Materials and Process Engineering for Printed and Flexible Opto-electronic Devices

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Northwestern University and Polyera Corporation (USA)

Outline

- **Part 1. Polyera Corporation and Introduction to Printed Opto-Electronics**
- **Part 2. Organic Transistors**
  - Structure and Operation
  - Materials and Process Requirements
  - Applications Printed TFTs and Circuits
- **Part 3. Organic Solar Cells**
  - Bulk-Heterojunction Structure
  - Printing Modules
- **Conclusions**
- **Acknowledgements**

Part 1.
Polyera Corporation

Company Overview

Our History

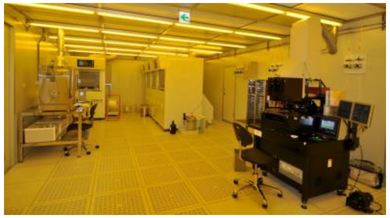
- Founded in August 2005 from NU technologies
- Efforts in OTFT (2005), OPV (2008), Oxide Semiconductors/OLETs (2011)

Our Facilities

- Skokie, USA
- Hsinchu, Taiwan

Chemistry and Materials Dev.

Formulation and Prototyping



Our Team

- Currently 61 employees
- 48 employees in R&D / technical support (25 PhDs)

Our Funding

- $4MM Series A, Dec 2007
- $5MM Series B, Aug 2010
- $24.5MM Series C, March 2012

Our Mission

Be a supplier of functional materials to the solution-processed semiconductor industry

Polyera Corporation. Materials Portfolio

Polyera

Core R&D Business

Organic Transistors

Printed Electronics

Organic Photovoltaics

Printed Solar Cells

Oxide Circuits

Oxide TFTs

CNT Transistors

Organic Light-Emitting Transistors

Printed Opto-Electronics

Fabricate (part of) opto-electronic devices using printing instead of vapor phase deposition/photolitography processes

Conventional Technology

- Very High Performance
- High Temperature Process
- Small Area
- Rigid/Breakable Devices
- High Capital Investment
- Long Production Run

Printed Technology

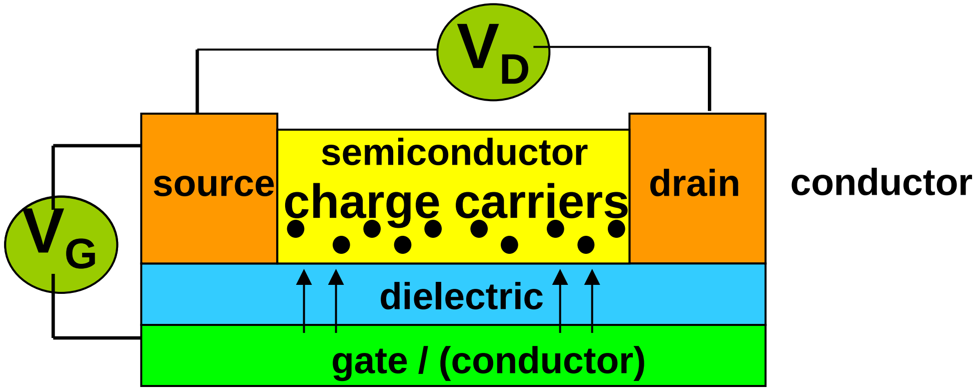
- Less Performance Are Needed
- Low Temperature Process
- Large Area
- Flexible Devices
- Short Production Run
- Designed for revolutionary products

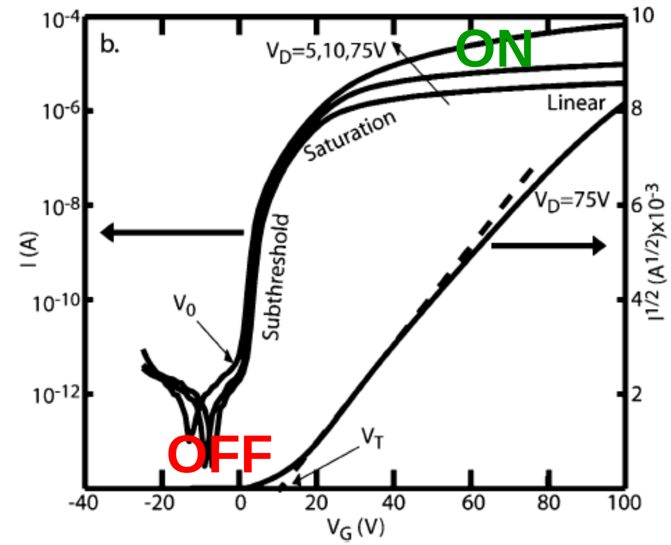
Science/Materials/Engineering Challenges

- Enhance Materials Performance
- Materials Formulated for Roll-to-Roll Processes, Environmentally Acceptable Solvents
- Maintain Performance on Inexpensive Substrates, Flexible Plastics
- Fabricate Commercially-relevant Device Architectures
- Understand Phenomena Based on Charge/Light-Soft Matter Interactions

Part 2.
Organic Transistors

Thin-Film Transistors Structure/Operation





OFF
$V_G = 0$

NO CHARGE CARRIERS BETWEEN s AND d => $I_D = 0$

ON
$V_G \neq 0$

CREATES CHARGE CHANNEL IN THE SEMICONDUCTOR LAYER => $I_D \neq 0$

Carriers: hole = p-channel (type); electrons = n-channel (type)

The key performance parameter is the Carrier mobility (μ)

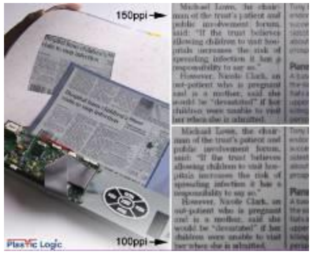
Printed TFTs need Printable p-/n-Semiconductors/Conductors/Dielectrics

Opportunities for Organic/Printed Transistors

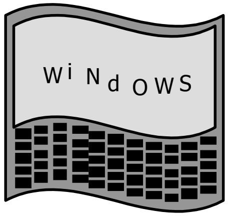
Low-Temperature Fabrication	**Fabrication on plastics, Energy saving**
Additive Process	**No materials waste**
New Products	**Inexpensive device assembly, Flexibility**

Ground-breaking New SAMSUNG Flexible AM OLED Screen.flv

Rigid, heavy and breakable -> Light, unbreakable and flexible



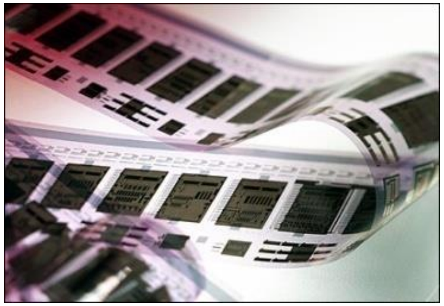
Rollable Newspapers



Paper Computer

Rollable Display

Military



Printed Circuits, RFID

a-Si Carrier Mobility ~ 0.5-1 cm^2/Vs is sufficient!

Transistor Performance Optimization

Great Opportunities for both Science and Technology and to collaborate!

Semiconductor

=> Modify chemical structure
=> Vary film deposition parameters

Facchetti, Husta *Adv. Mater.* **2012**, *24,* 3678
Facchetti, Marks, Ratner, Wasielewski, *Adv. Mater.* **2011**, *23*, 268
Facchetti, Kanatzidis, Marks, T. J. *Nature Mater*. **2011**, *10*, 382
Facchetti, Muccini *Nature Mater.* **2010**, *9*, 496
Facchetti, Morpurgo ... **2009**, *131*, 2462
Facchetti, Y...

1. Chemistry

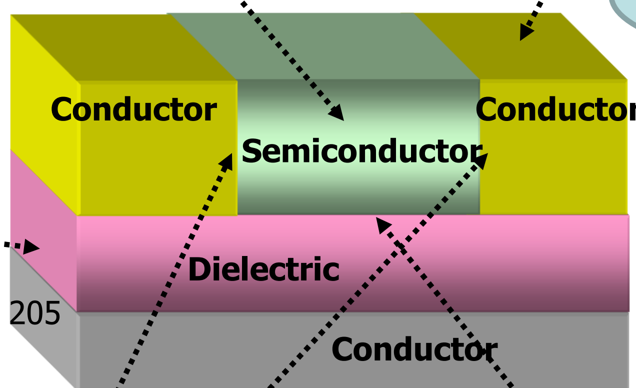
2. Physics

Conductor

=> Workfunction

Facchetti, Sirringhaus *Chem Mater* **2010**, *22*, 1559
Facchetti, Muccini *J. Phys. Chem.*

5. Prototyping



Dielectric

=> Morphology, leakage, k

Facchetti, Ponce, Marks *Chemical Reviews* **2010**, *110*, 205
Facchetti, Marks *Chem. Mater.* **2009**, *21*, 1173
Facchetti, Marks *J. Am. Chem. Soc.*, **2008**, 130, 6867
Facchetti, Marks *PNAS.* **2005**, *102*, 4678.

Device Design

=> Structure
=> Geometry

Noh, Facchetti *Organic Electronics* **2013**
Facchetti, A.; Noh, Y.-Y. *J. Pol.* ... **2011**, *49*, 62
... APL **2009**,
... APL **2008**, *93*, 263303

4. Integration

3. Process Engineering

Contact-Semiconductor Interface

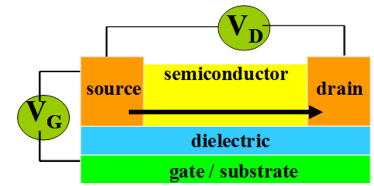
Facchetti, Morpurgo *Appl. Phys. Lett.* **2010**, *97*, 143307
Facchetti, Schol *Adv. Funct. Mater.* **2008**, *18*, 3645
Facchetti, Marks *Nano Letters.* **2006**, *6*, 2447

Dielectric-Semiconductor Interface

Facchetti, Marks *Adv. Funct. Mater.* **2010**, *20*, 50
Facchetti, Marks Salleo *Nature Mater*, **2009**, *8*, 952
Facchetti, Marks *Science* **2007**, *318*, 76.

1. Chemistry: Materials Design, Synthesis, Screening

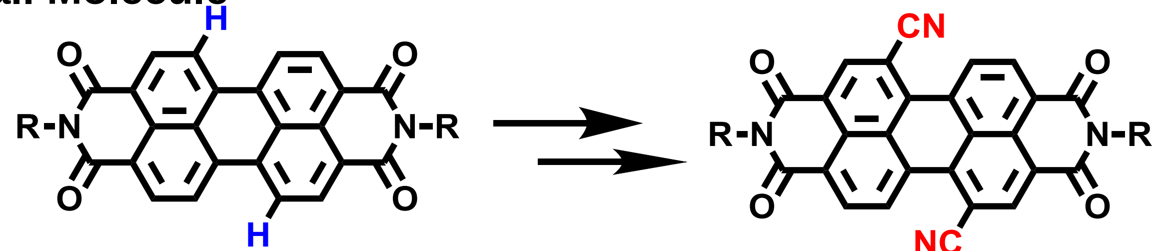
Semiconductor: Small Molecule, Polymers



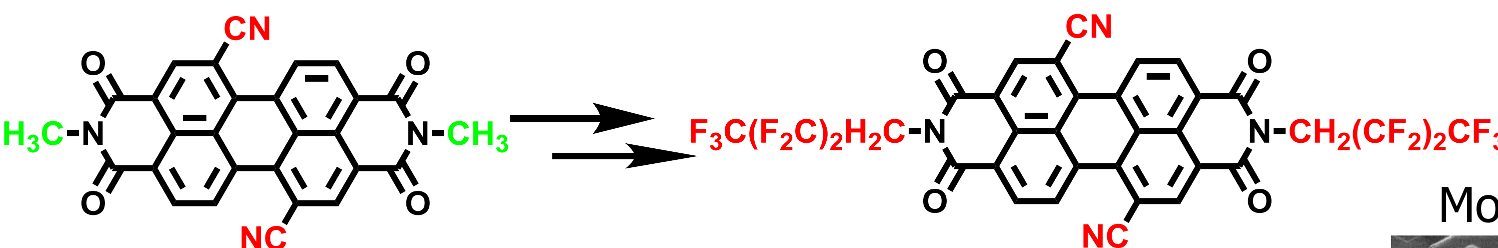
Criteria For Achieving High Performance

- Proper HOMO/LUMO energy level
- Sufficient intermolecular interactions
- Favorable film morphology

Small Molecule



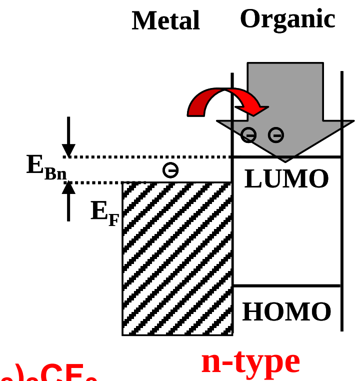
Air unstable **Air stable !**



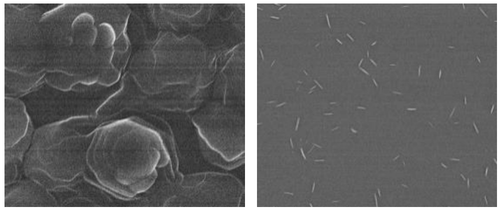
Low-Mobility
$\mu \sim 0.000001\ cm^2\ V^{-1}\ s^{-1}$

High-Mobility!
$\mu \sim 1\ cm^2\ V^{-1}\ s^{-1}$

Energetic aspect

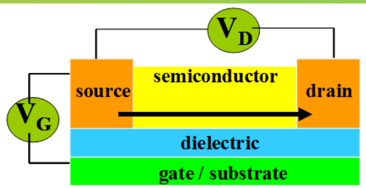


Morphology aspect



Facchetti, Wasielewski, Marks et.al. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900
Facchetti, Marks, Wasielewski et.al. *Chem. Mater.* **2007**, 19, 2703

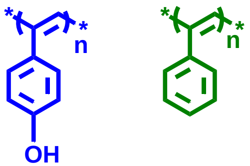
1. Chemistry: Molecular Design, Synthesis, Screening



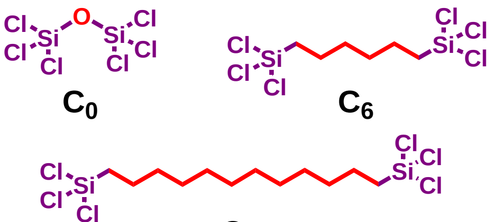
Dielectric: Molecular, Polymeric, Hybrid

Criteria For Achieving High Performance

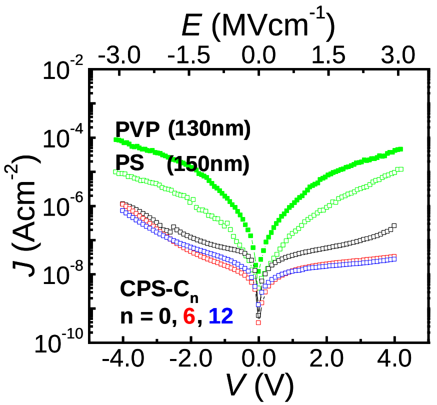
- Excellent insulator
- High capacitance
- Good morphology
- Good adhesion



PVP PS



C_0 C_6 C_{12}

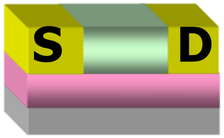


Conductors: Molecular, Polymeric, Hybrid

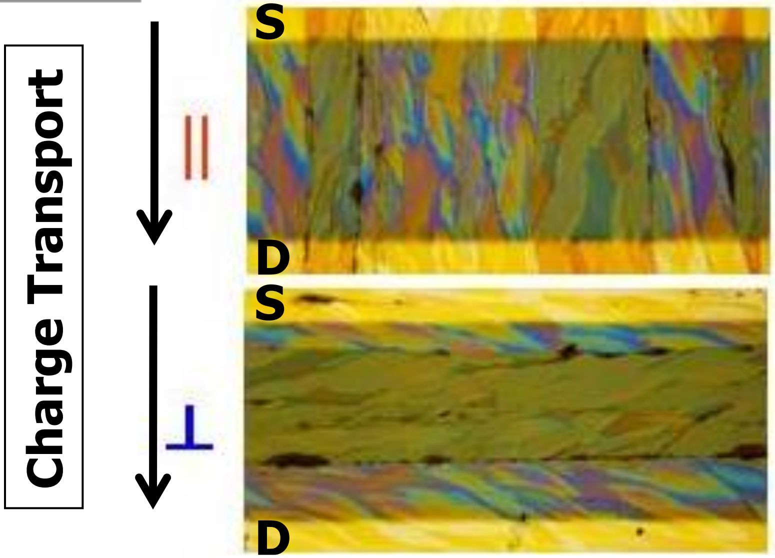
Criteria For Achieving High Performance

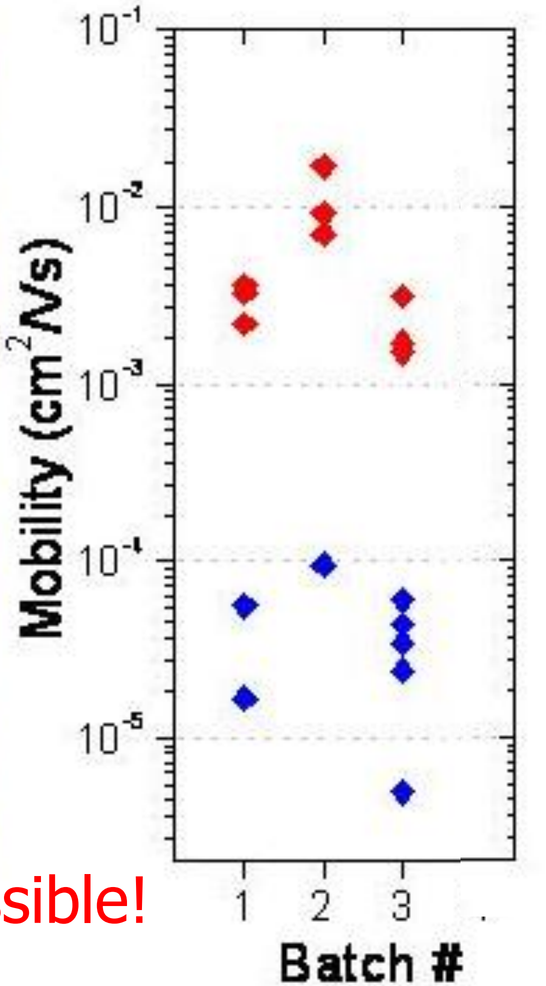
- High conductivity
- Good charge injection (SD)
- Low/reproducible contact resistance (S/D)
- Stable interface

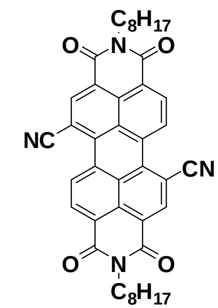
2. Applied Physics: Understand Charge Transport Anisotropy



TFTs with Aligned PDI8-CN2 Films







High Performance

Low Performance

‖ vs. ⊥ much more efficient

Mobility increase by 3-8x is possible!

Facchetti, Marks, Salleo et.al. *Nature Mater* **2009**

2. Applied Physics: Understand Performance Limits

$PDIF\text{-}CN_2$ Single Crystal FETs

- Photolithographically structured neg. resist (SU-8/25)

↓

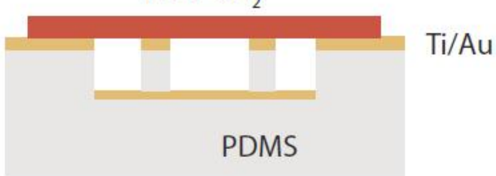
- Filled with Polydimethylsiloxane (PDMS) elastomer

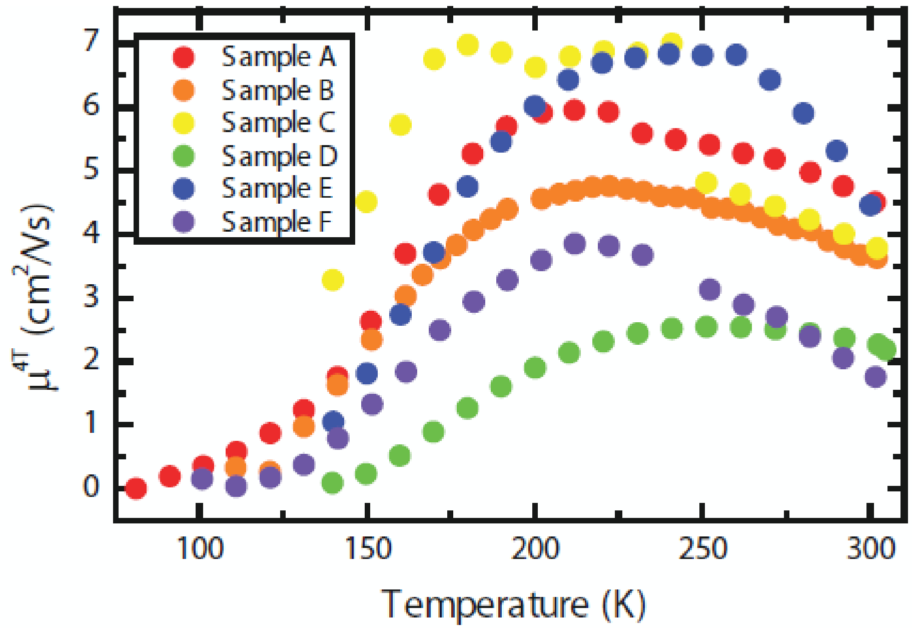
↓

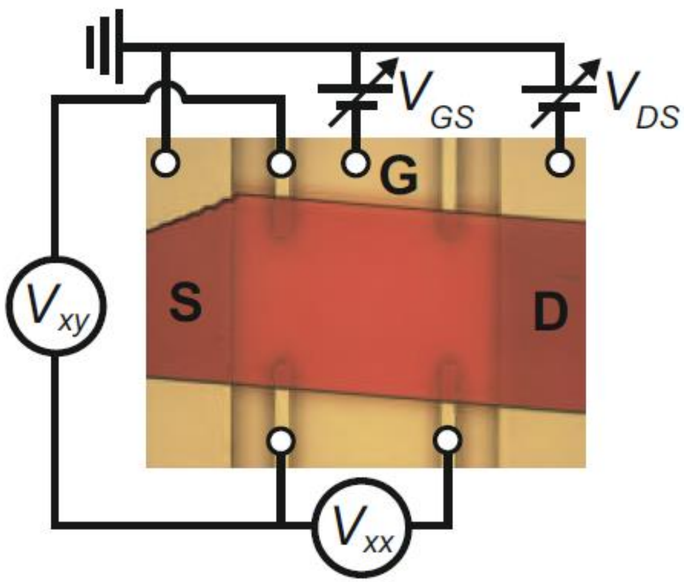
- 3 nm Ti, 20 nm Au evaporated on PDMS

↓

- Single crystal laminated manually to substrate







> Band-like transport

> Mobility ~ 7 cm^2/Vs possible

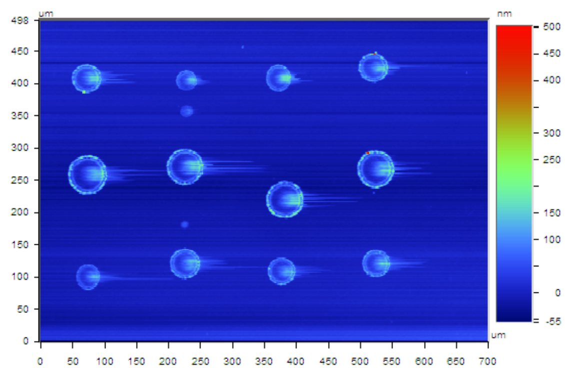
Facchetti, Morpurgo et.al. *Adv. Mater.* **2012**

Takeya, Facchetti *Adv. Mater.* **2011**, *23(32)*, 3681

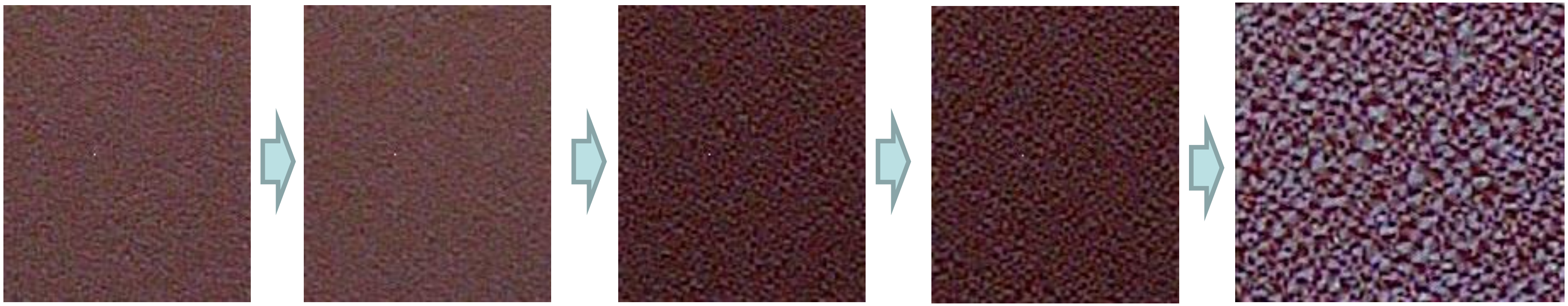
Facchetti, Morpurgo et.al. *JACS* **2009,** *131*, 2462

3. Process Eng.: Ink-jet Printing Molecular Semiconductors

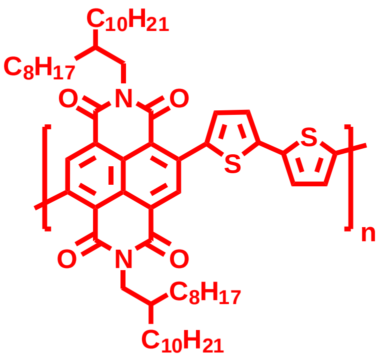
- Formulation
- Viscosity
- Surface Tension
- Surface Energy
- Printing Speed
- Droplet Size
- Temperature

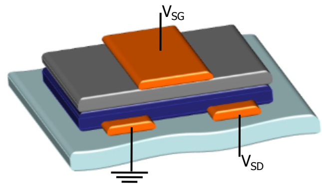


Target OSF morphology

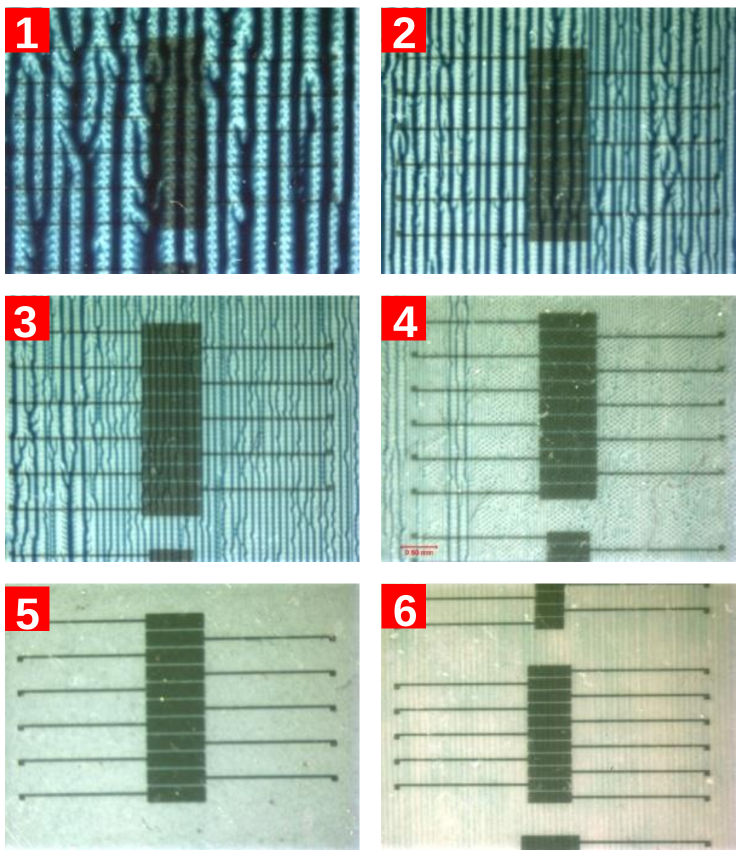


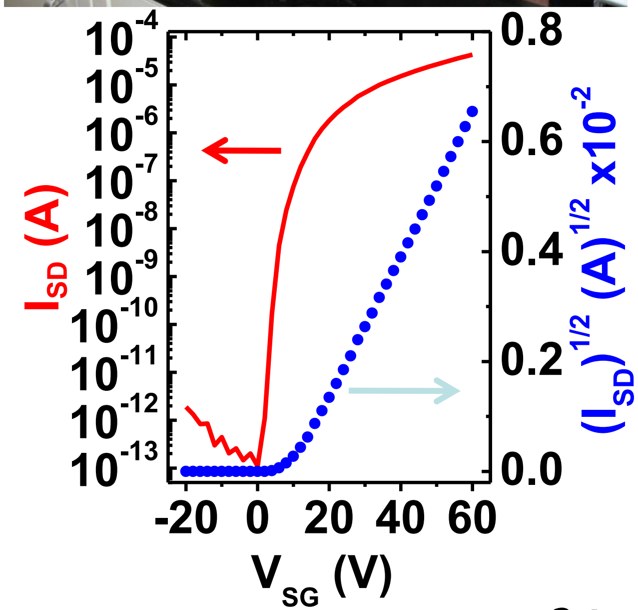
3. Process Eng.: Gravure Printing Polymeric Semiconductors





Optimizing semiconductor formulations



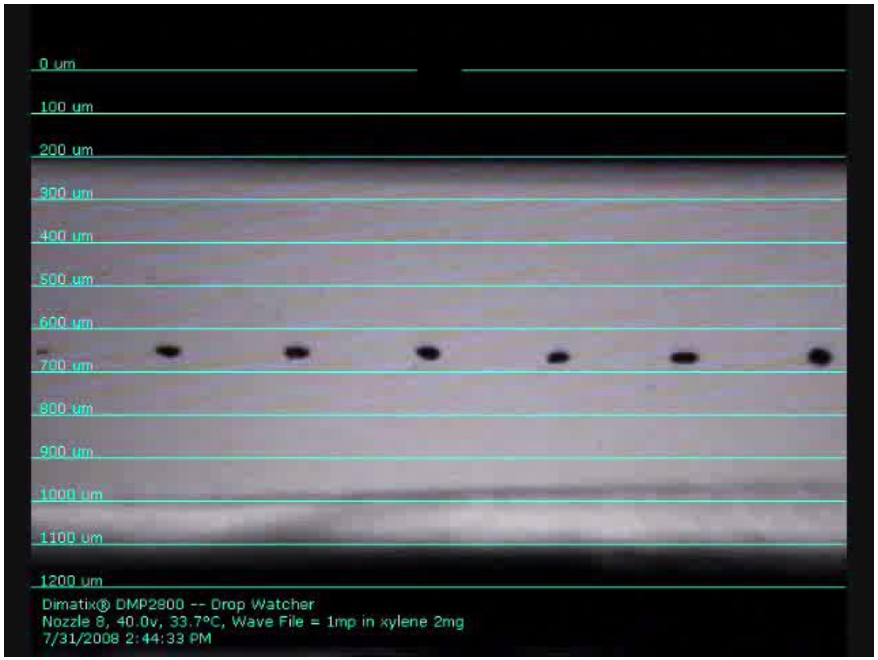


μ = 0.2-0.85 cm^2/Vs

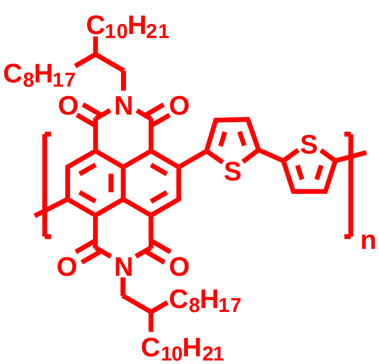
Facchetti et al. *Nature* **2009** *457*, 659

3. Process Eng.: Printing Polymers vs. Small Molecules

Bad formulation



Good formulation

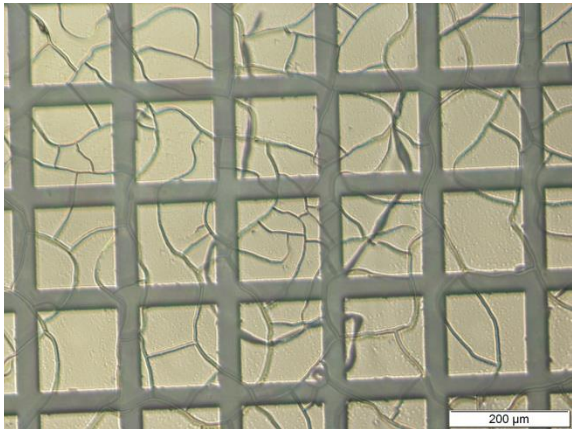


Mw ~ 60K Da

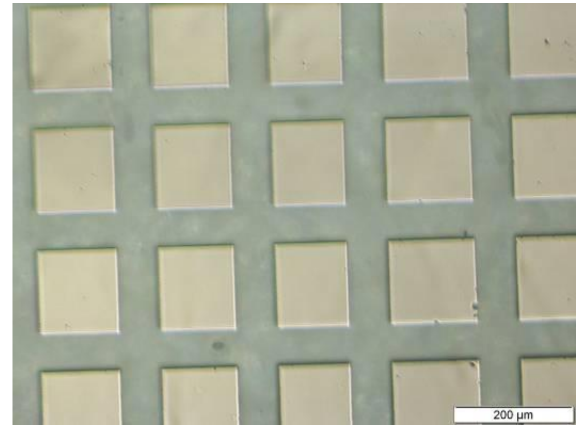
Mw ~ 25K Da

4. Process Eng.: Printing Dielectrics

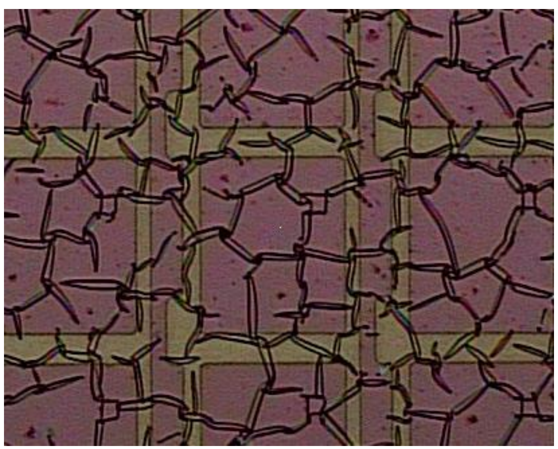
Unoptimized formulation

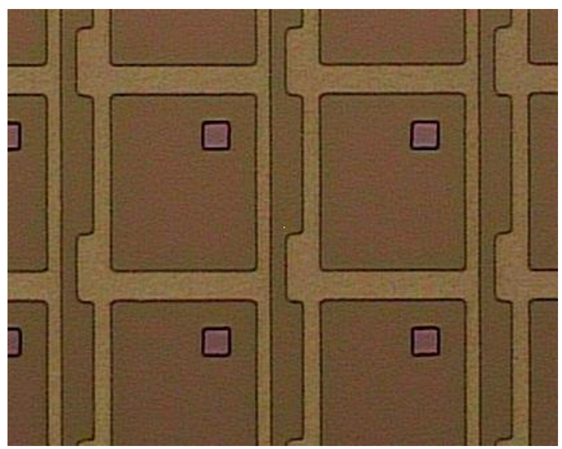


Optimized formulation

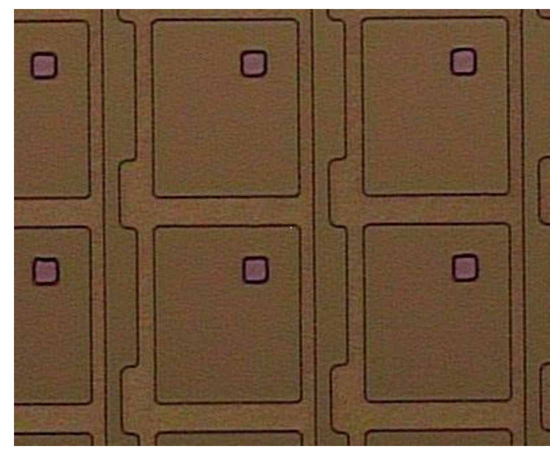


Unoptimized curing

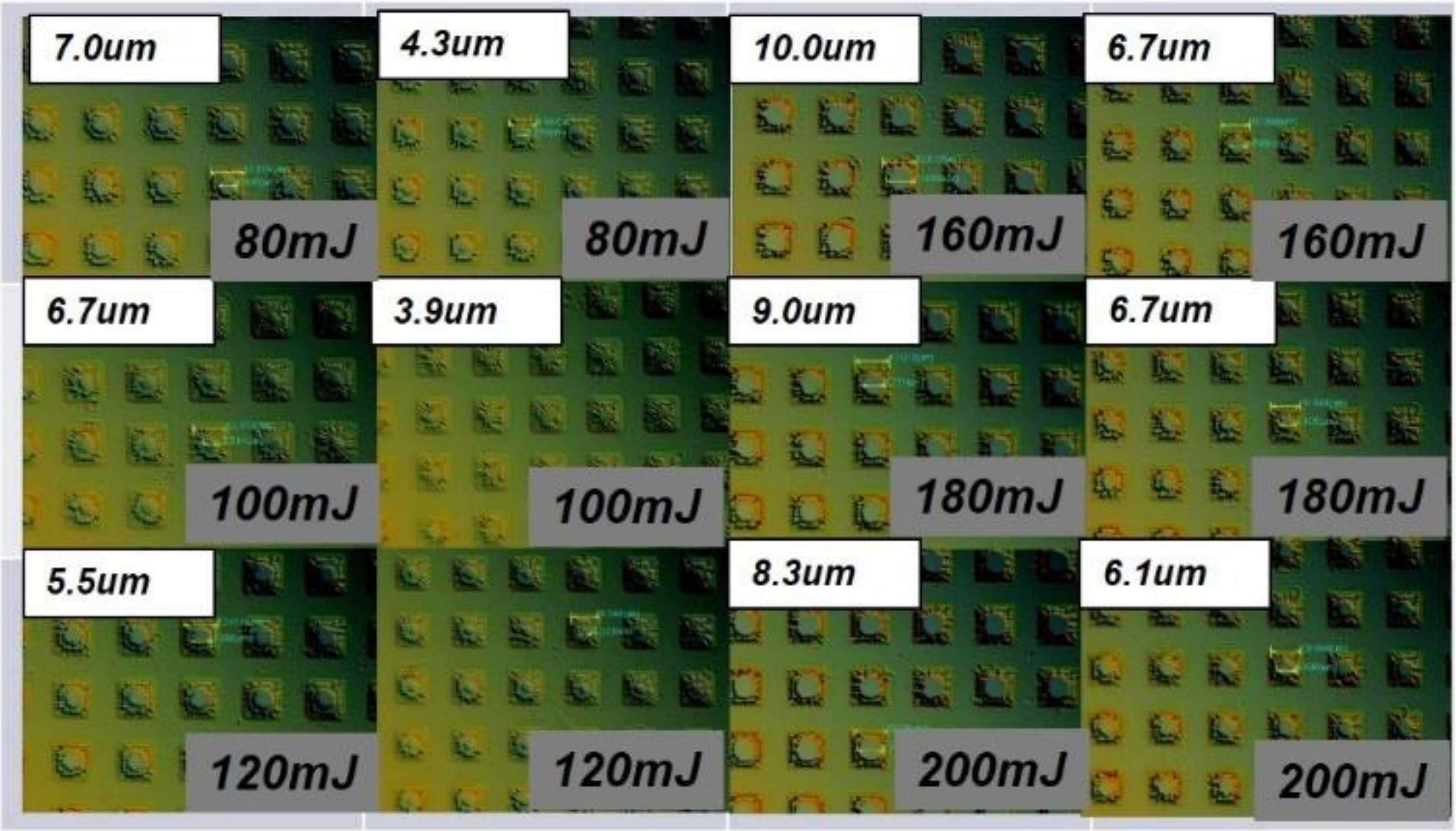




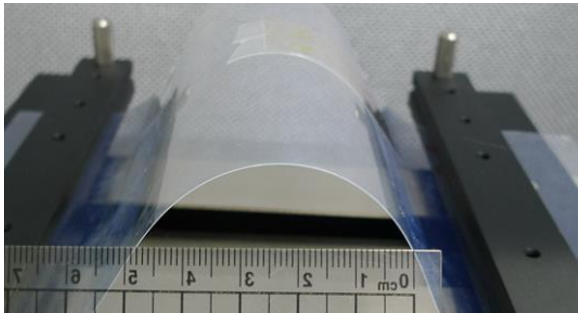
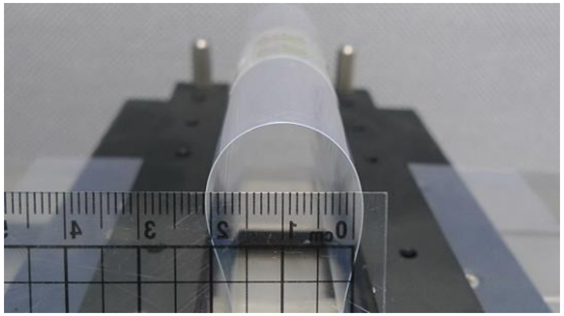
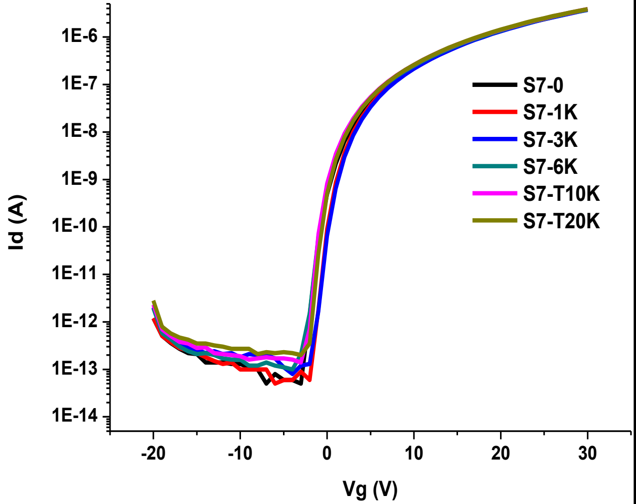
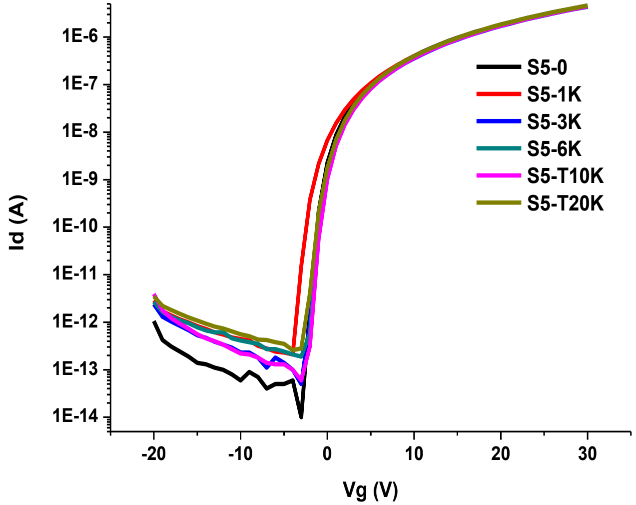
Optimized curing



4. Integration: Multistack deposition, Via Holes



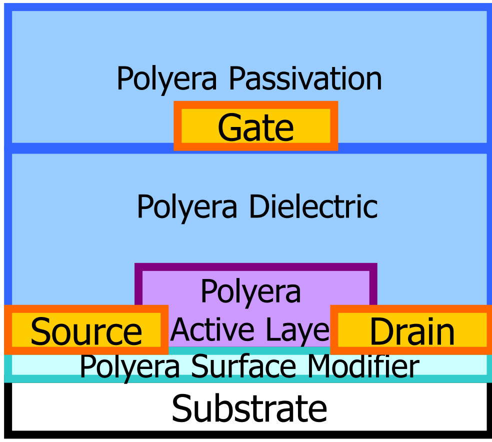
4. Integration: Mechanical stress tests

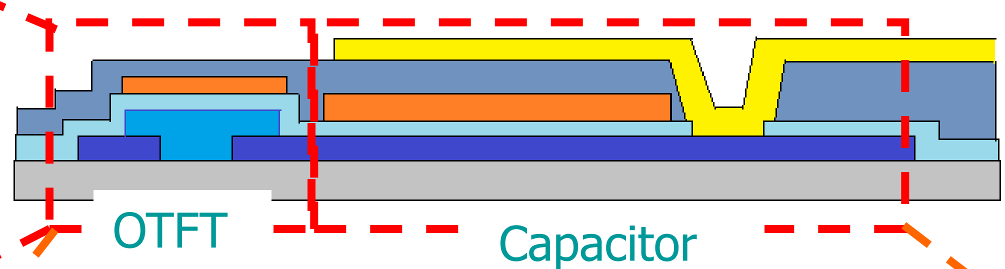
	Diameter: 5 cm	Diameter: 2 cm
Bending curve (diameter)		
Bending frequency	20 times/min	20 times/mins
Times	Initial→20,000 times	Initial→20,000 times
IV result IMG_0965 - Copy (1).mp4		

Testing 5 mm at customer sites

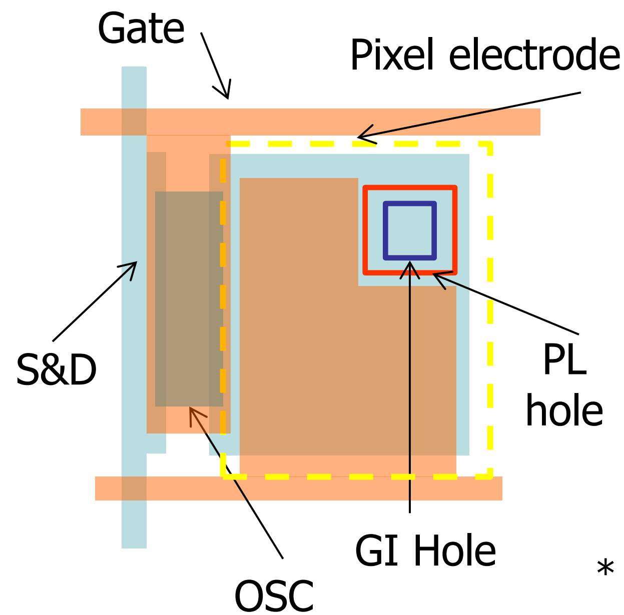
4. Prototyping: Flexible Displays

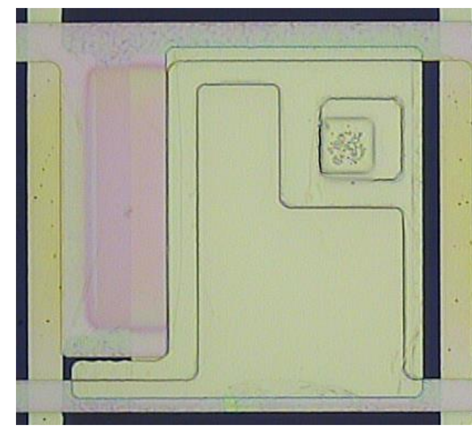
500.000 OTFTs
T < 120 °C



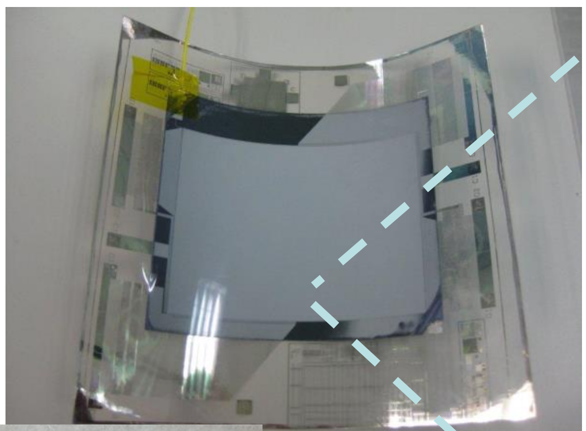


One Pixel





* Microscope image of a pixel



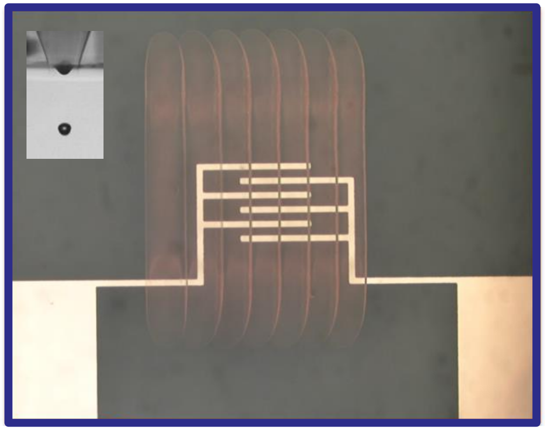
- Polyera 1st gen. backplane for 6” EPD
- (800x600 pixels)

IMG_0965 - Copy (1).mp4

4. Prototyping: Printed Circuits for Sensors

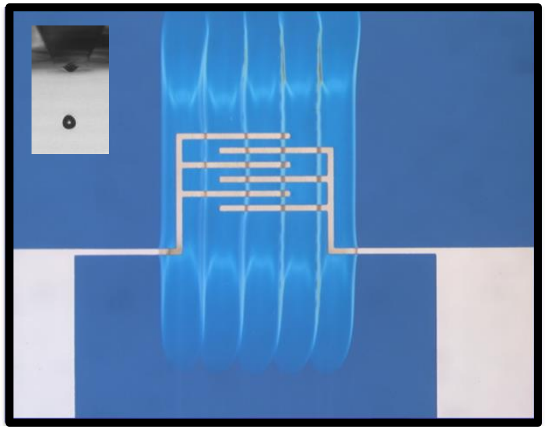
Need p- and n-type semiconductors with comparable performance in printed TFTs

P-channel

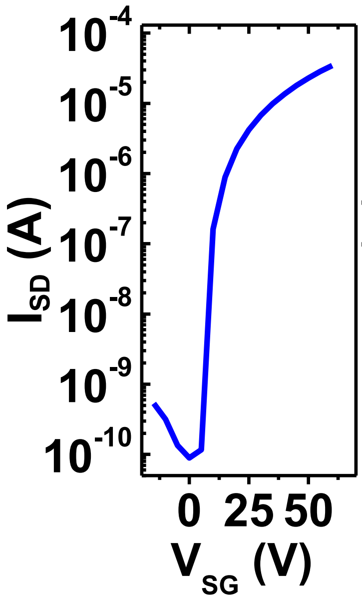


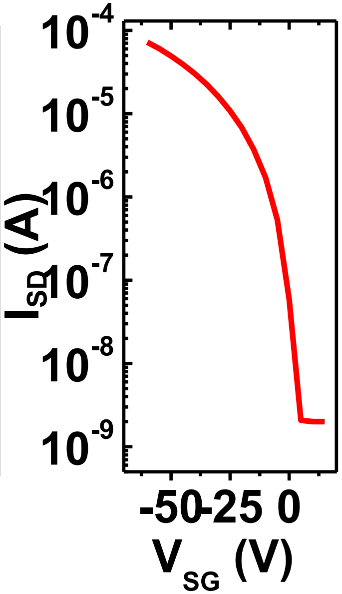
0.75 cm2/Vs

N-channel

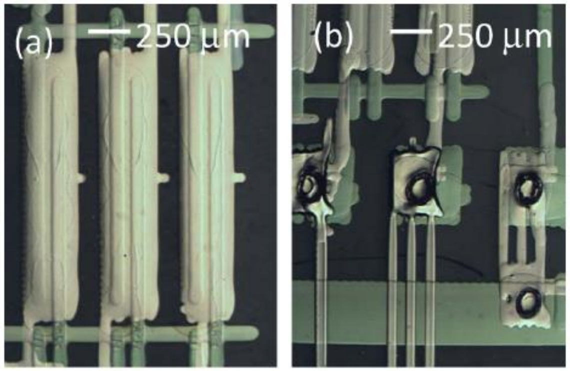


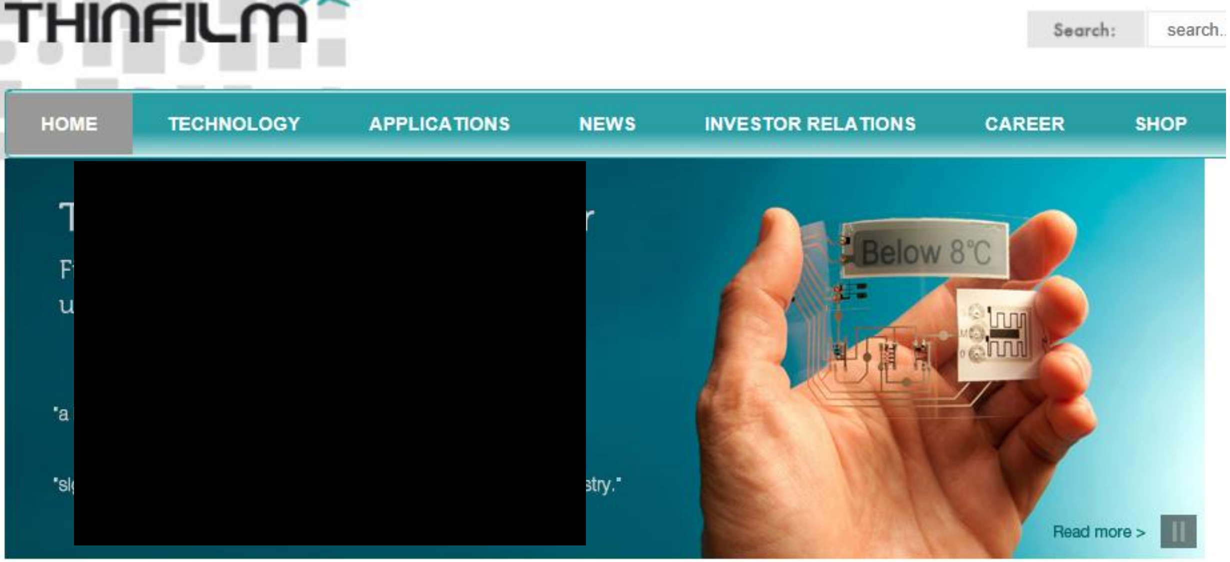
0.85 cm2/Vs





THINFILM

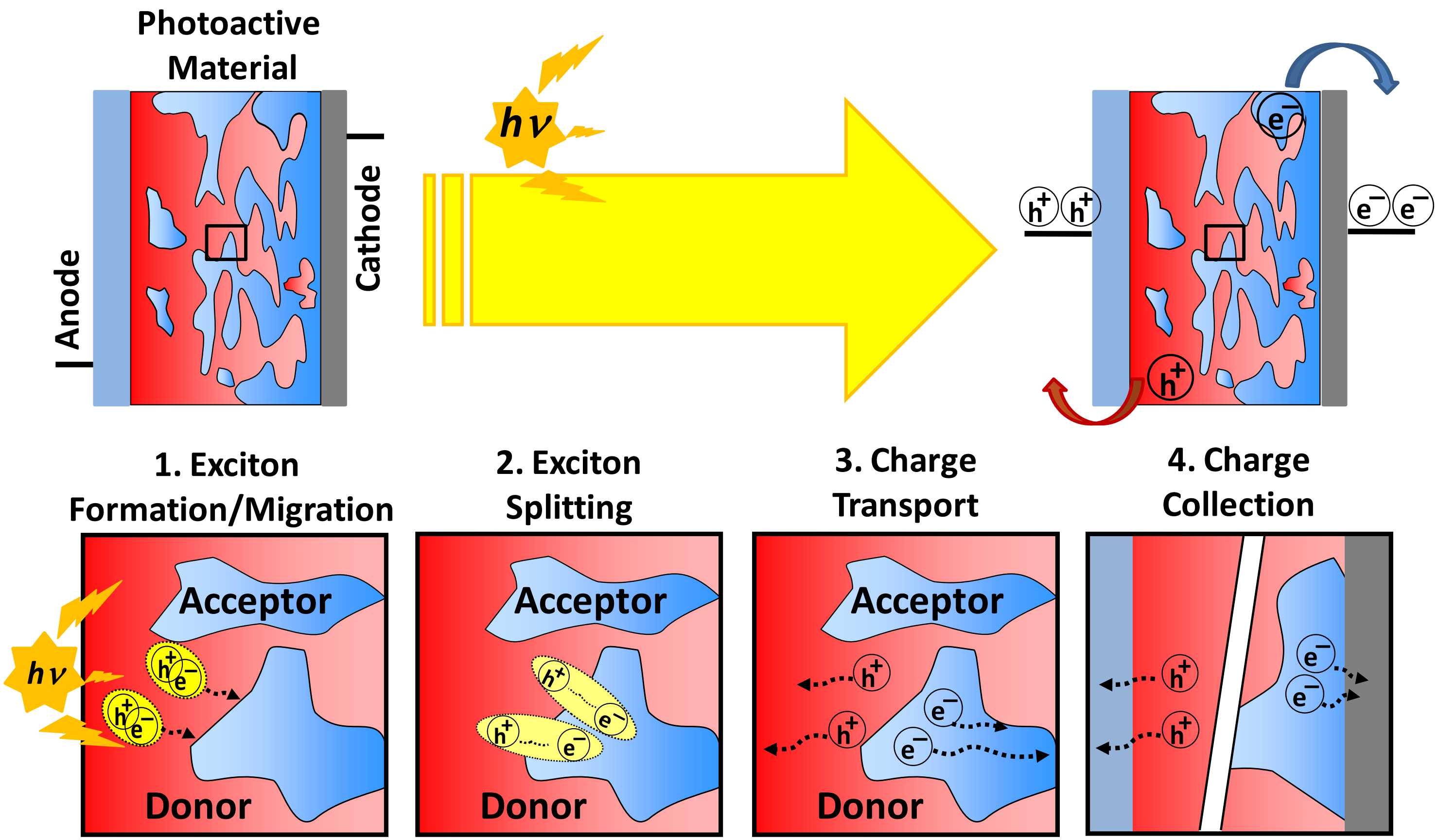




Part 3.
Organic Solar Cells

Organic Photovoltaic Cells

Solar energy into electrical energy (photons to charges)



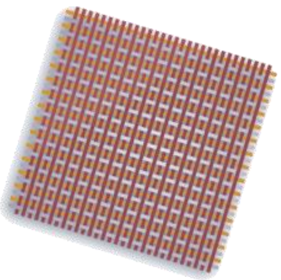
$$power\ \ conversion\ efficiency\ \eta = \frac{electrical\ \ power\ \ generated}{incident\ \ optical\ \ power}$$

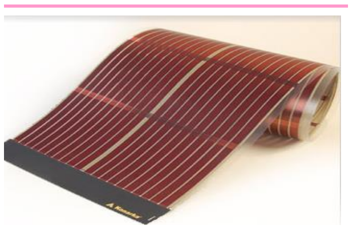
$$= \frac{V_{OC} I_{SC}}{P_{in}} ff$$

Opportunities for Printed Solar Cells

Low power applications
like watches, calculators, etc.
http://www.citizenwatch.com
http://zzd99.en.alibaba.com

Charge iPods and other portable
devices anywhere, day or night
http://www.solio.com





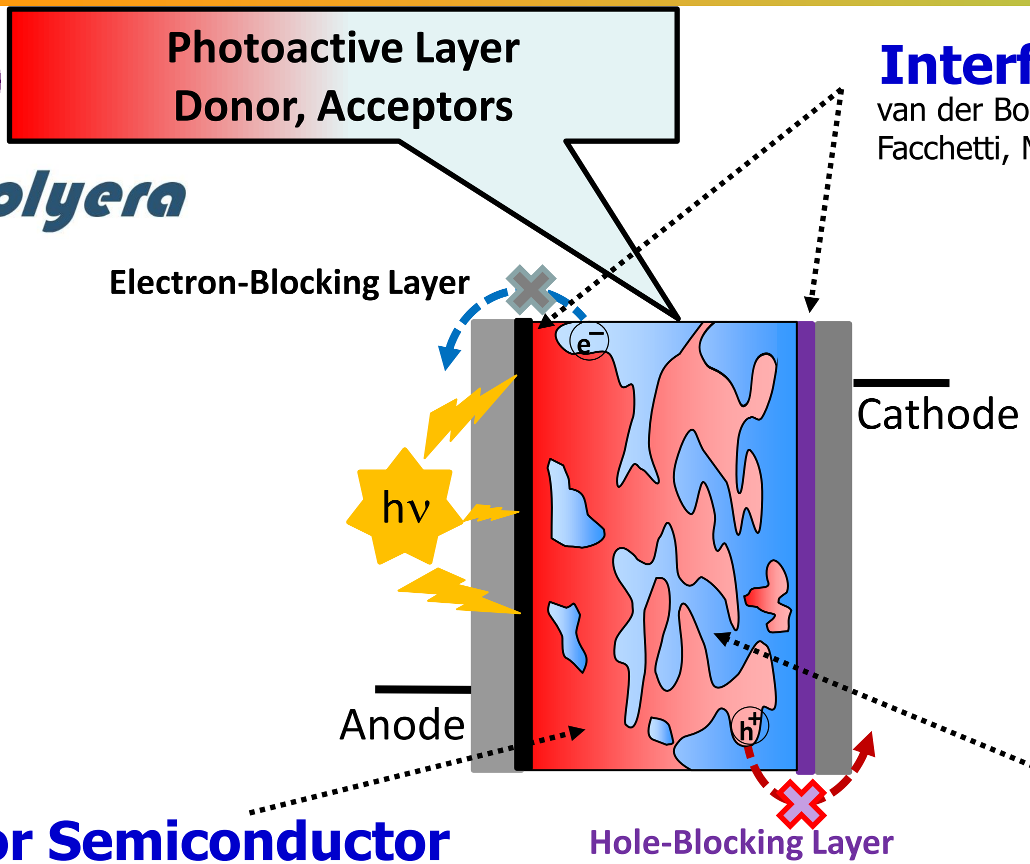
Flexible OPV woven
into a fabric

Flexible solar cells on a military tent
http://www.afrlhorizons.com/Briefs/Jun04/ML0319.html

Building integration

PCEs ~ 5 % is sufficient!

Organic Photovoltaic Cells



Interface

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Donor Semiconductor

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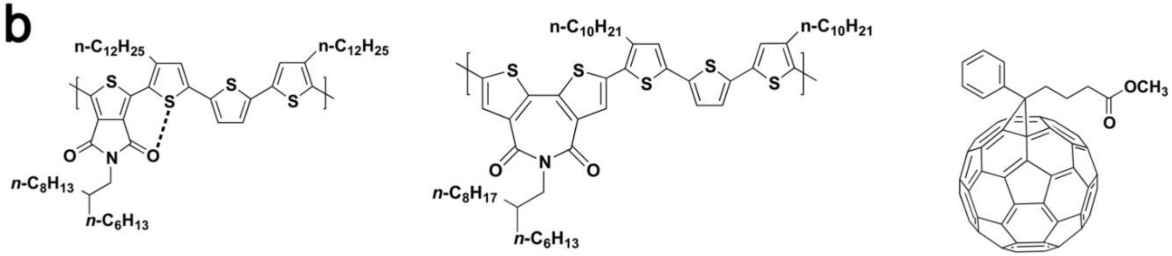
Donor-Acceptor Semiconductor Design

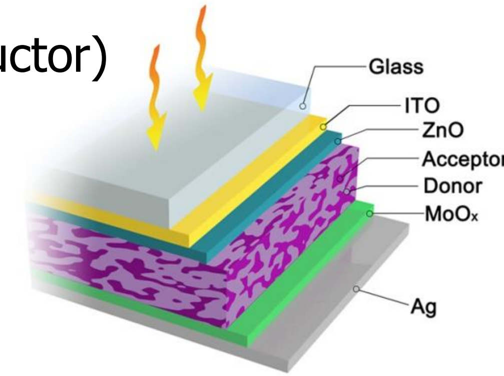
DONOR
(hole semiconductor)

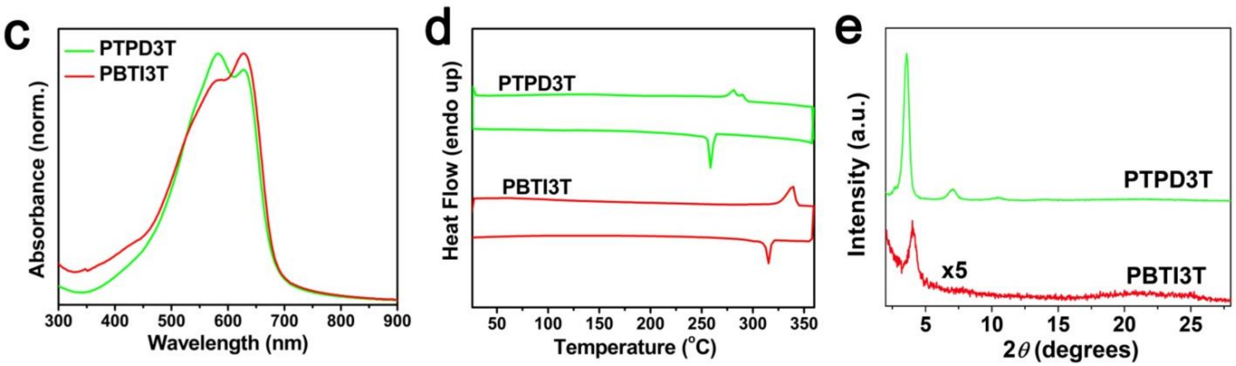
ACCEPTOR
(electron semiconductor)

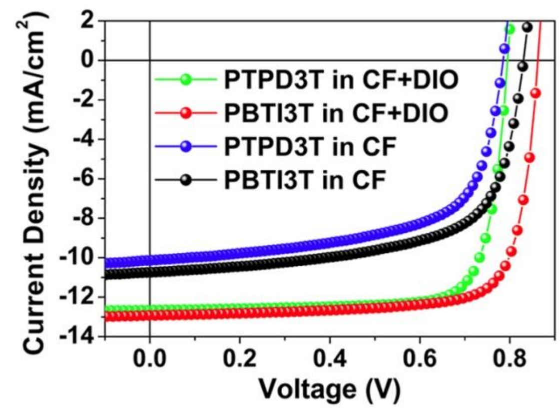
b



PTPD3T PBTI3T $PC_{71}BM$



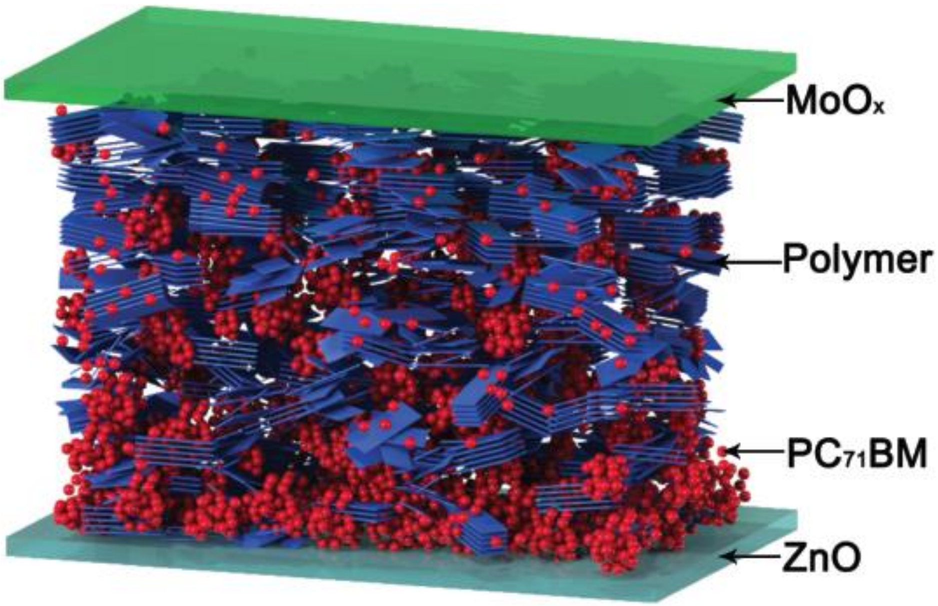




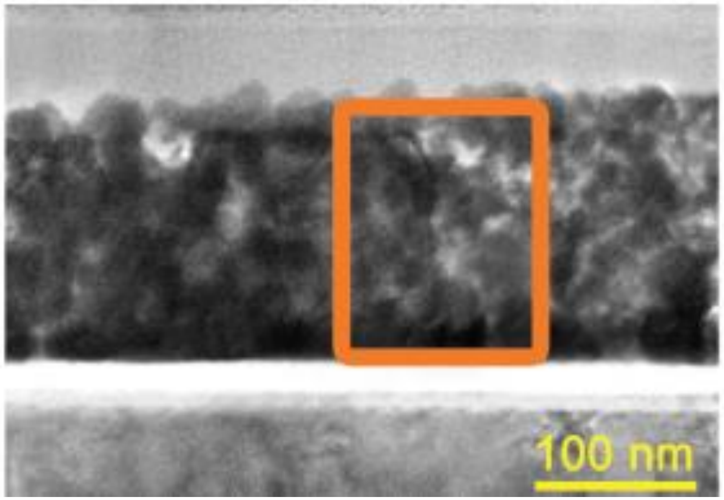
Polymer	μ_h (TFT) (cm^2/Vs)	μ_h (SCLC) (cm^2/Vs)	V_{oc} (V)	J_{cs} (mA/cm^2)	*FF* (%)	PCE (%)*
PTPD3T	5.87×10^{-2}	1.2×10^{-3}	0.795	12.5	79.6	7.90
PBTI3T	2.74×10^{-3}	1.5×10^{-3}	0.859	12.9	77.8	8.66

Facchetti, Marks *Nature Photonics* **2013** in press

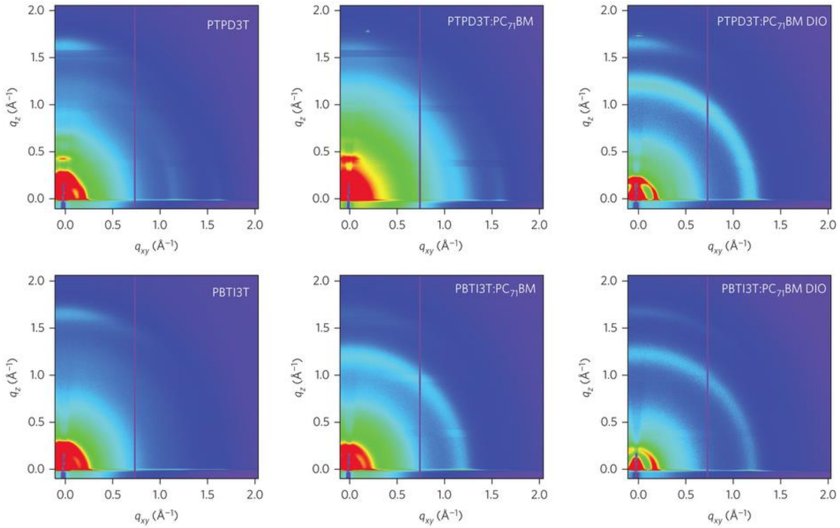
Understand/Control Protoactive Blend Microstructure



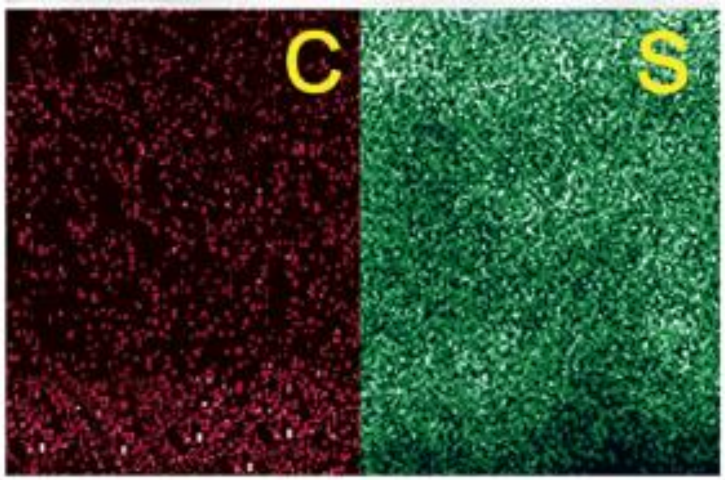
Cross-sectional TEM specimen (FIB) prepared:
- Darker contrast may indicate $PC_{71}BM$
- Preferred aggregation at bottom (ZnO) interface



WAXRD
- Crystalline, face-on oriented



EDS mapping in active layer
- More C and less S content near ZnO interface

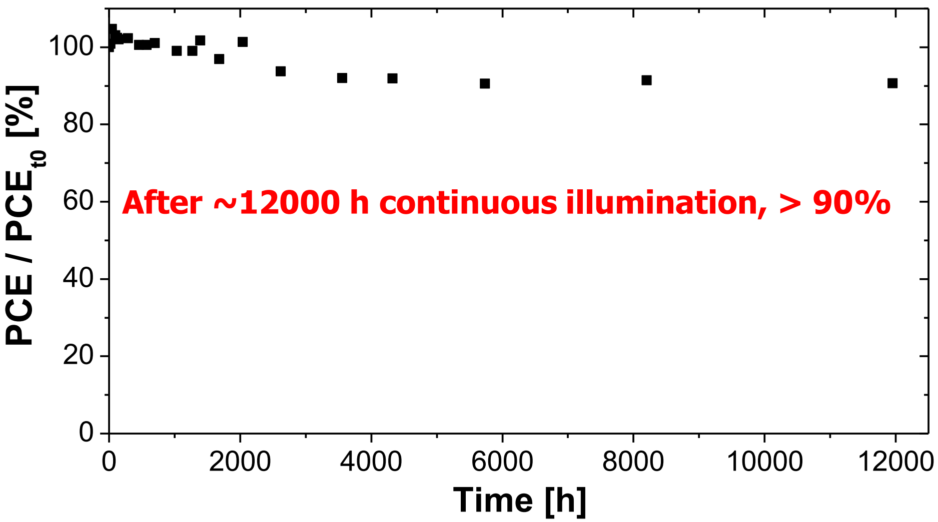


Facchetti, Marks *Nature Photonics*, **2013** in press

Understand/Control Processing, Monitor Stability

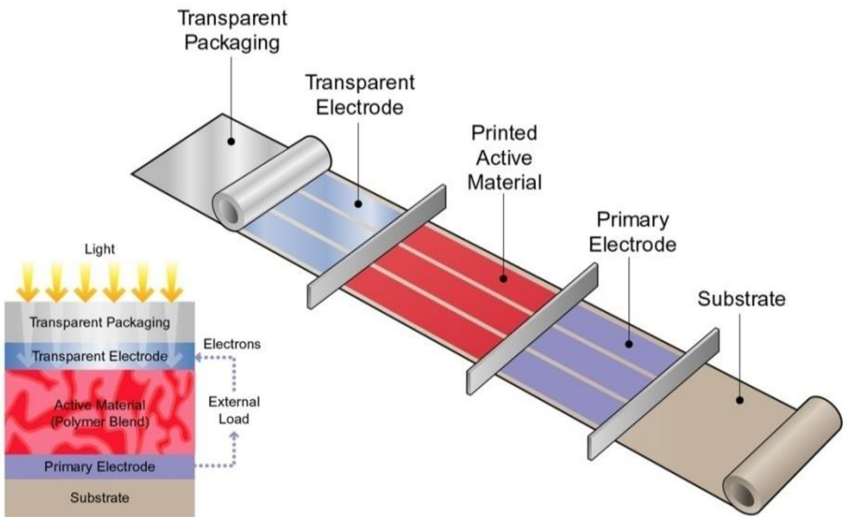
- Active layer coated under N_2 or air
- Spin casting and doctor blading
- Same performance in air and N_2

PCE ~ 8%



Printing OPV Modules

- Technology Overview



- Patented roll-to-roll process:
  - Continuous printing/coating
  - Flexible substrates
  - Lower capital & labor costs
  - Low-temp/low-energy/low carbon manufacturing
  - Uses existing coating & printing equipment

Conclusions

Challenges

Printed TFTs, Circuits

- Scale-up current generation of materials
- Engineering the process in a FAB line
- Develop second-generation material set

Organic Solar Cells

- Develop suitable donor-acceptor semiconductors
- Long-term stability
- Cost-effective encapsulation

Opportunities

- Understand/control light/transport phenomena in soft matter
- Create a new industry

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