

# West Lafayette, Nous Voila



Birck Nanotechnology Center Distinguished Lecture, Purdue University,  
West Lafayette, IN, Dec. 3, 2018

# Organic Photonics and Electronics: The Endless Frontier

Bernard Kippelen

**Georgia  
Tech**



Center for  
Organic Photonics  
and Electronics

# Atlanta: A Fast Growing Technology Hub

TECHLANTA



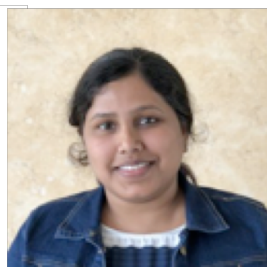
# Kippelen Research Group



Canek Fuentes  
Principal  
Research  
Scientist



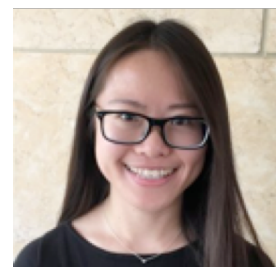
Xiaoqing Zhang



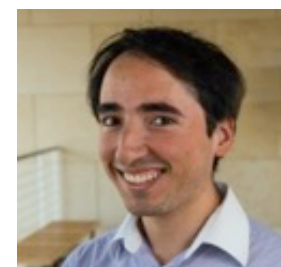
Silja Abraham



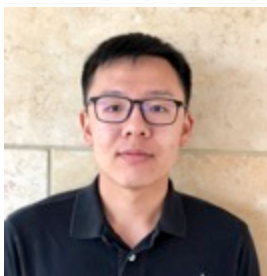
Wen-Fang Chou



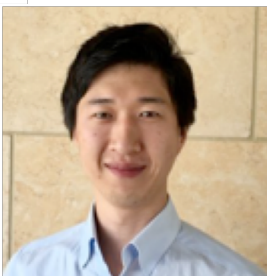
Xiaojia Jia



Felipe Larrain



Yi-Chien Chang



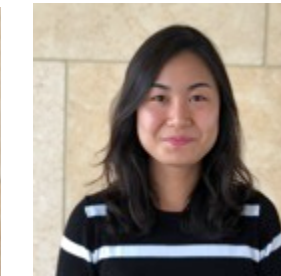
Youngrak Park



Victor Rodriguez



Oliver Moreno



Gunhee Kim



# Outline

- Motivation and external drivers
- Recent advances:
  - Electrode engineering
  - Organic light-emitting diodes
  - Thin-film transistors

# Global Macro Trends

Increasing **population**: 7.6 Billion today, 8.5 Billion by 2030

Increasing **energy** demand:  
16 TW in 2007 (0.5 ZJ), 28 TW by 2050 (0.9 ZJ)

Population shift from rural to urban areas  
Aging population  
Increasing economic disparity



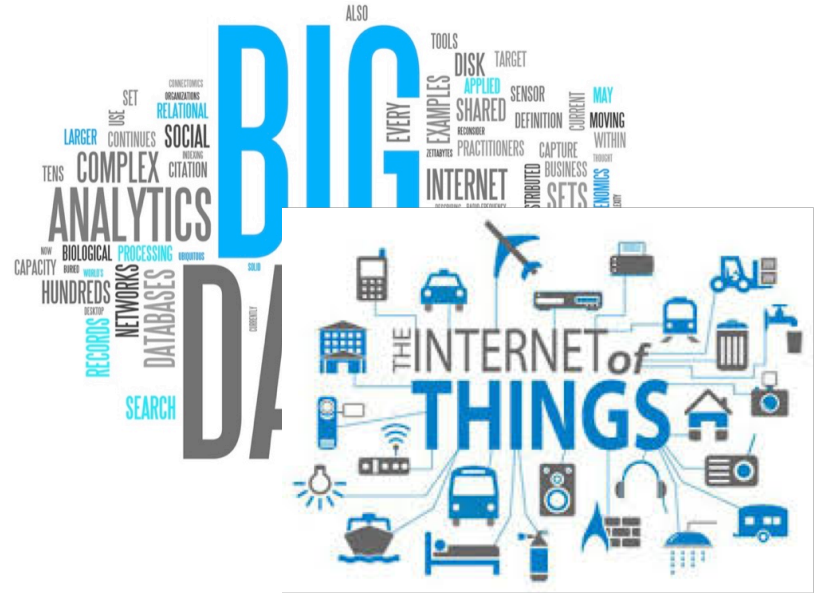
# An Economy in Flux



Source: Financial Times Global 500 rankings; Based on market capitalization

# Technology Trends

- Artificial Intelligence
- Internet of Things
- Cybersecurity
- Blockchain
- Quantum computing
- Immersive experience
- CRISPR:Cas9
- Smart materials



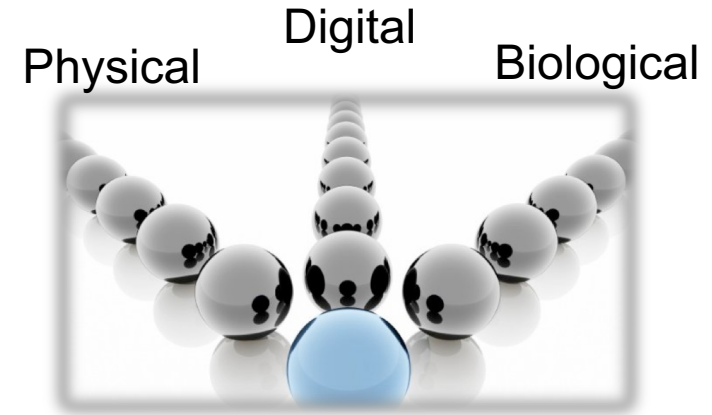
What is the Next Big Thing?



# What's Next: Fourth Industrial Revolution\*



Source: [www.transconflict.com](http://www.transconflict.com)



*An accelerated  
convergence*

(\*) Coined by Klaus Schwab, Founder of the World Economic Forum

# Grand Challenges and Opportunities



Improve the quality of life through sustainable development:

- *Profit (economics)*
- *People (societal)*
- *Planet (environment)*

# From “Digital” to “Deep Tech”



Katsushika Hokusai's *The Great Wave off Kanagawa*

[1] “From Tech to Deep Tech,” Boston Consulting Group and Hello Tomorrow report.

[2] *The 4th Industrial Revolution*, Klaus Schwab, Crown Publishing Group 2016.

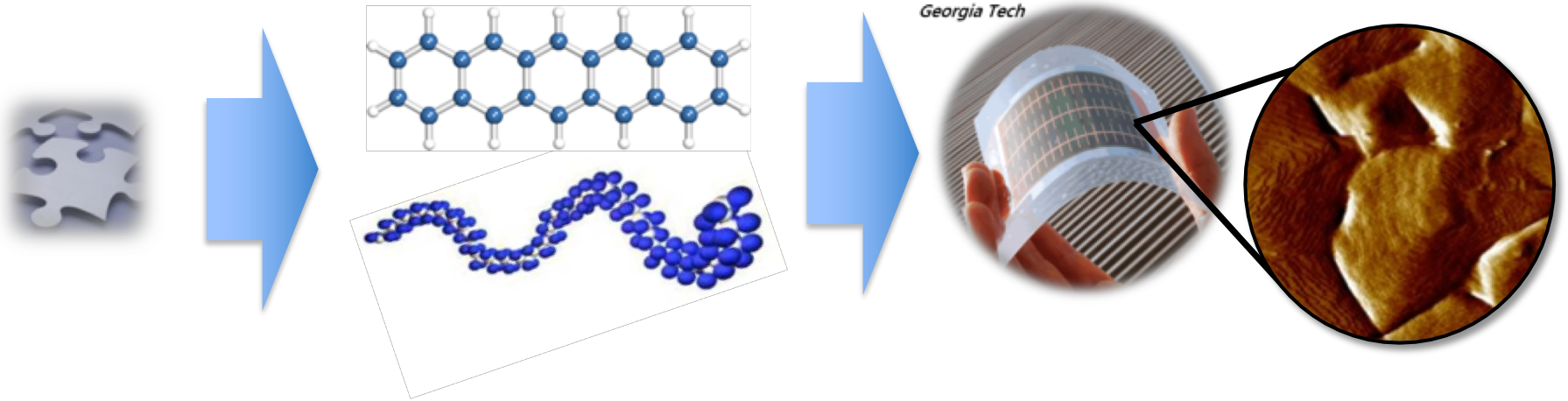
## ***Digital innovation wave:***

wider dissemination enabled by hyper-connected world

## ***Next Deep Tech wave:***

disruptive solutions built around unique, protected technological or scientific advances

# Organic Molecules and Polymers



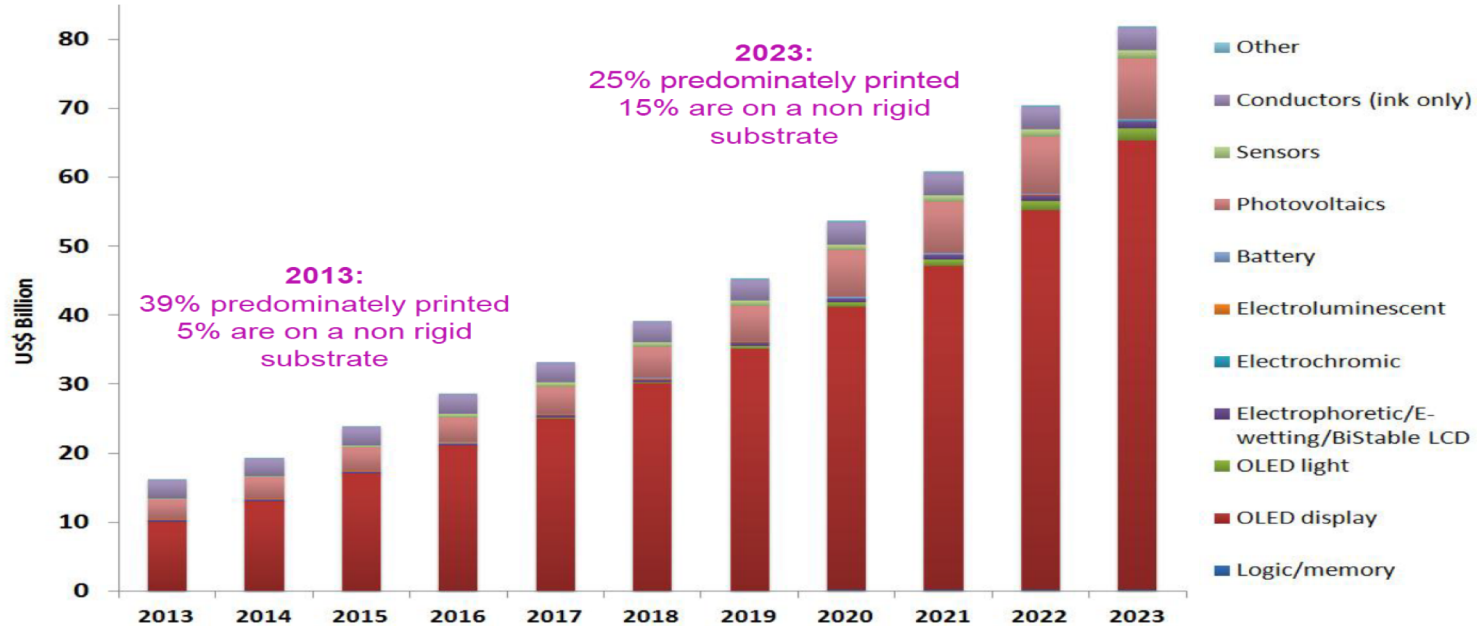
**Carbon-based compounds  
with tailored optical, electrical and  
mechanical properties**

**Semiconductor films processed at  
room temperature from vacuum or  
solution.**

# Printed Electronics Market Forecast

## IDTechEx 2013-2023 Forecast

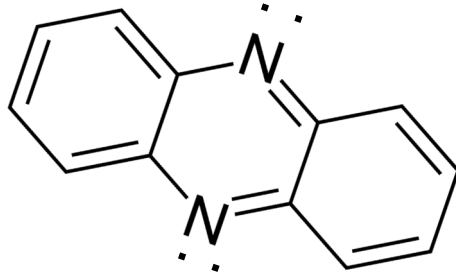
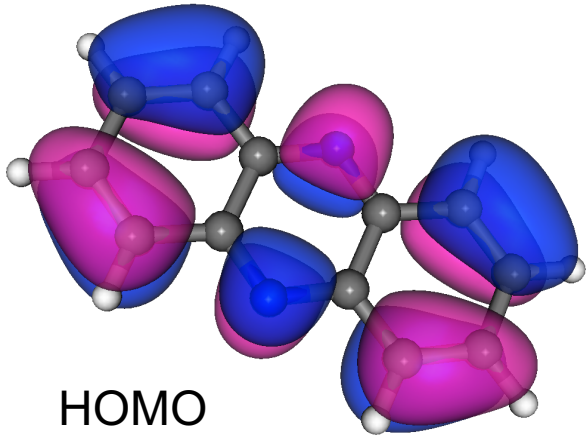
See [www.IDTechEx.com/pe](http://www.IDTechEx.com/pe)  
for full details



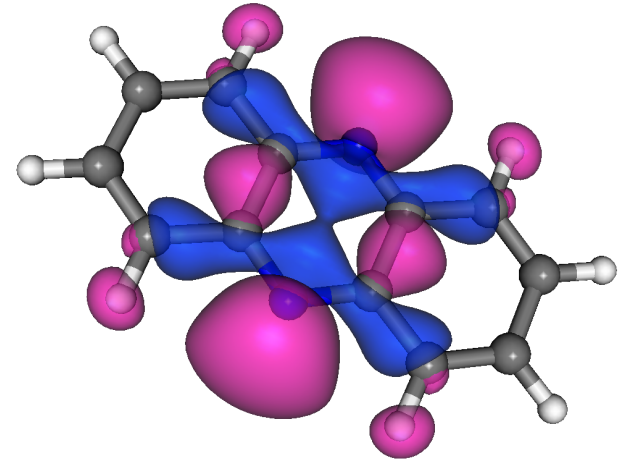
Source: IDTechEx report "Printed, Organic & Flexible Electronics 2013-2023" [www.IDTechEx.com](http://www.IDTechEx.com)

# Organic Semiconductors: Conjugated Molecules and Polymers

$\pi$  orbital

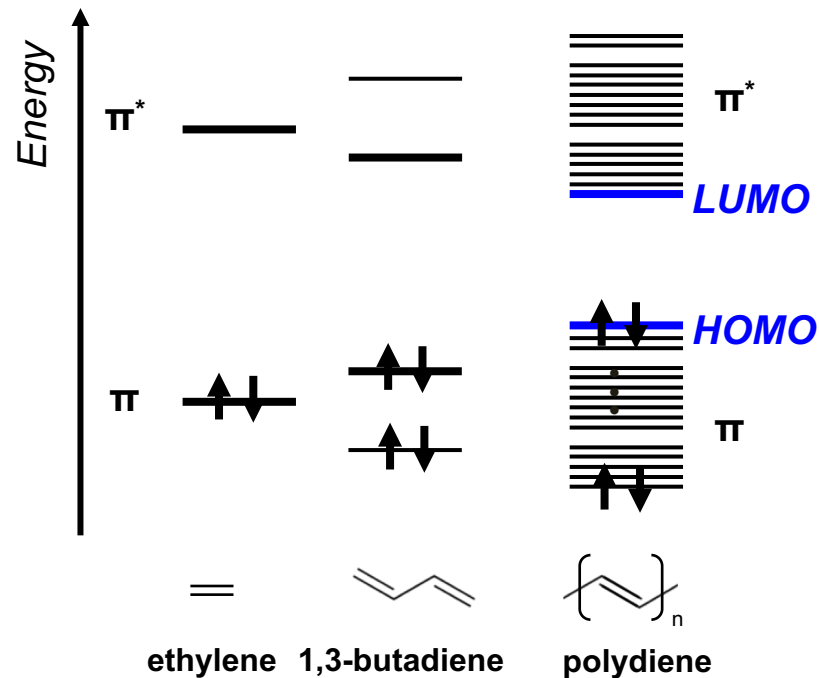
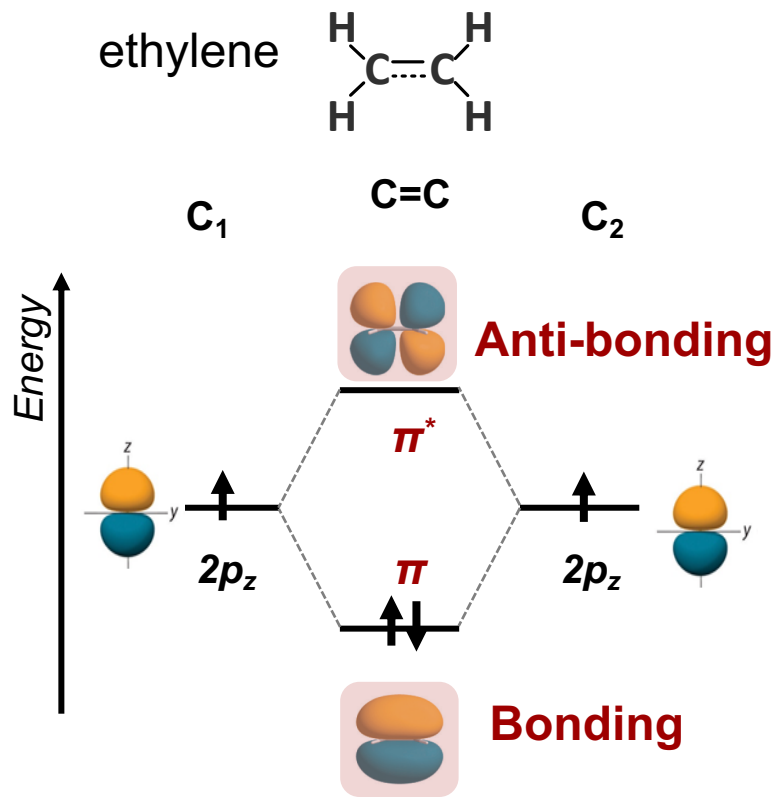


$n$  orbital

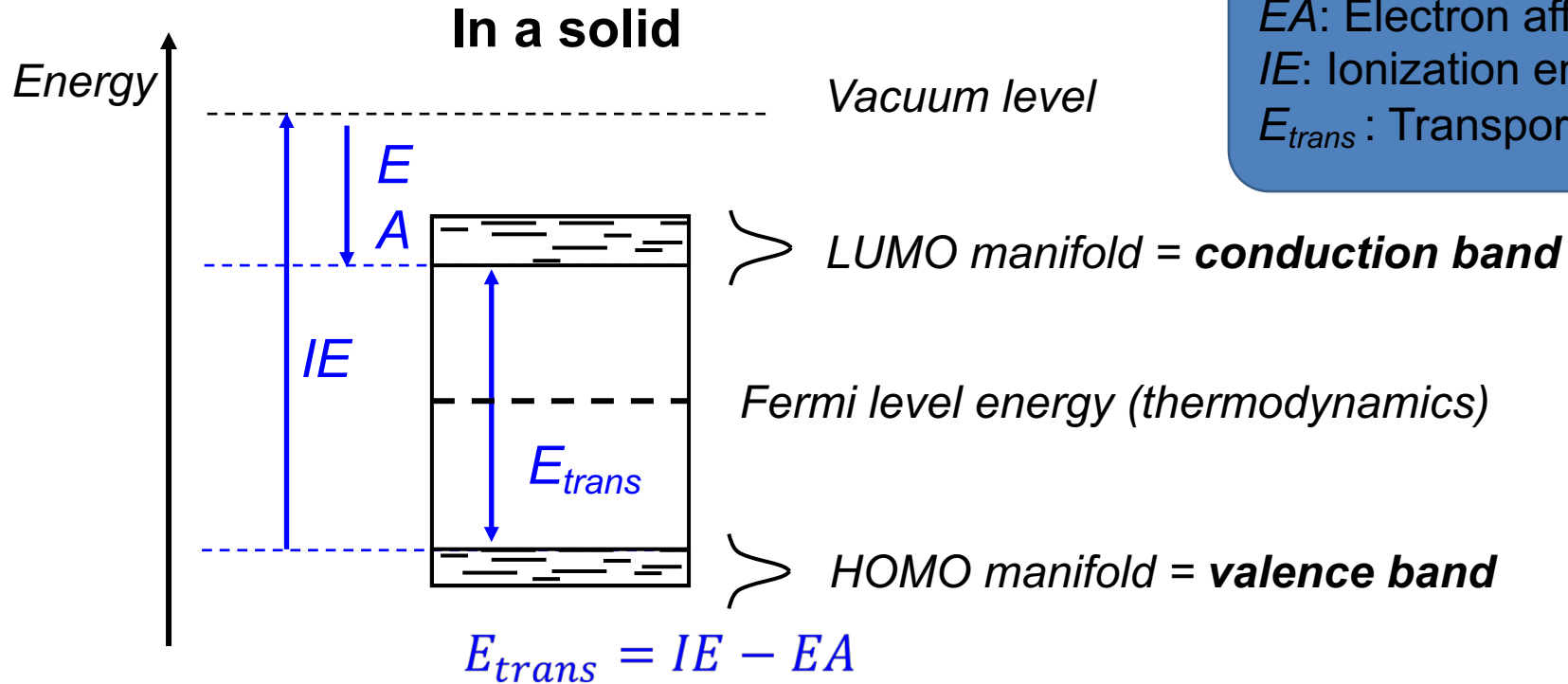


Drawings: courtesy of Wolfram Ratzke, Lupton Group, Univ. of Regensburg

# Frontier Molecular Orbitals



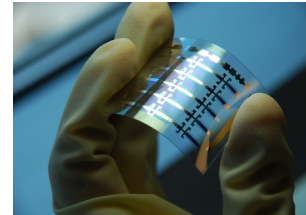
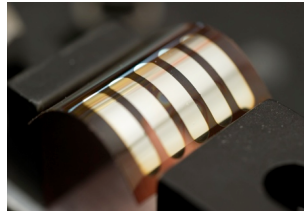
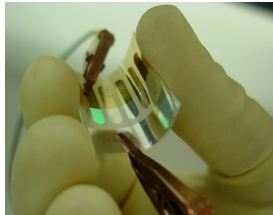
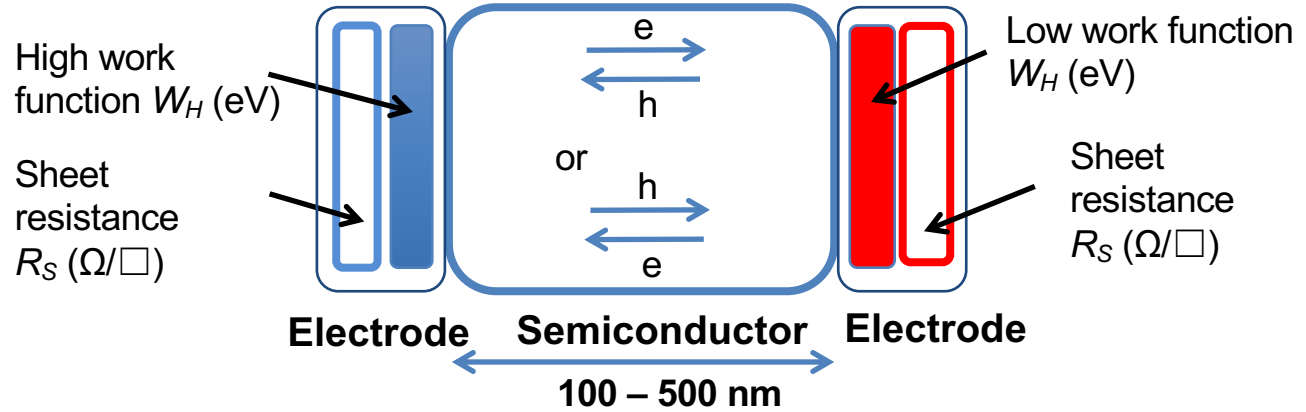
# Organic Semiconductors: Transport Bands



$EA$ : Electron affinity  
 $IE$ : Ionization energy  
 $E_{trans}$ : Transport gap



# Solid-state Organic Optoelectronic Devices

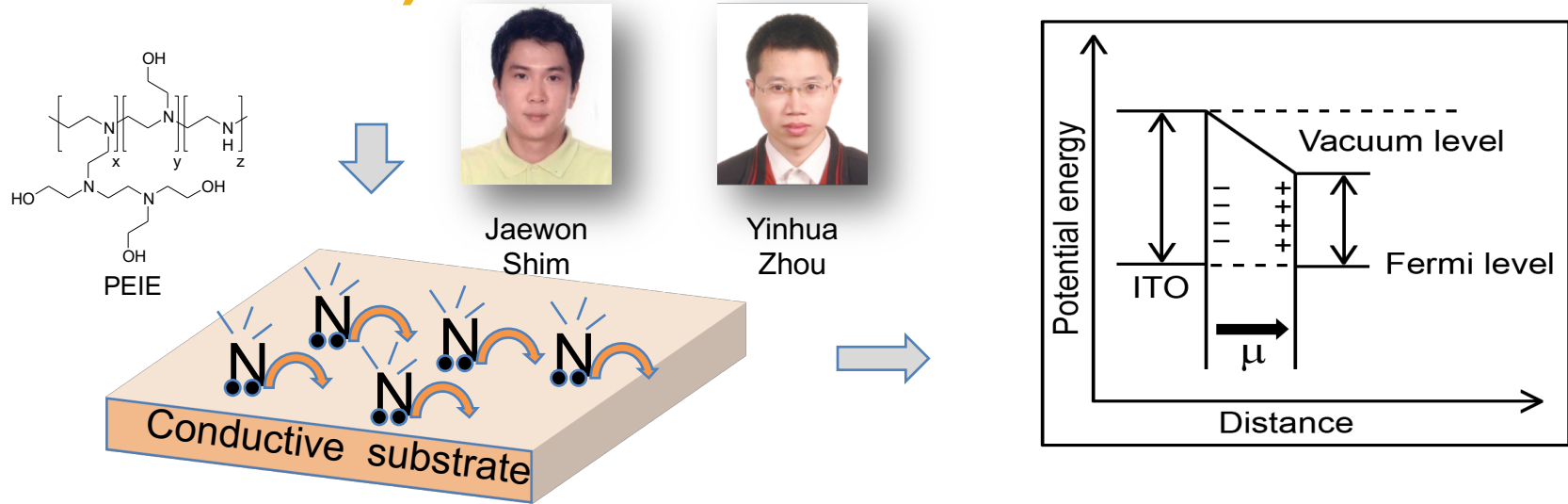


Electrodes for charge injection (OLED, OFET) or charge collection (OPV) are essential device-enabling building blocks

# Outline

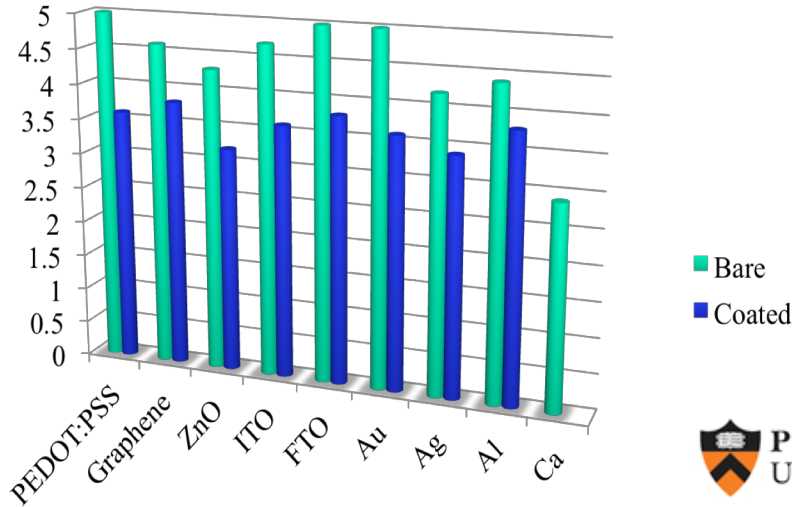
- Motivation and external drivers
- Recent advances:
  - Electrode engineering
  - Organic light-emitting diodes
  - Thin-film transistors

# Simple Method to Produce Stable Low Work Function Electrodes (Electron Collection)

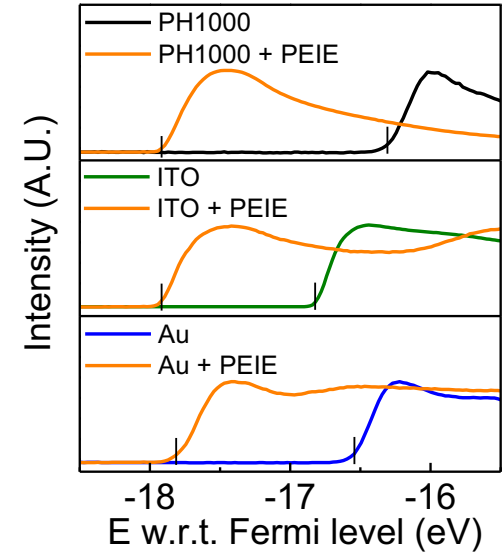


Y. Zhou, J. Shim, S.R. Marder, J.L. Bredas, S. Graham, A. Kahn, B. Kippelen et al. *Science*, 336, 327 April 20 (2012).

# A Universal Method

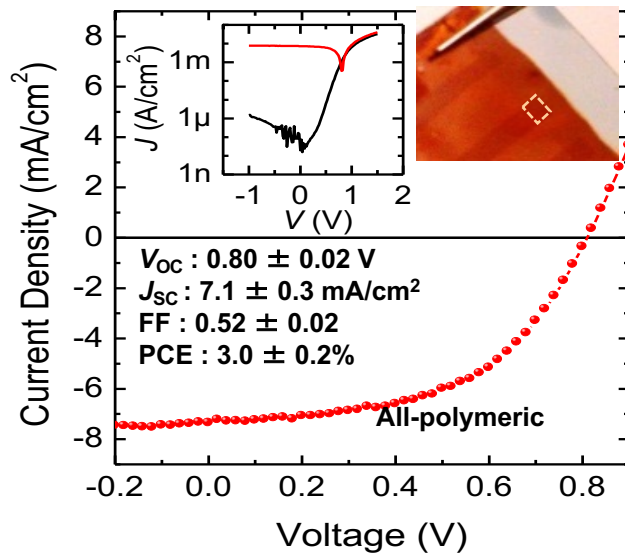
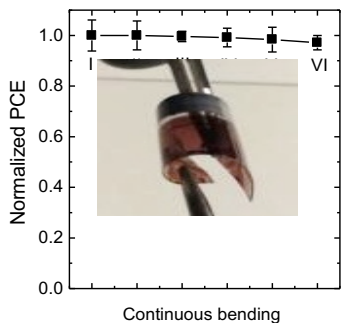
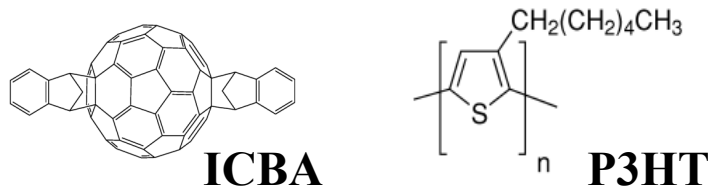
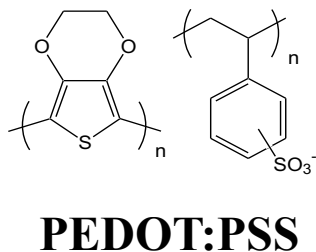
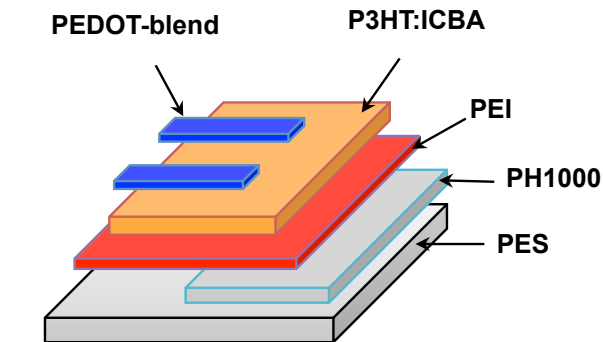


UPS measurements: Kahn group  
Secondary photoelectron cutoffs



Reduction in work function up to 1.5 eV

# All-organic Solar Cell



Y. Zhou, J. Shim, S.R. Marder, J.L. Bredas, S. Graham, A. Kahn, B. Kippelen et al. *Science*, 336, 327 April 20 (2012).

# All-organic Solar Cells in the News

Forbes / Tech

APR 25, 2012 @ 04:04 AM 16,404 VIEWS

## New Technique Creates First Plastic Solar Cell



Jennifer Hicks  
CONTRIBUTOR

I write about science, robotics & innovative technologies in Europe.

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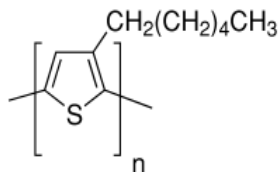
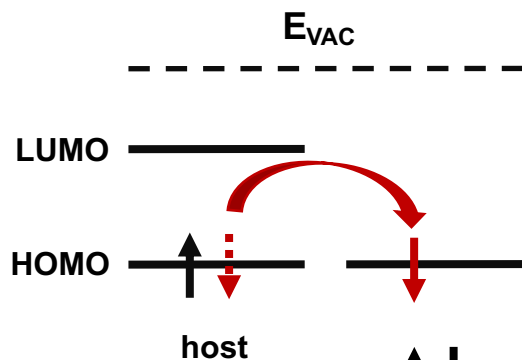
Georgia Tech's Bernard Kippelen and his team developed the first completely plastic solar cell. Courtesy: Virginie Drujon-Kippelen

The growth of the solar industry has been limited by the supply of the polysilicon material used to make solar panels. In 2006, more than half of the world's supply of polysilicon was used for production of renewable electricity. In 2008, only twelve factories produced solar-grade polysilicon. In 2011, the industry produced an excess of polysilicon. And now, another shift — the creation of a plastic solar cell.

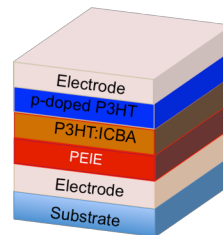
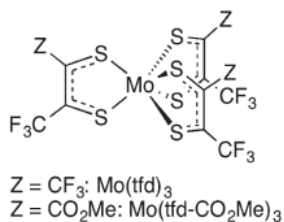
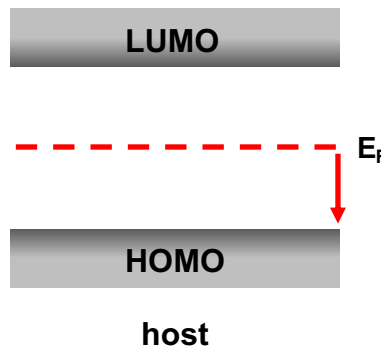


Y. Zhou, S.R. Marder, J.L. Bredas, S. Graham, A. Kahn, B. Kippelen et al. *Science*, 336, 327 April 20 (2012).

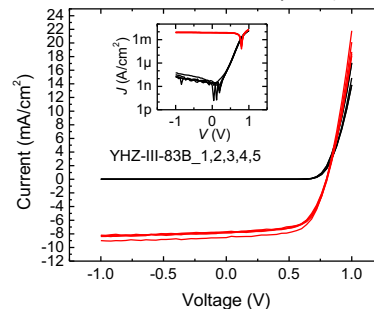
# Electrical Doping of Organic Semiconductors



p-type doping

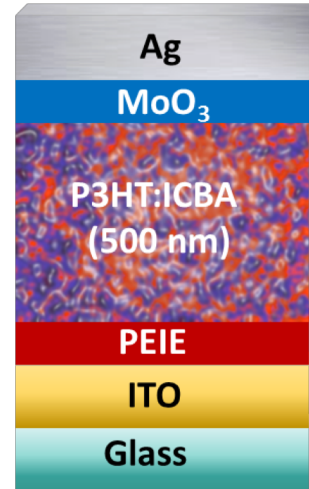
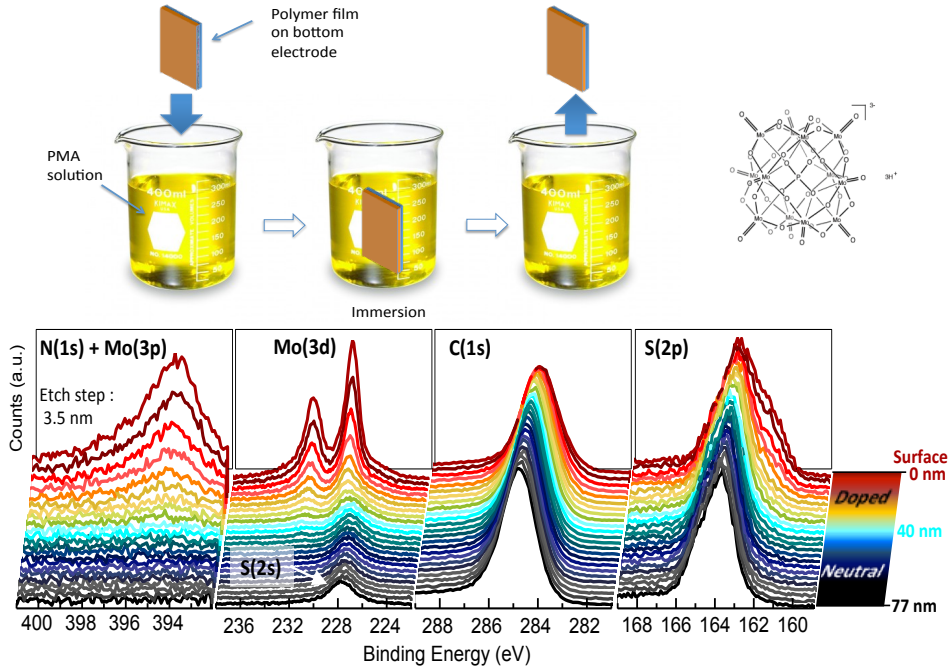


ITO/PEIE/P3HT:ICBA/P3HT: dopant (4 wt%)/Ag

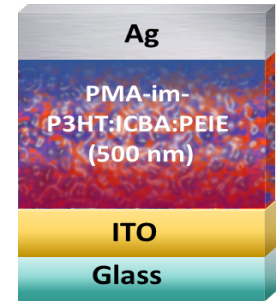


Dai, A., et al. *Adv. Funct. Mater.* **24**, 2197-2204, (2014).

# Simple Method for Electrical Doping



Single layer solar cell



V.A. Kolesov et al., *Nature Materials* 16, 474, April 2017. Doi: [10.1038/nmat4818](https://doi.org/10.1038/nmat4818)



# Outline

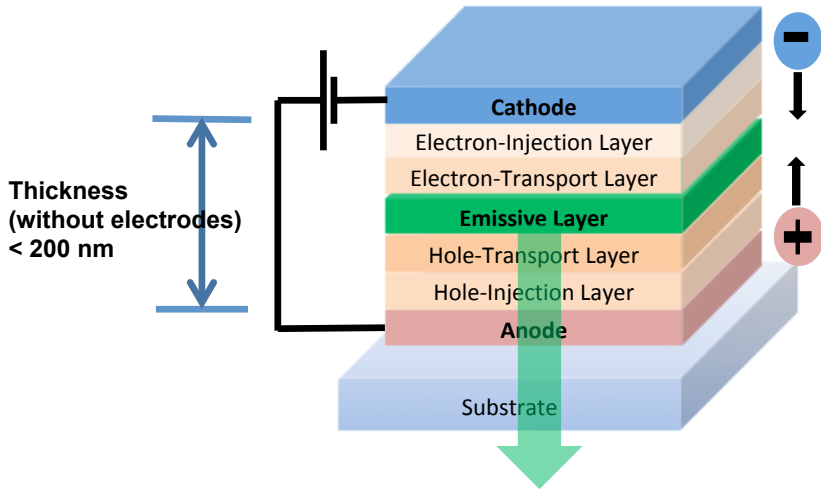
- Motivation and external drivers
- Recent advances:
  - Electrode engineering
  - Organic light-emitting diodes
  - Thin-film transistors

# OLEDs: Light Sources of the Future



Diffuse light, UV free, large area, ultra-thin, flexible, transparent

# OLED Science and Technology



- Materials
- Device architecture
- Manufacturing technology
- Integration: packaging and bonding (interconnects with backplane, barrier coatings, functional films)

# Electroluminescence for Beginners

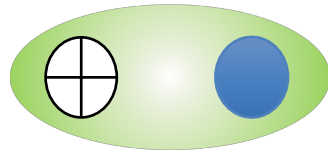
Step 1:



Charge injection and transport



Step 2:

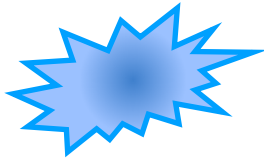


Excited state formation

**Easy**

Bohr, Heisenberg,  
Pauli

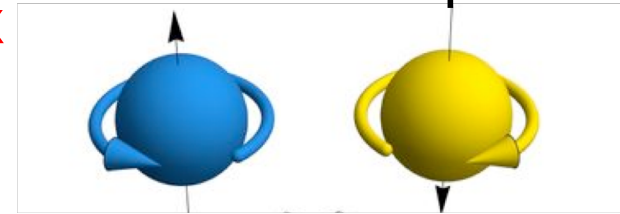
Step 3:



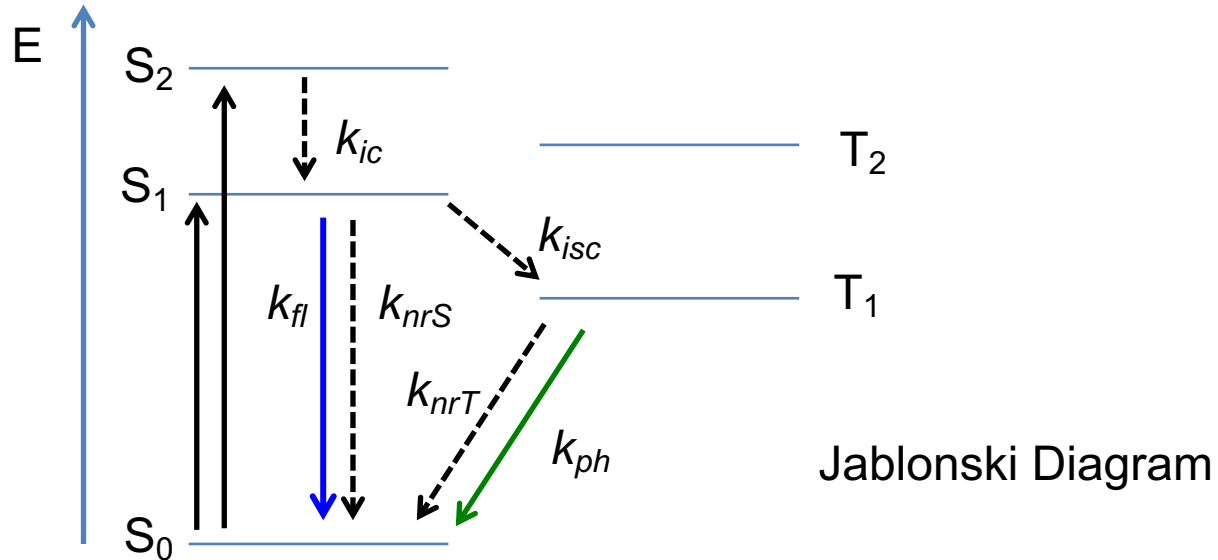
Light emission

**Complex**

Electron spin

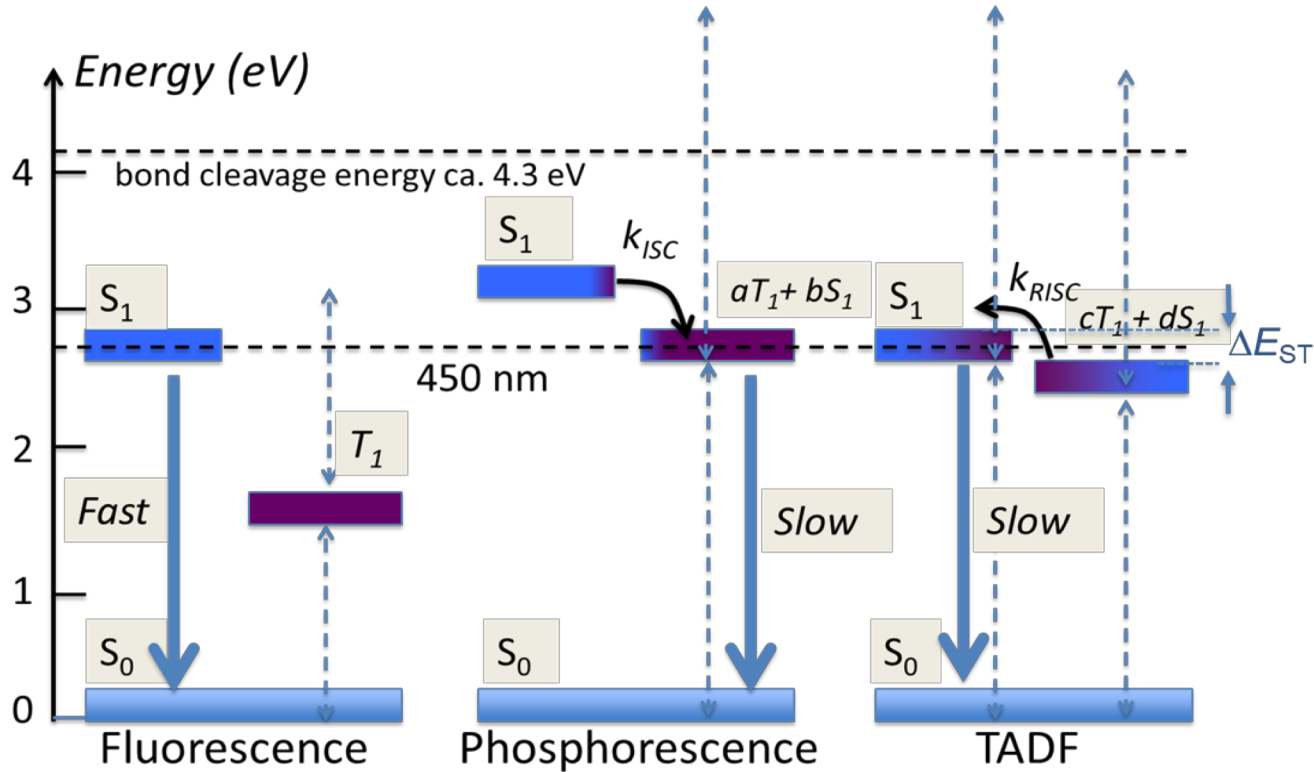


# Photophysics of Organic Molecules



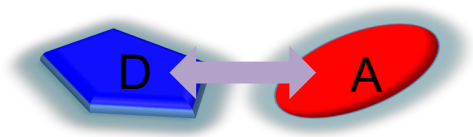
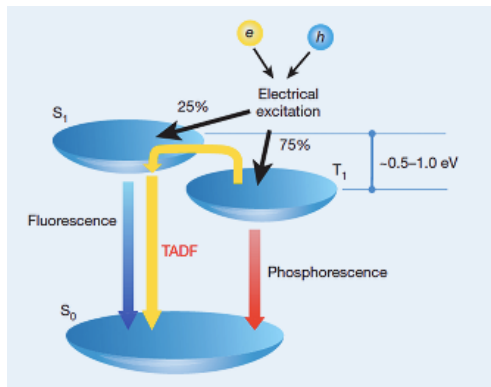
Simplified electronic state diagrams for planar all-carbon conjugated compounds: neglects non-bonding orbitals and charge-transfer states

# Light Emission in Organic Molecules



# Thermally Activated Delayed Fluorescence

All-organic compounds that do not contain precious heavy metals, an alternative to phosphorescence



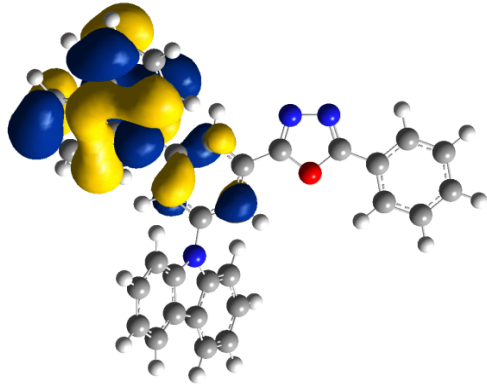
Design criteria based on engineering a weak coupling between donor and acceptor-like moieties.

$$k_{\text{RISC}} = A \exp(-\Delta E_{ST}/k_B T)$$

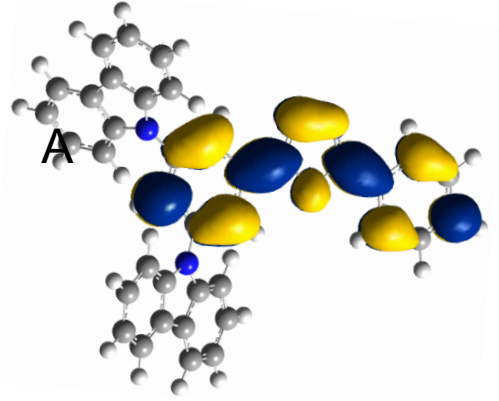
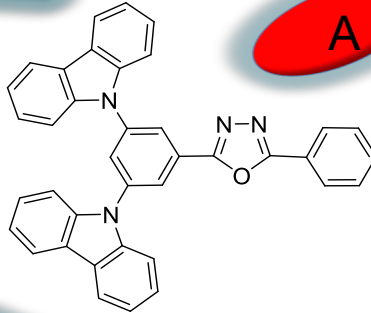
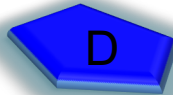
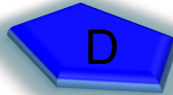
Uoyama, H., Goushi, K., Shizu, K., Nomura, H., Adachi, C. *Nature*. 492, 234 (2012).

Nakanotani, H., Masui, K., Nishide, J., Shibata, T., Adachi, C., *Scientific Reports*. 4, 2127 (2013).

# Material Design Strategy



HOMO: carbazole-like



LUMO: oxadiazole-like

US 9,133,177 B2 issued Sep. 15, 2015

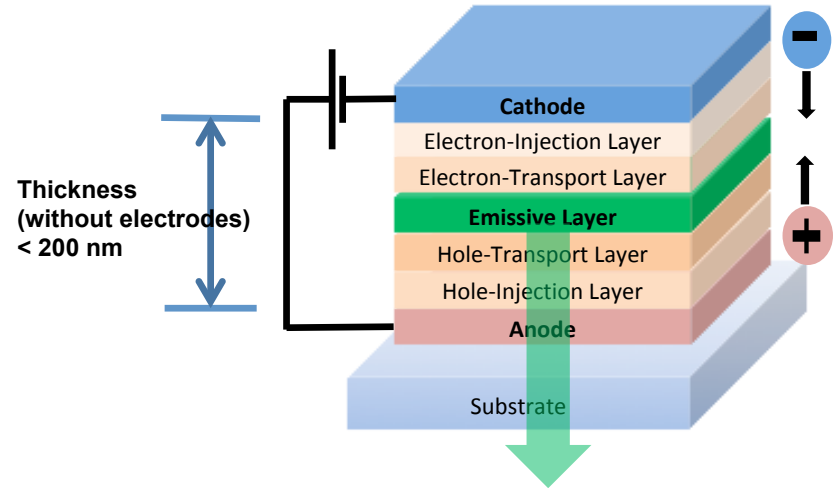
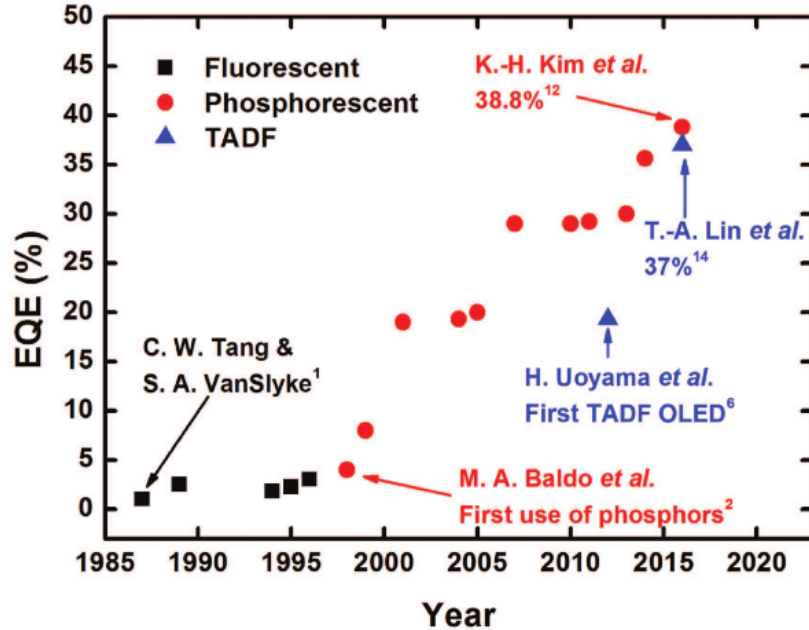
Collaboration with Bredas Group, Georgia Tech

Computed at the DFT B3LYP/6-31 G\*\* level



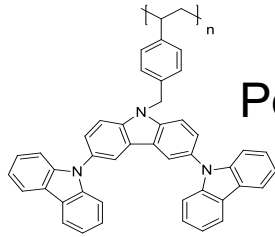


# TADF: Organic Light-emitting Diodes

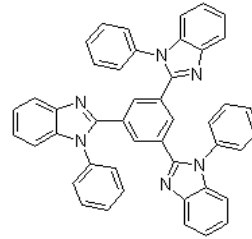


Kim, Kwon-Hyeon & Jang-Joo Kim, *Advanced Materials* (2018)

# TADF Devices with Carbazole/Sulfone Host

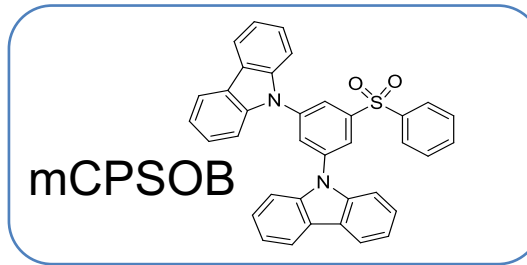
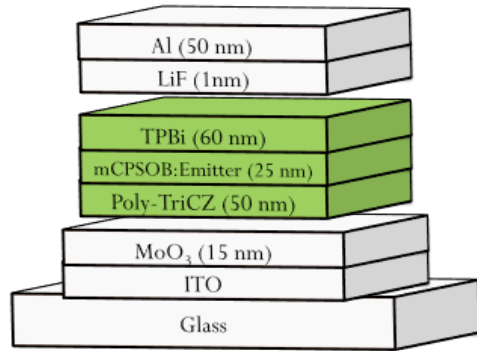


Poly-TriCZ

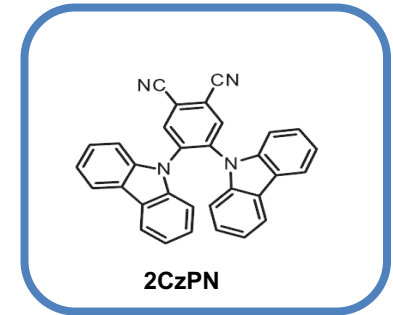
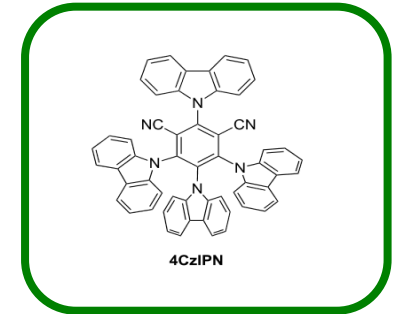


TPBi

Bottom emission, top cathode

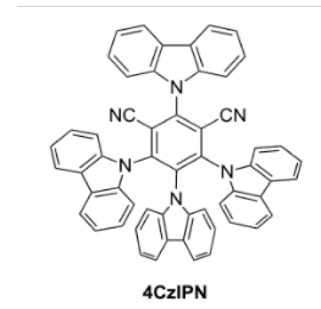
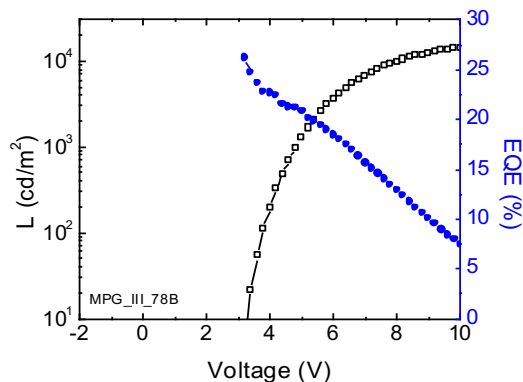
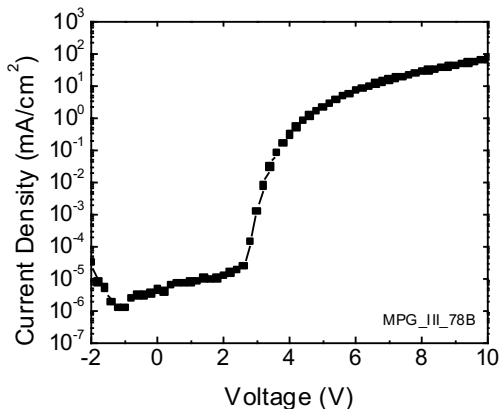


Collaboration with the Marder Group



Uoyama, H., Goushi, K., Shizu, K., Nomura, H., Adachi, C. *Nature*. 492, 234 (2012).  
Nakanotani, H., Masui, K., Nishide, J., Shibata, T., Adachi, C., *Scientific Reports*. 4, 2127 (2013).

# Green-emitting TADF OLEDs

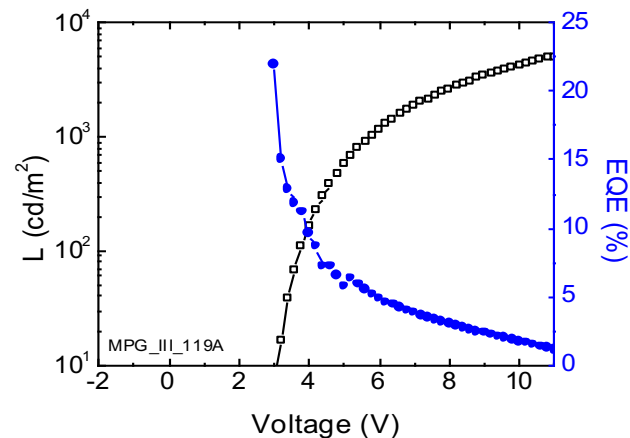
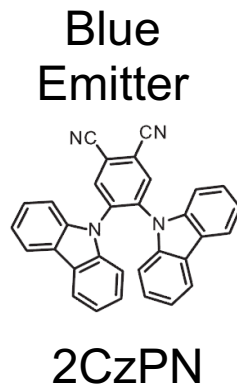
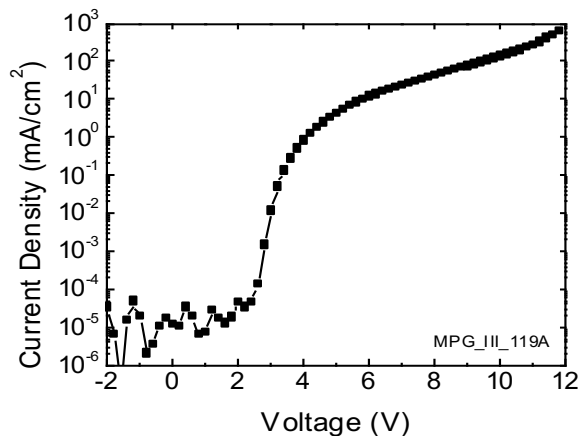


Device	Luminance (cd/m <sup>2</sup> )	Volt (V)	EQE (%)	cd/A	Lm/W	mA/cm <sup>2</sup>
<b>4CzIPN</b>	6	3.2	26.2	79.5	78.1	0.01
	110	3.8	22.3	69.2	57.2	0.16
	965	4.8	21.1	64.2	42.0	1.50
	10365	8.2	12.3	37.4	14.3	27.7

$\Delta E_{ST} = 83 \text{ meV}$

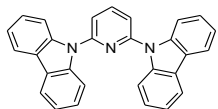
M. Gaj, B. Kippelen et al. Org. Electron. 16, 109-112 Jan. (2015)

# Blue-emitting TADF OLEDs

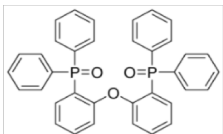


Device	Luminance ( $\text{cd}/\text{m}^2$ )	Volt (V)	EQE (%)	$\text{cd}/\text{A}$	$\text{lm}/\text{W}$	$\text{mA}/\text{cm}^2$
2CzPN	6	3.0	22.0	53.8	56.4	0.01
	111	3.8	11.1	27.2	22.5	0.41
	1040	5.8	5.1	12.5	6.8	8.30
	5070	11.0	1.2	2.7	0.8	185.1

# High-efficiency Blue-emitting OLEDs

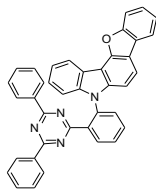


**YZ-I-10 (PYD2)**  
 $\Delta E_{ST} = 0.61 \text{ eV}$



**DPEPO**  
 HOMO: -6.1 eV  
 LUMO: -2.0 eV  
 $E_T = 3.3 \text{ eV}$

**Host**

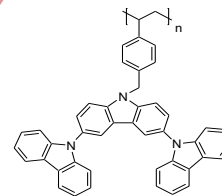


**oBFCzTrz (YZ-XI-49)**  
 $\Delta E_{ST} = -0.14 \text{ eV}$

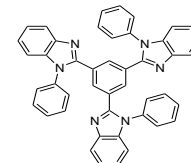
**Emitter**

Al/Ag (50 /100 nm)
LiF (1 nm)
TPBi (50 nm)
TP3PO (4 nm)
<b>Host : emitter (25 nm, X %)</b>
Poly-TriCZ (80 nm)
MoO <sub>3</sub> (15 nm)
ITO
Glass

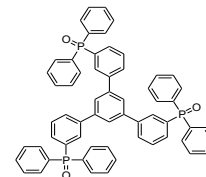
**Transport materials**



**HTL**  
**Poly-TriCZ**



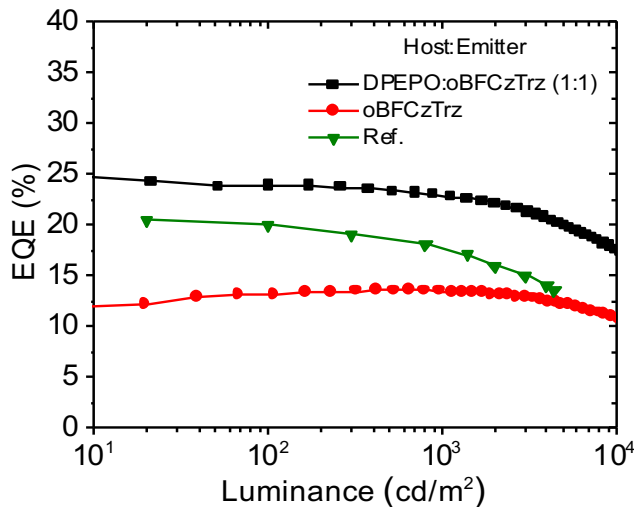
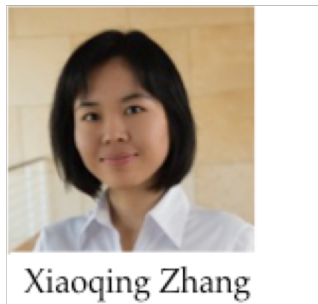
**ETL**  
**TPBi**



**HBL**  
**TP3PO**

Ref. [1] Dong Ryun Lee, et.al., ACS Appl. Mater. Interfaces 2016, 8, 23190–23196

# Optimized Performance



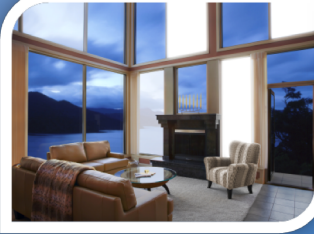
- **Blends EML:**  
Higher EQE & smaller roll-off
- **Pure material EML:**  
Roll-off is negligible

Emissive layer	EQE(%)				Von (V) @10 cd/m²	$\eta_c$ (cd/A) @ 1000 cd/m²	$\eta_p$ (lm/W) @ 1000 cd/m²
	Max,	@ 10	/ 100	/1000 /10000 cd/m²			
DPEPO: oBFCzTrz (1:1)	25.5,	25.5/24.2/22.8/16.4			3.3	57.9	35.0
oBFCzTrz	13.5,	12.1/ 13.2/ 13.5/ 10.8			4.2	36.3	17.8

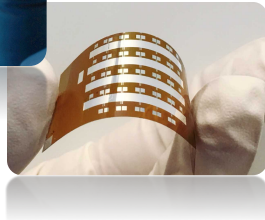
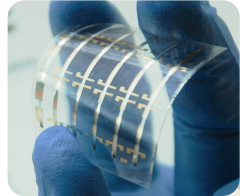
Ref. [1] Dong Ryun Lee, et.al., ACS Appl. Mater. Interfaces 2016, 8, 23190–23196

# Towards Adaptive Lighting

Lighting  
technology

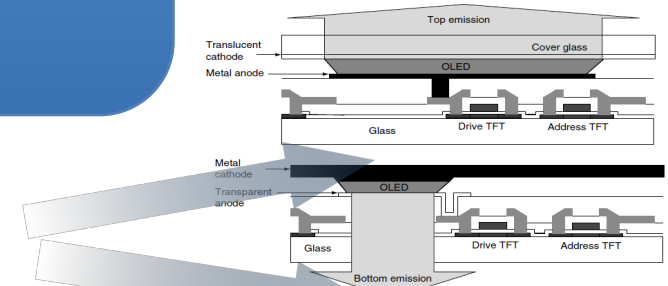


Convergence of  
functionalities



Organic thin-  
film  
transistors

Display  
technology



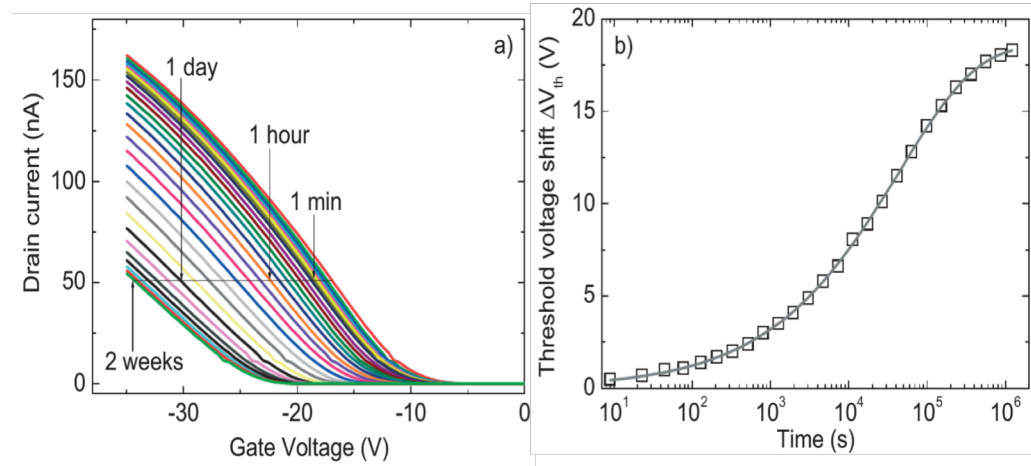
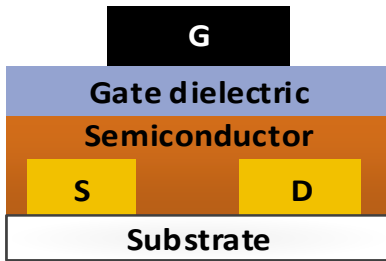
W. D. Bower, *Active Matrix Liquid Crystal Displays*, 1st ed. Burlington: Newnes, 2005.

# Outline

- Motivation and external drivers
- Recent advances:
  - Electrode engineering
  - Organic light-emitting diodes
  - **Thin-film transistors**



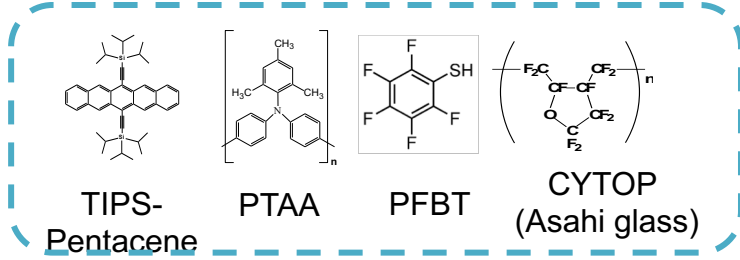
# Organic Field-Effect Transistors: The Problem



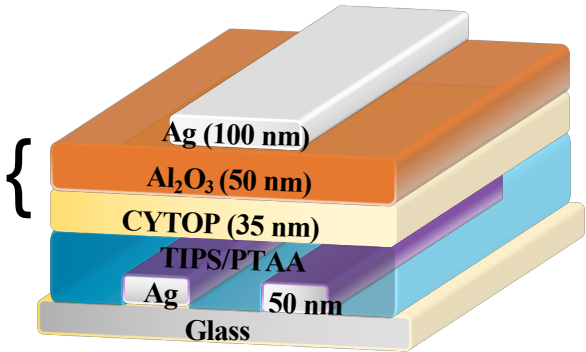
Stability challenge: charge trapping leads to shifts in threshold voltage

$$\Delta V_{TH}(t) = \Delta V_{TH,1\infty} \cdot \left\{ 1 - \exp \left[ - \left( \frac{t}{\tau_1} \right)^{\beta_1} \right] \right\}$$

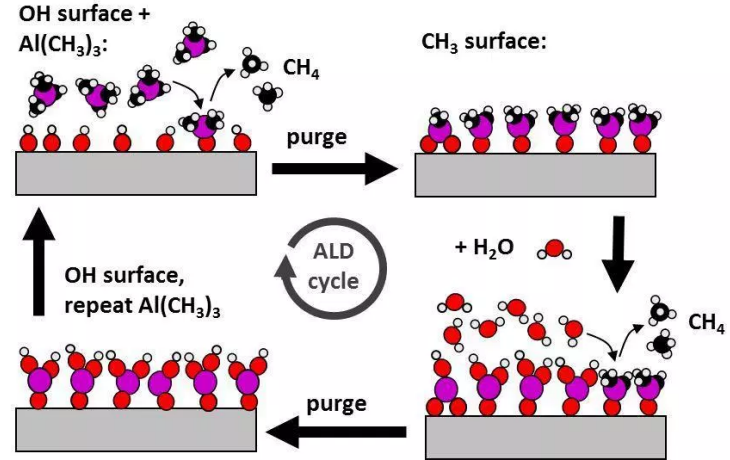
# OFETs with Bilayer Gate Dielectric



Bi-layer gate dielectric



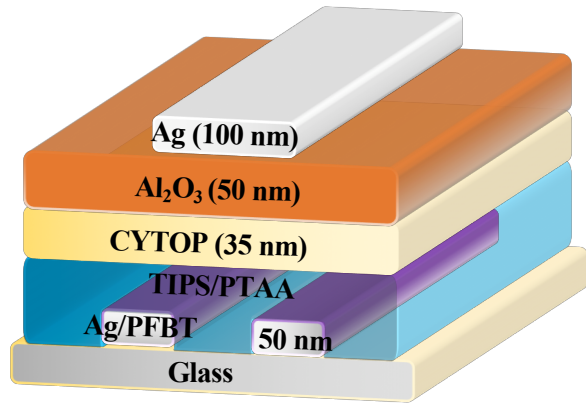
## Atomic Layer Deposition (ALD) of



**Pioneered the use ALD in OFETs.**

- US Patent # 9,368,737 B2, issued Jun. 14, 2016.
- D. K. Hwang et al., *Advanced Materials* 2011, 23, 1293.
- X.-H. Zhang et al., *Organic Electronics* 2007, 8, 718.

# Architecture for Stability Optimization

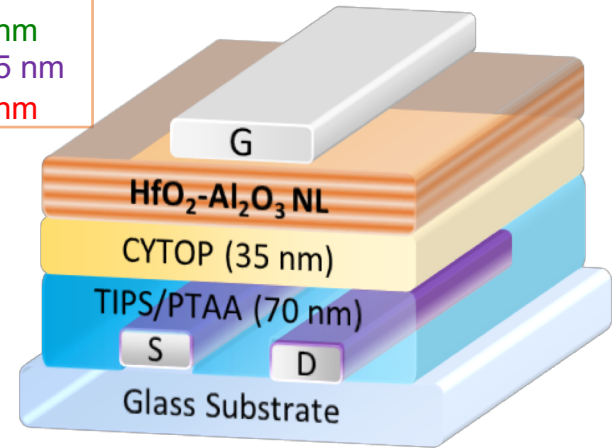
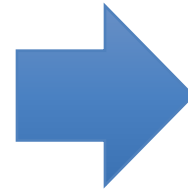


Group A:

A\_33: 33 nm

A\_27: 27.5 nm

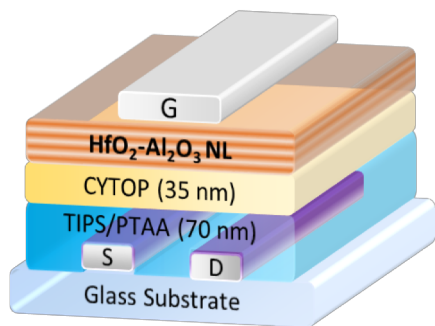
A\_22: 22 nm



Oxide layer: Al<sub>2</sub>O<sub>3</sub> (grown by ALD)  
Problem: corrosion in humid environment  
and high temperature

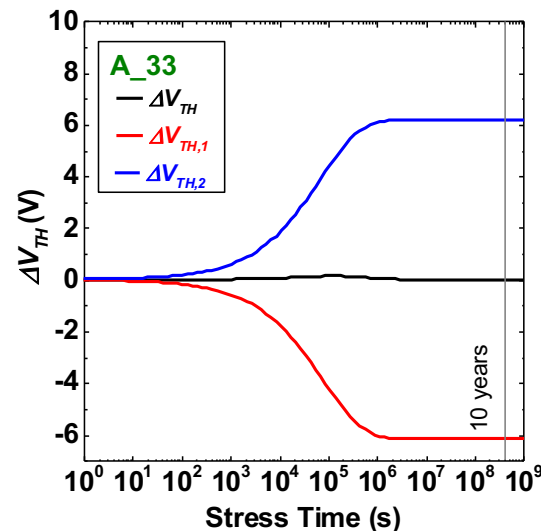
Oxide layer: HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>  
nanolaminate (grown by ALD)  
with different thickness

# Compensation Effect in OFET with Bilayer Gate Geometry



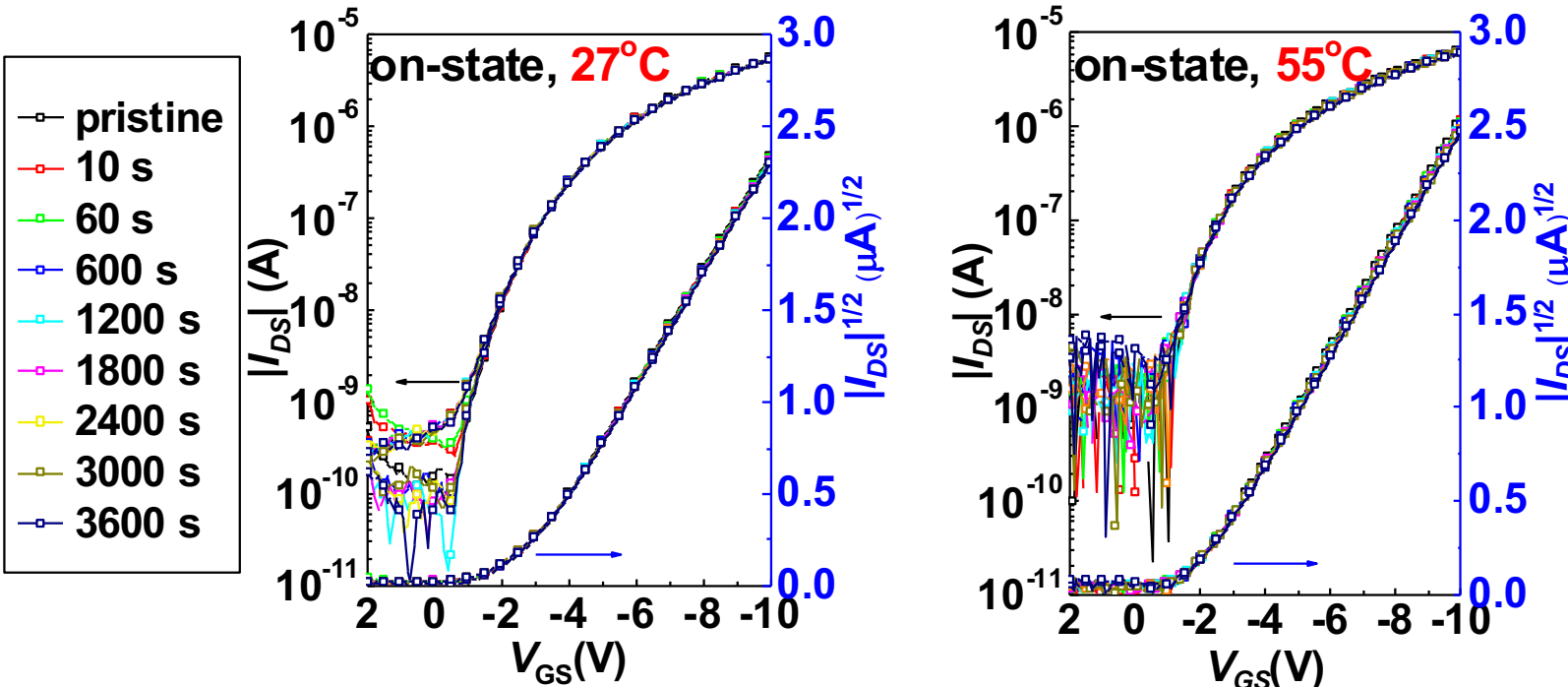
$$\Delta V_{TH}(t) = \underbrace{\Delta V_{TH,1\infty}}_{\text{charge-trapping effect (decrease)}} \cdot \left\{ 1 - \exp \left[ - \left( \frac{t}{\tau_1} \right)^{\beta_1} \right] \right\}$$

$$+ \underbrace{\Delta V_{TH,2\infty}}_{\text{(increase)}} \cdot \left\{ 1 - \exp \left[ - \left( \frac{t}{\tau_2} \right)^{\beta_2} \right] \right\}$$



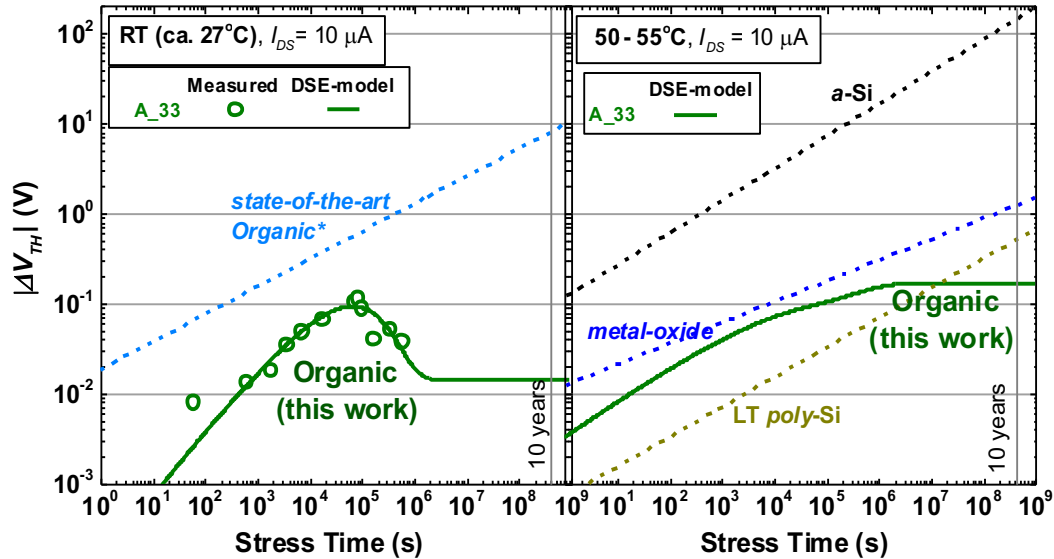
Compensation due to two mechanisms with opposite effect

# Bias Stress Tests @ Higher Temperature



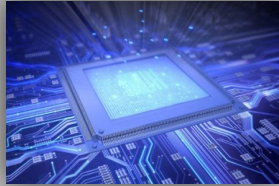
On-state (**A\_33**) ( $V_{DS} = V_{GS} = -10$  V)

# Stability of Thin-film Transistors

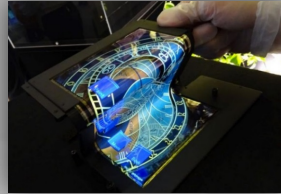


X. Jia, C. Fuentes-Hernandez, C.-Y. Wang, Y. Park, B. Kippelen, Science Advances 2018, 4, aao1705.

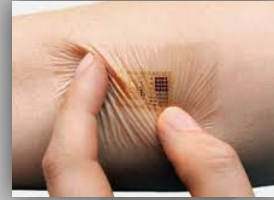
# Technology Roadmap



Photolithography and etching - **Rigid**



All additive direct writing and 3D printing - **Flexible**



Conformal, stretchable and wearable - **Soft**

Implantable, in vivo electronics - **Biocompatible**

**Georgia Tech**  Center for Organic Photonics and Electronics

2005

2015

2025

# Synopsis: Lessons Learned

- Science is your friend, keep exploring
- When you go in the lab be prepared for the unexpected
- Do not disregard outliers in your data sets
- Challenge the conventional wisdom and push the frontiers



*Louis Pasteur*



# Thank you

