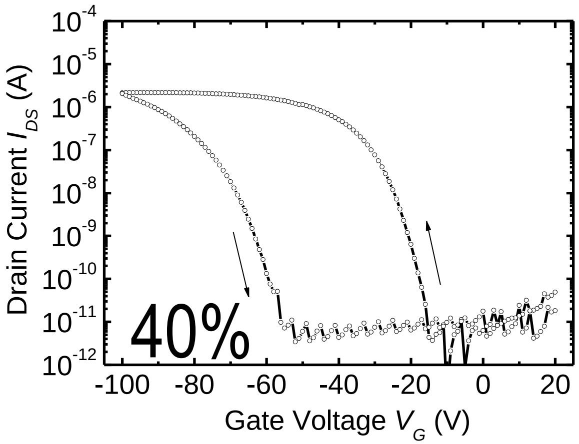
Transfer characteristics of the Device with/without Au NPs

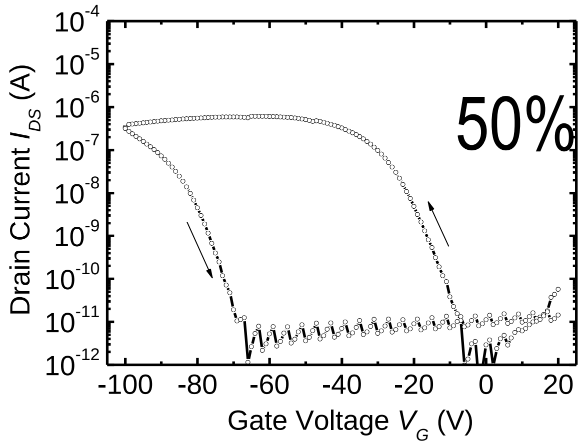


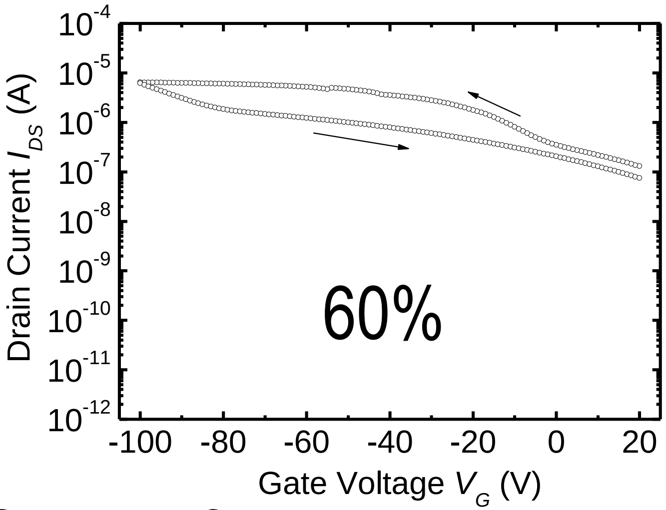


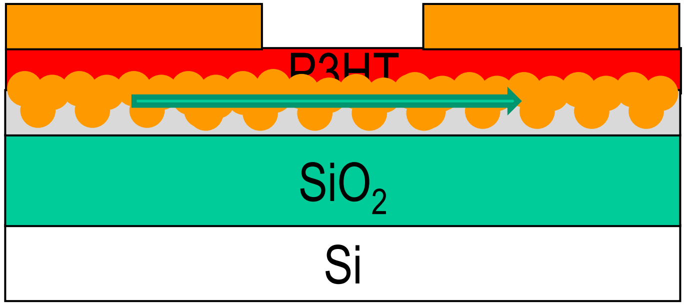
Transfer characteristics of the Device with/without Au NPs





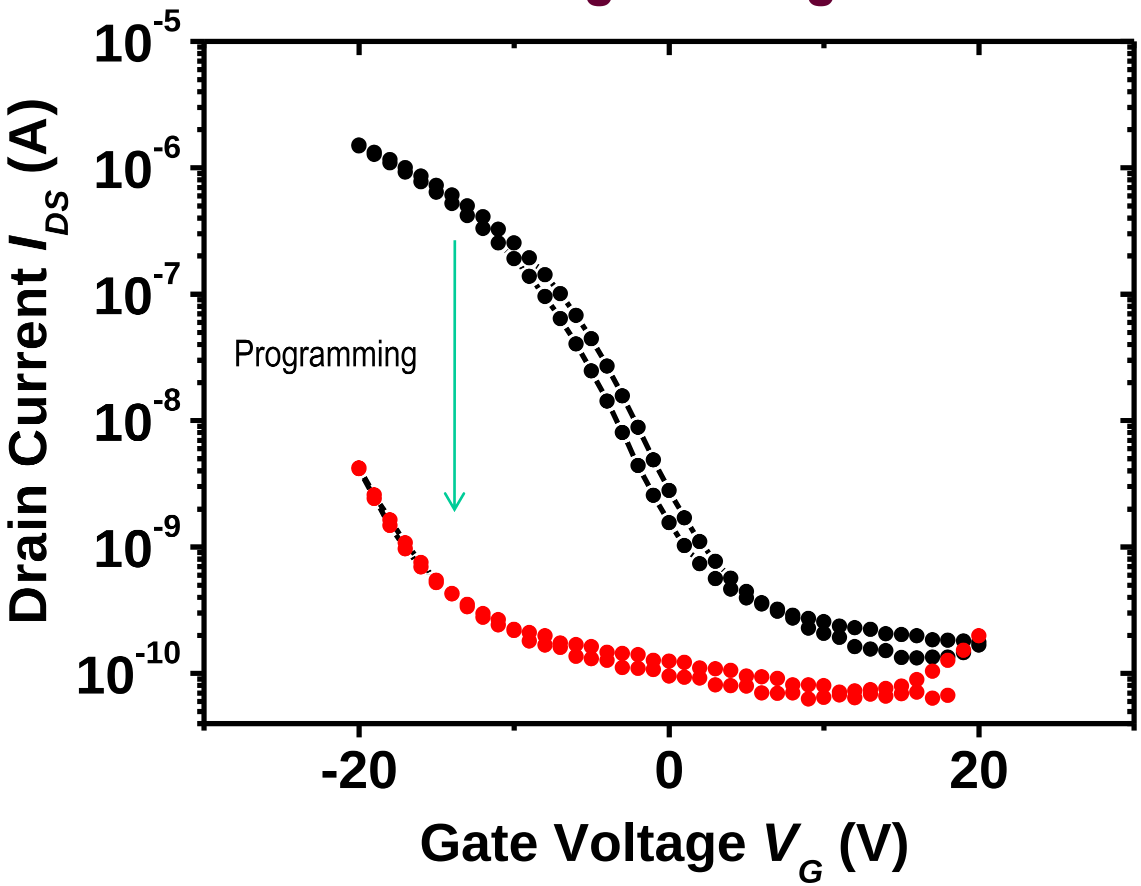


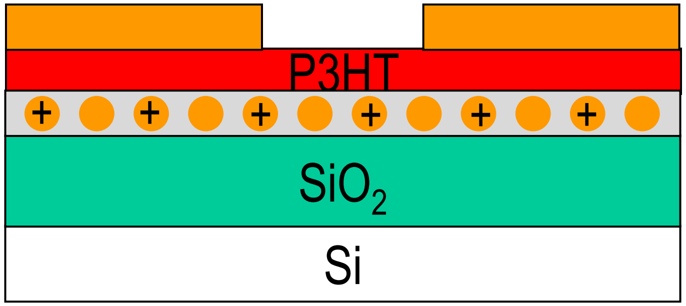




Current flow in the percolated Au layer – conductive films

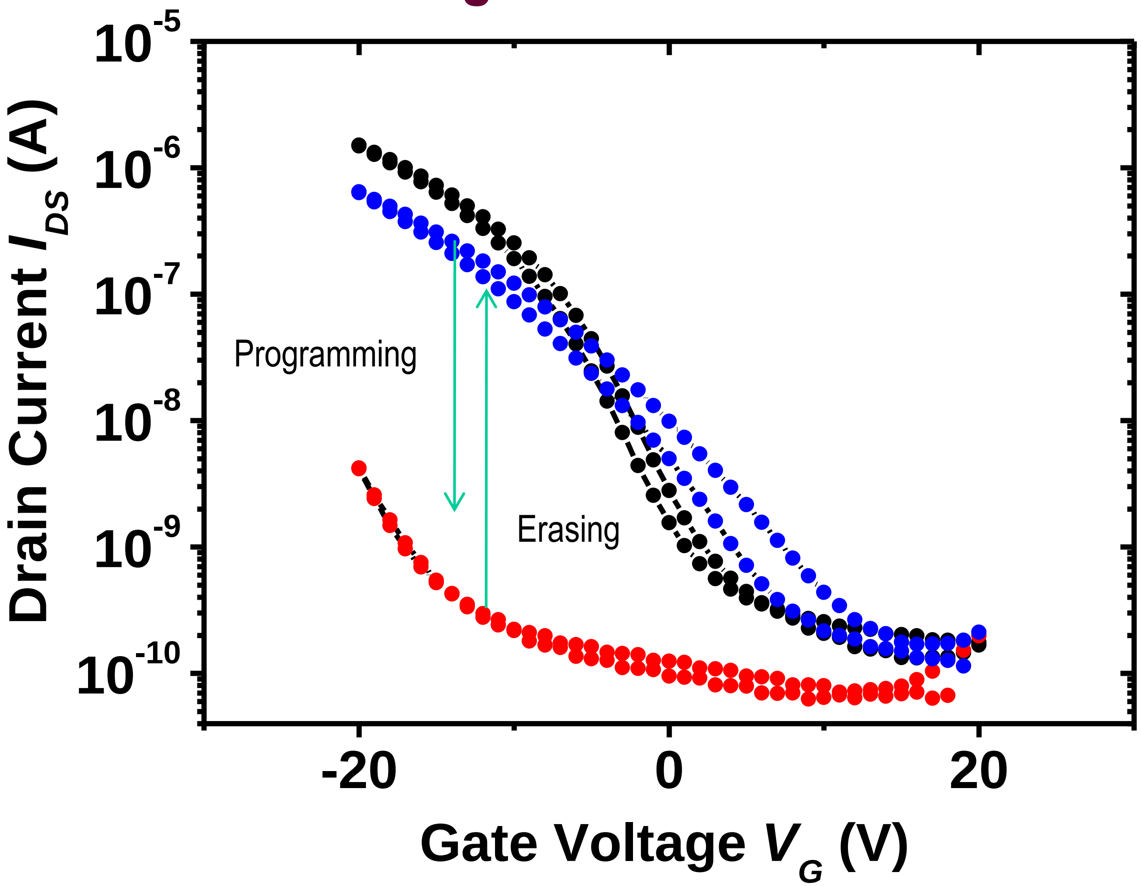
Device Programming

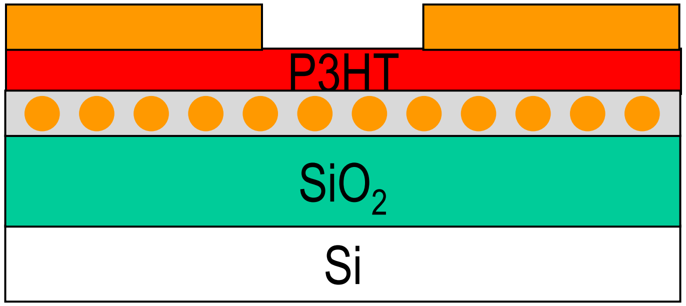




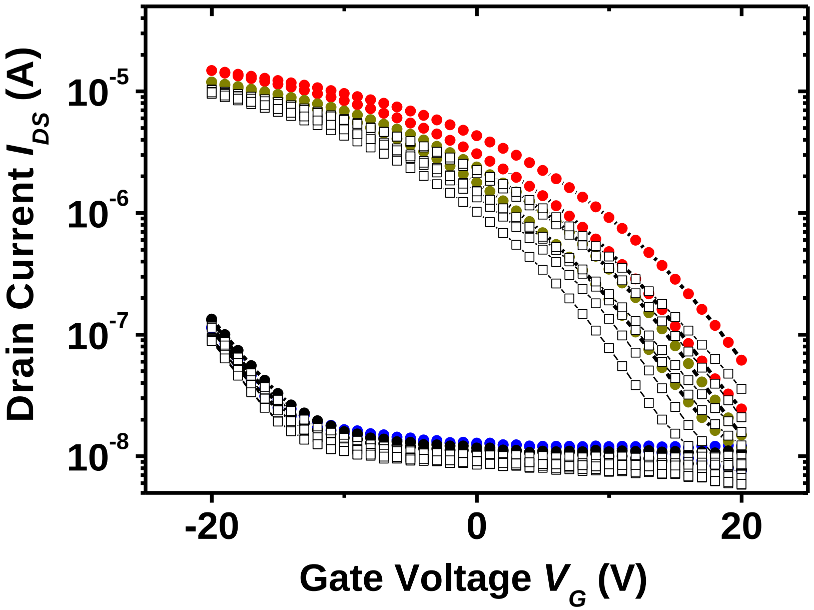
CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

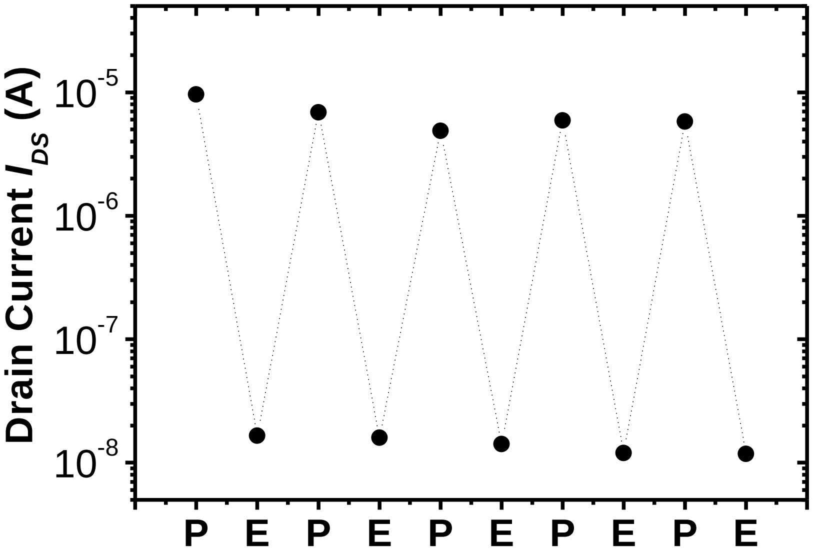
Program / Erase





Program – Erase Cycles



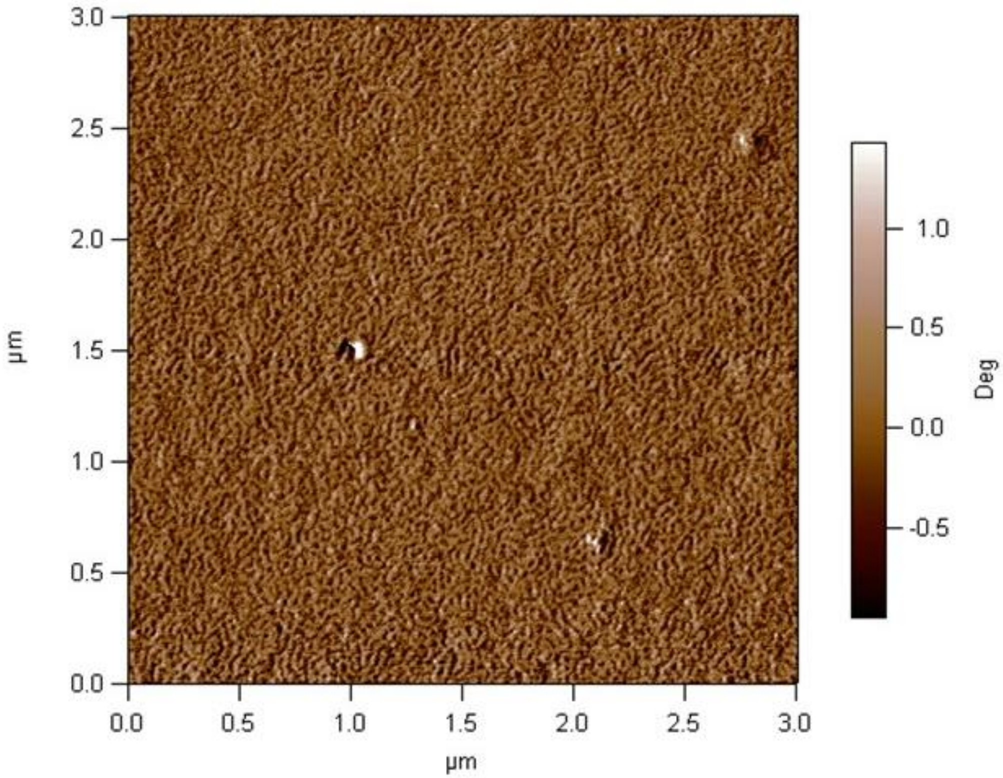


The programming and the erasing are reversible

R2R Processing of Single Domain Block Copolymer Thin Film

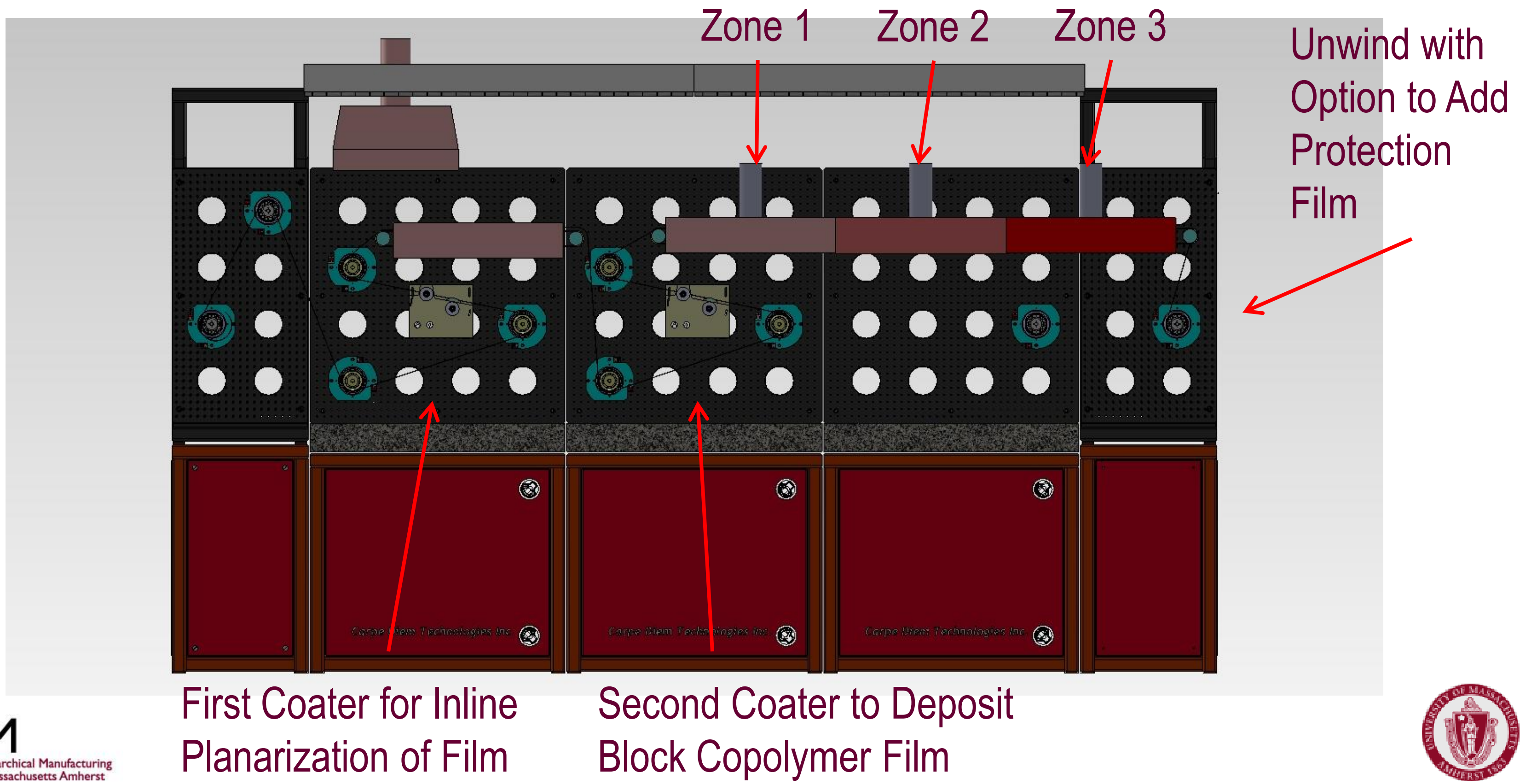
MiniLabo Microgravure Coater

PS-*b*-P2VP (55k-b-25k) on Teonex PEN 125 um
Planerized Film : Phase Image



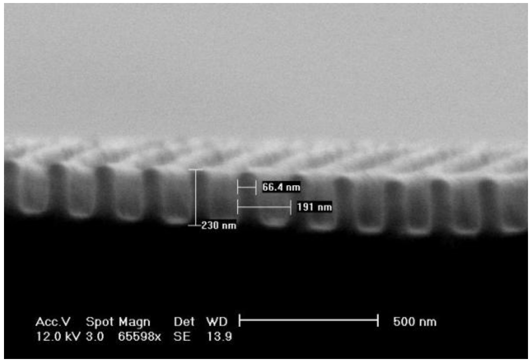
Roll-to-Roll Coating of Ordered Hybrids

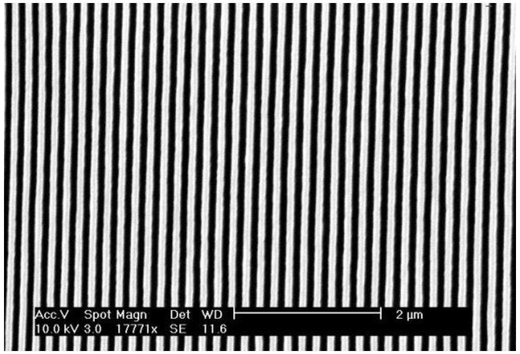
- Two interchangeable gravure or Mayer rod coaters placed in series
- First coater used to apply a planarization layer
- Second coater used to apply thin block copolymer or hybrid layer on planarized film.
- Three independently controlled ovens (with room for expansion to six) used to apply temperature and environmental gradient along web.



Device-Level Patterning by R2R

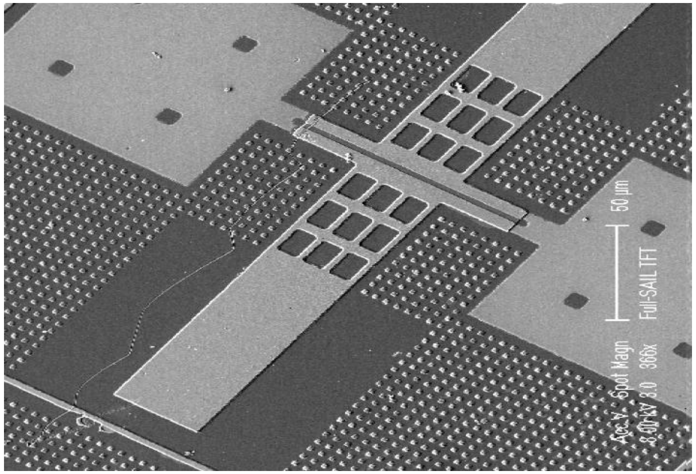
L. Jay Guo, Michigan
UV R2RNIL



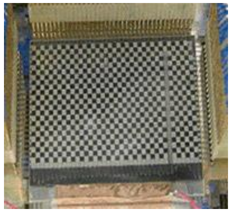


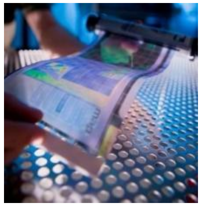
Guo, Adv Mat. 2008

HP SAIL TFT Backplane



Taussig, HP Labs

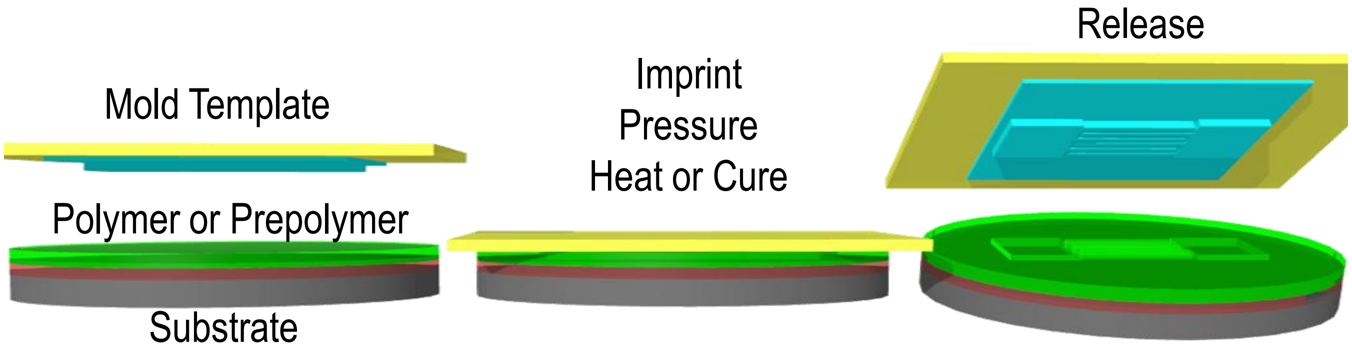




Imprint Lithography

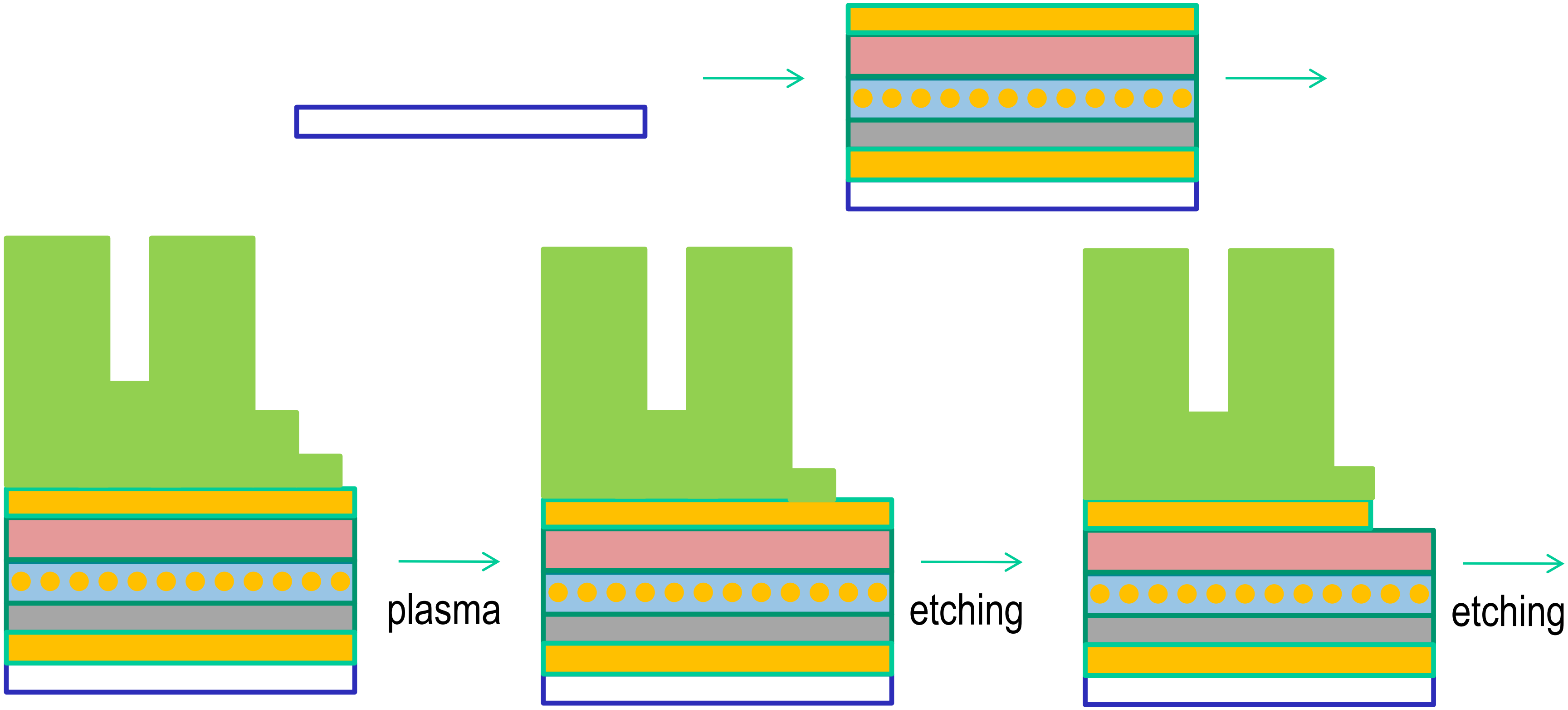
Imprint lithography is generally practiced in one of two modes

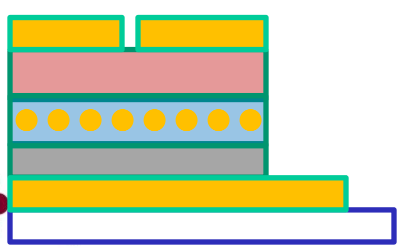
- Thermal Imprint Lithography
  - Emboss pattern into thermoplastic or thermoset with heating
- UV-Assisted Imprint Lithography
  - Curing polymer while in contact with hard, transparent mold
  - <u>Low thermal budget, less mold adhesion problems, high speed</u>



"New approaches to nanofabrication: Molding, printing, and other techniques"
Chemical Reviews, **2005**, *105(4)*, 1171-1196.

Patterning of Flexible Floating Gate Memory – No Alignment Required

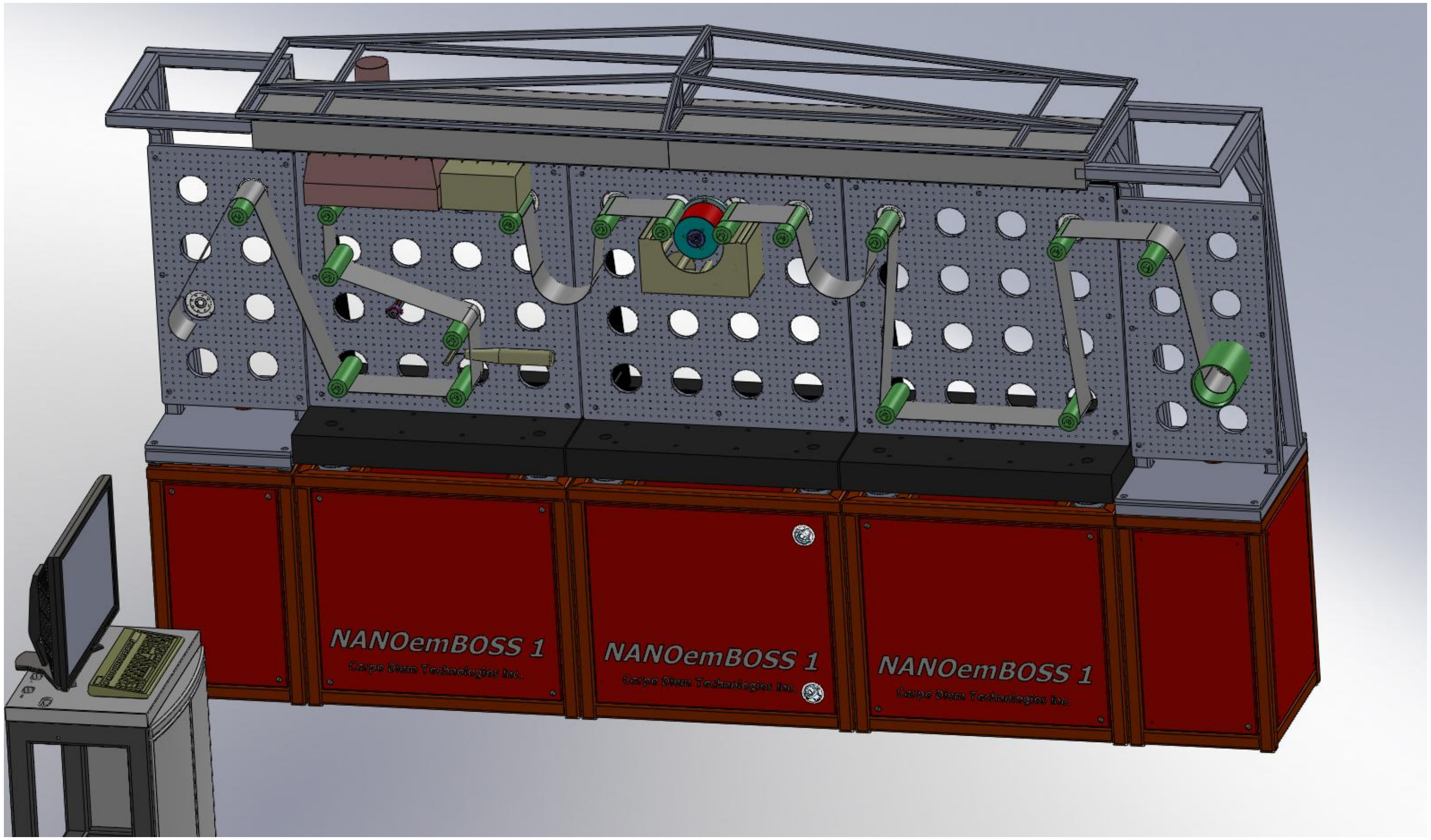




Patterning limits will determine device density

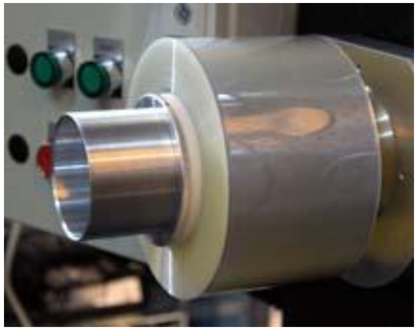
UMass / CHM R2R NIL Tool

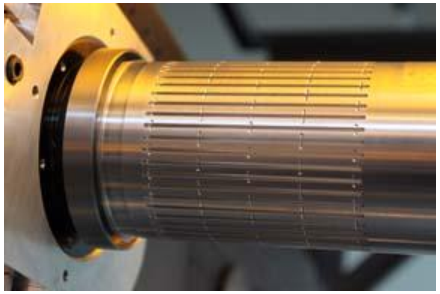
- **K.R. Carter and J. Rothstein are CHM Test Bed Coordinators**
- UMass NANOemBOSS R2RNIL Tool has been designed and constructed with Carpe Diem Technologies (Franklin, MA)
- Tool is uniquely designed for coating and imprinting with nanoscopic precision



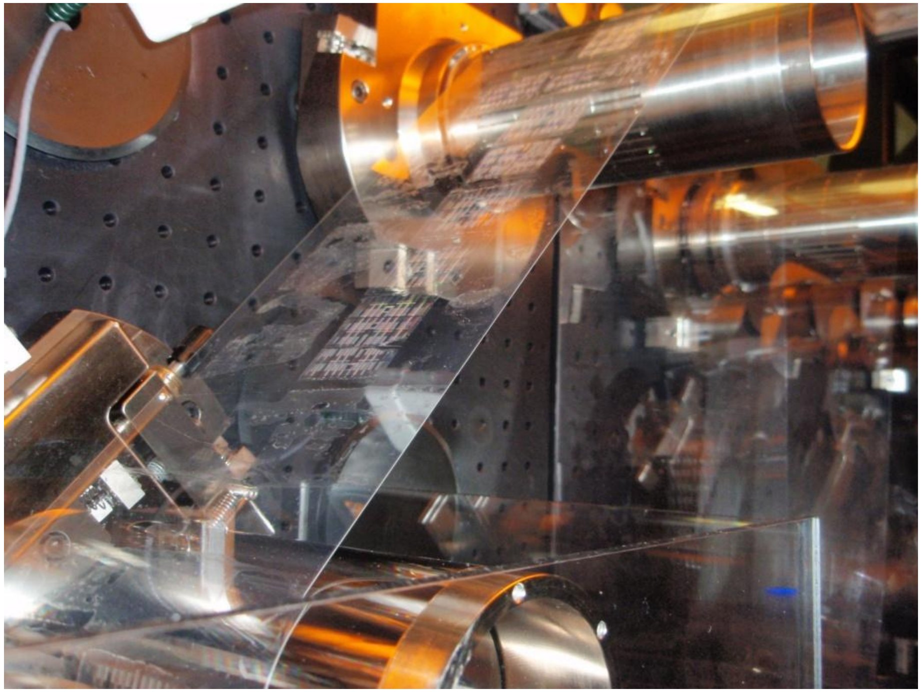
Roll-to-Roll Process Facility

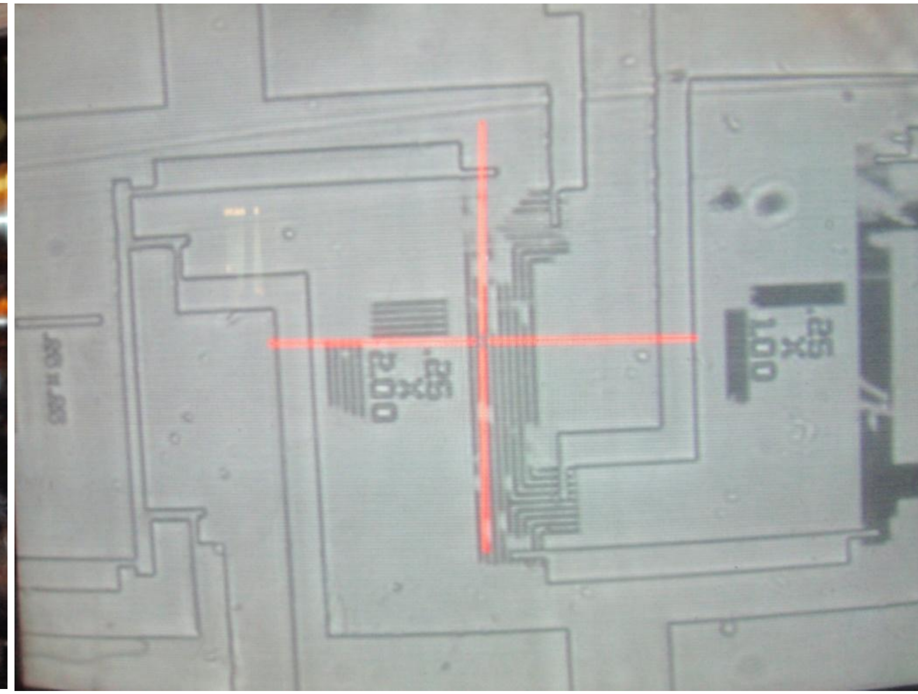
- UMass NanoEmboss R2RNIL tool is installed at UMass.





First Run – May 25, 2011



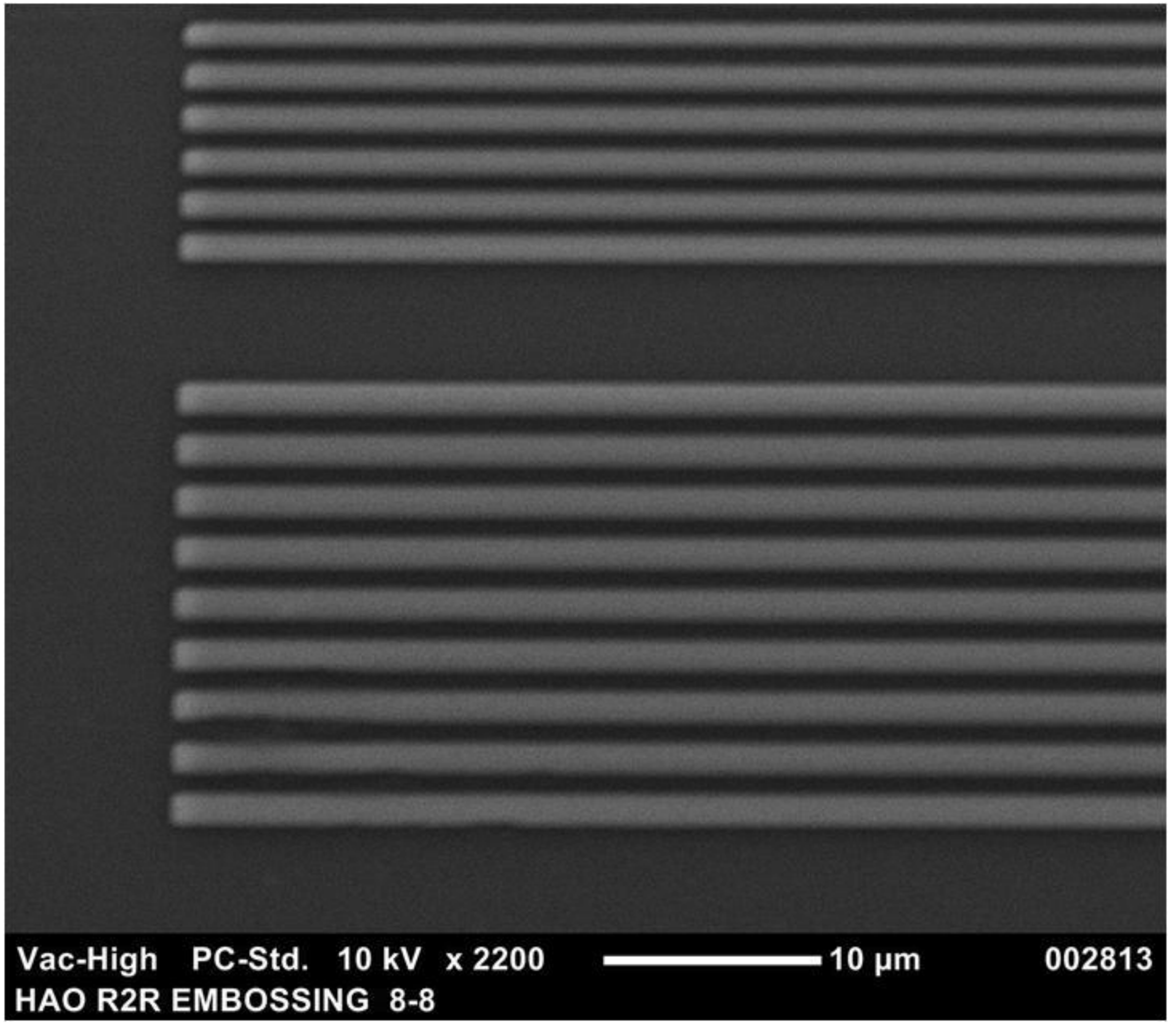


- We successfully imprinted 2 micron features from a PDMS mold to a web moving at 12inch/min.

CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

Hao Zhang, Jacob John

R2R NIL Results



Hao Zhang, Jacob John

Challenges for R2R Manufacturing of Nanostructured Materials and Devices

- **Materials and Process Costs**
- **Planarization and Base / Barrier Layers**
  - includes transparent conducting films, coat-able dielectrics
- **Creation of Ordered Nanoscale Hybrid Materials as Active Layers**
  - directed and/or additive driven self-assembly
- **Continuous Device Level Patterning**
  - roll-to-roll nanoimprint lithography
- **Availability of Collaborative Demonstration Facilities / POC Projects**
  - UMass CHM R2R Tool Platforms
  - PVs, Flexible Memory as Example Devices

some more difficult than others, but no obvious show stoppers