Orthogonal Processing: A New Strategy for Patterning Organic Electronics

ERC Teleconference

3/September/2009

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Organic Electronics

Will enable simple, low cost electronics and photonics

Will make dumb object smart

Will complement Si-based electronics

(+) Ease of processing

(+) Tunability of electronic properties

(+) Integration with biological systems

(-) Low-end performance

(-) Lifetime

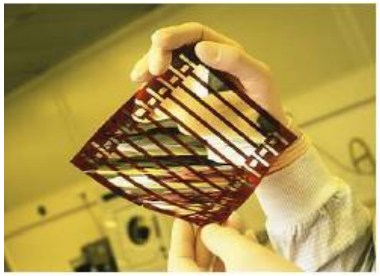
OTFTs

DuPont

OLEDs

Kodak

OPVs



Siemens

Outline

- Patterning issues in organic electronics?
- *Orthogonal Processing* employing
  - Supercritical carbon dioxide
  - Hydrofluoroethers and tuned fluorinated materials
- Applications and possibilities

Overview on Patterning of Solution Processable Organic Materials

technique	resolution	materials compatibility
photolithography	30 nm	photoresists, functional organics
inkjet printing	10-20 μm	organic conductors, low molecular weight polymers, wax, others
soft printing	0.1-2 μm	SAMs, thin metals, organic and inorganic semiconductors
imprint lithography	<10 nm	moldable resists, functional organics
capillary molding	2-5 μm	resists, low-viscosity inks, functional organics
laser imaging	5 μm	organic conductors, semiconductors and electroluminescent materials
embossing	1 nm	moldable resists, functional organics

E. Menard, *et al.*, *Chem. Rev.* 2007, 107, 1117.
J. R. Sheats, *J. Mater. Res.* 2004, *19*, 1974.

Patterning by Photolithography

Advantages of photolithography

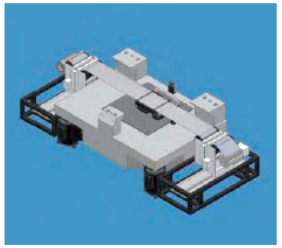
- Long history in Si industry
  - Optimized Process
  - Experienced operators
  - Cheaper depreciated equipment
- Parallel process
- Large area
- High Resolution
- Good registration (alignment between layers)

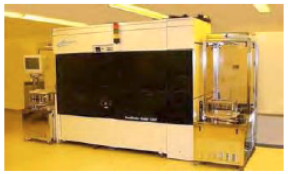
Precision Lithography: Capability

AzoresCorp, 2006

- Based on proven FPD stepper
- 8" width, can handle up to 24" with new chucks
- g-line (436 nm)
- 4 μm L/S
- 230 to 760 mm/min
- 400 ppm distortion compensation
- Requires hole-punch pattern for pre- alignment:

CAMM

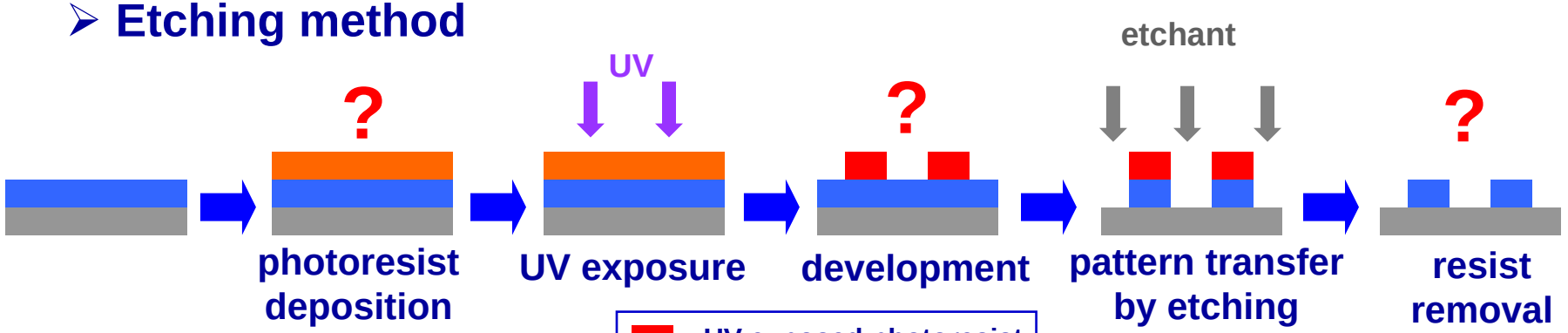




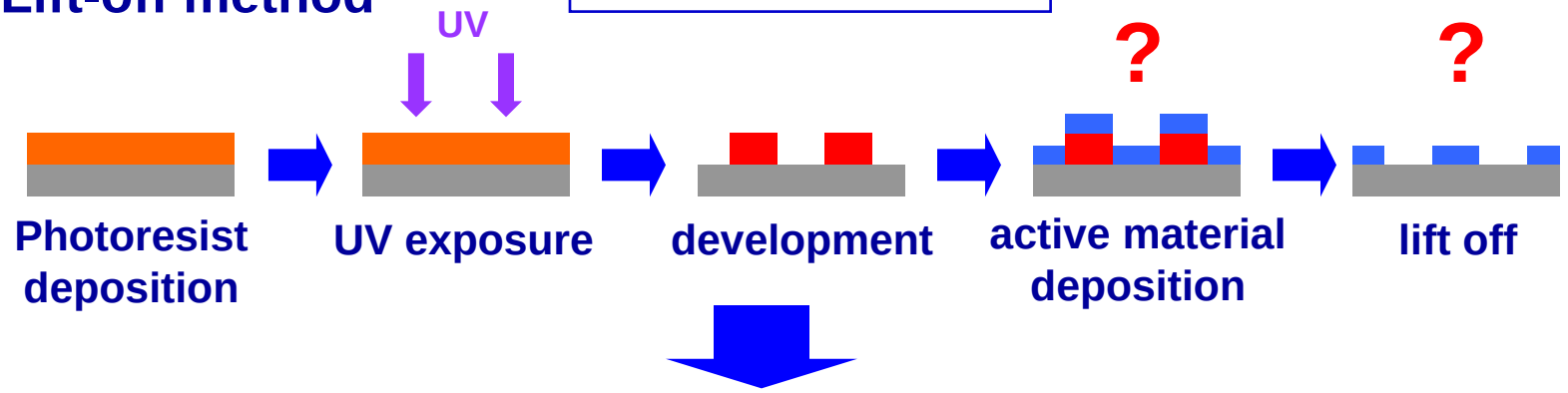
But… Chemical compatibility issues between process chemicals and organic electronic materials!

Problems in Photolithographic Patterning of Organic Materials

➢ Etching method



➢ Lift-off method



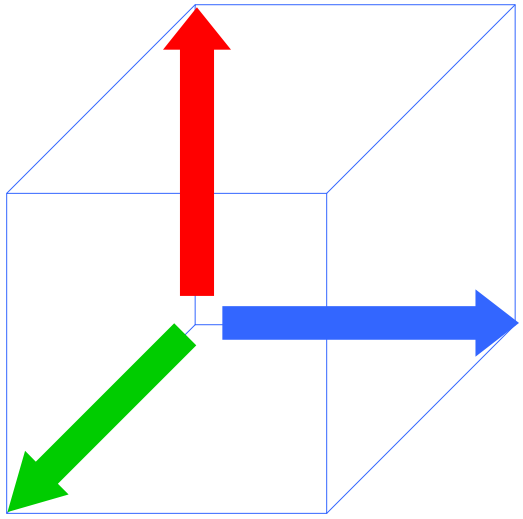
Development of lithographic conditions in chemically non-damaging solvent system

Orthogonal Patterning

Research Objectives

To develop processes and materials for the fabrication of organic/flexible electronic devices employing chemically benign, environmentally-friendly process solvents

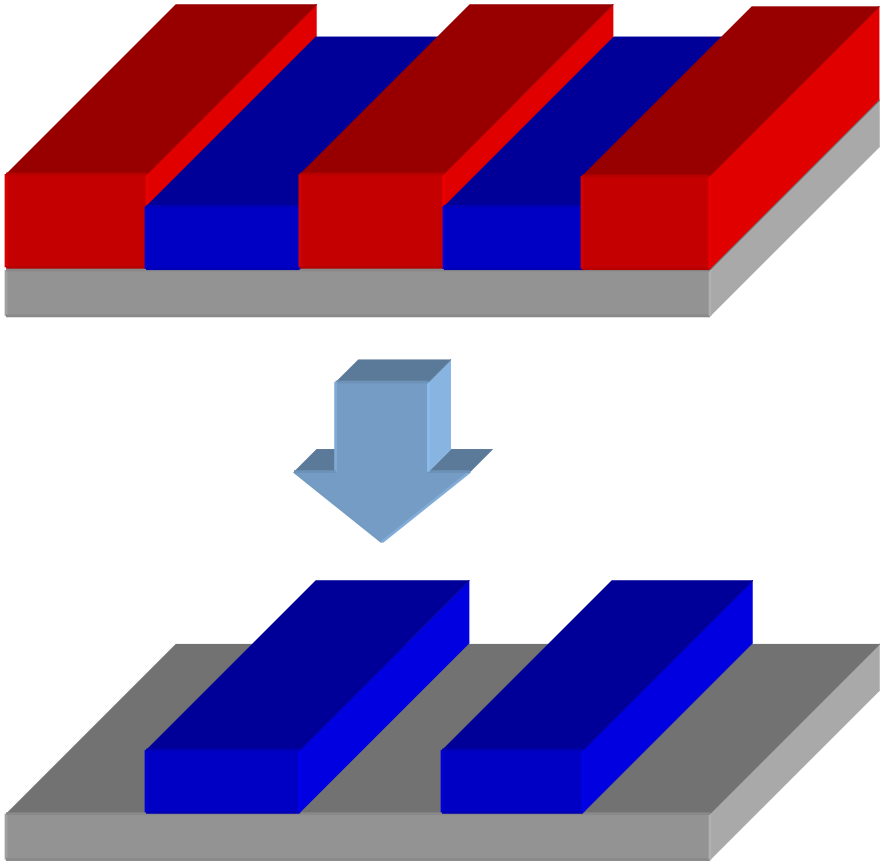
Orthogonal solvents
($scCO_2$ & fluorous liquids)



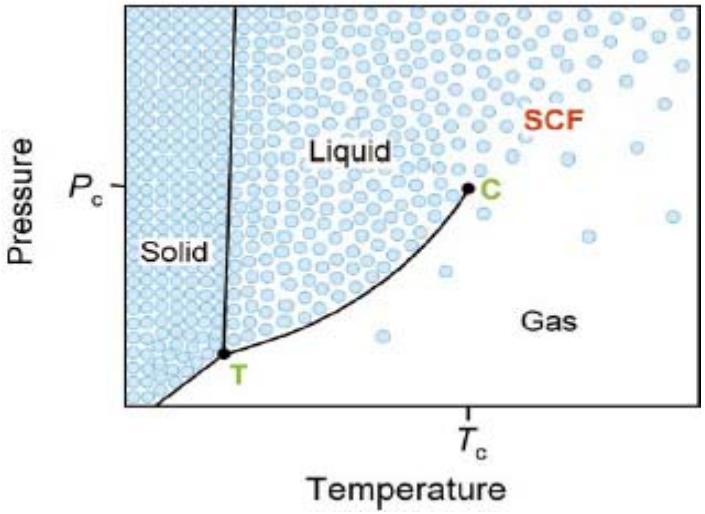
Hydroxylic solvents

Non-polar organic solvents

- ✓ ***Patterning Organic Electronic Materials employing Fluorinated Photoresists in Hydrofluoroethers***

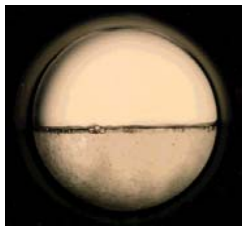


Supercritical Carbon Dioxide ($scCO_2$)

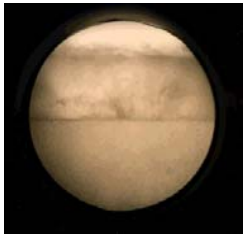


(T_c = 31.1 ºC, P_c = 72.8 bar)

J. Mater. Chem. 2000, **10**. 207.



Below critical point
- separate liquid and gas phases



Near critical point
- meniscus begins to fade

Above critical point
- no meniscus, homogeneous phase

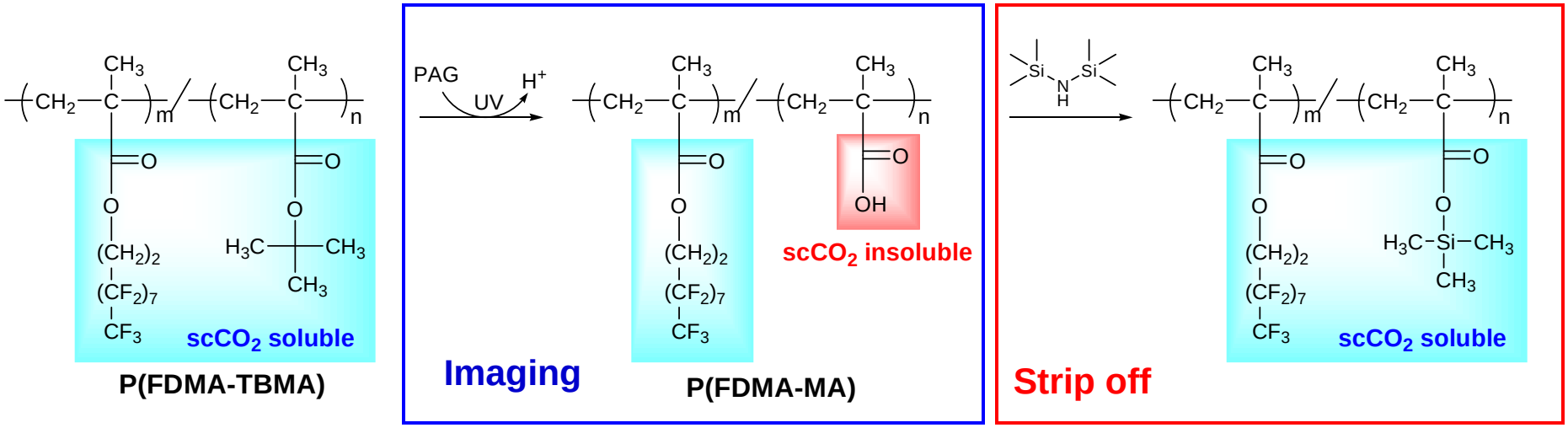
J. Chem. Soc., Perkin Trans. 1, 2001, 917.

- **Most non-fluorinated materials are stable in $scCO_2$**
- **Environmentally safe**
- **Cheap and readily available**

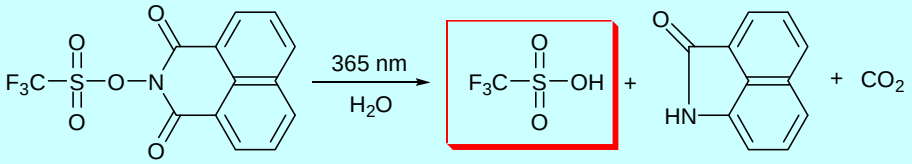
$scCO_2$ is promising to develop photoresist patterns!

Photoresist Processable in $scCO_2$

Mechanism



Acid generation from PAG

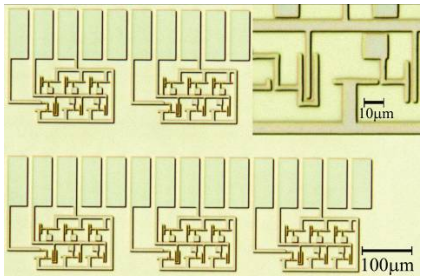


Chemical Physics Letters, 2007, **443**, 323.

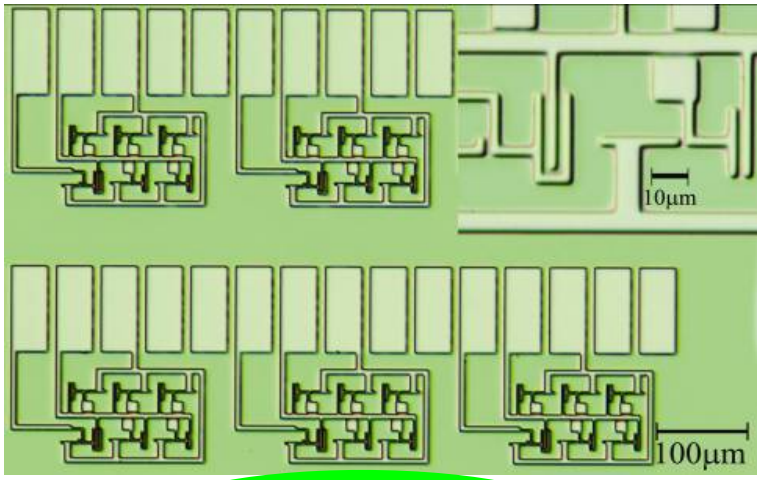
H. S. Hwang, *et al., J. Mater. Chem.*, 2008, 18, 3087.

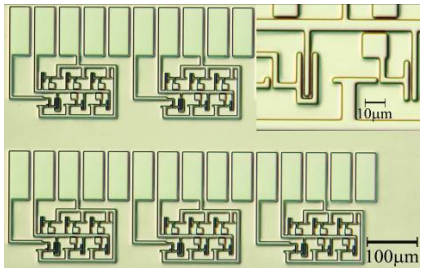
Lithographic Evaluation of Resist

Good adhesion and pattern development on PEDOT:PSS film

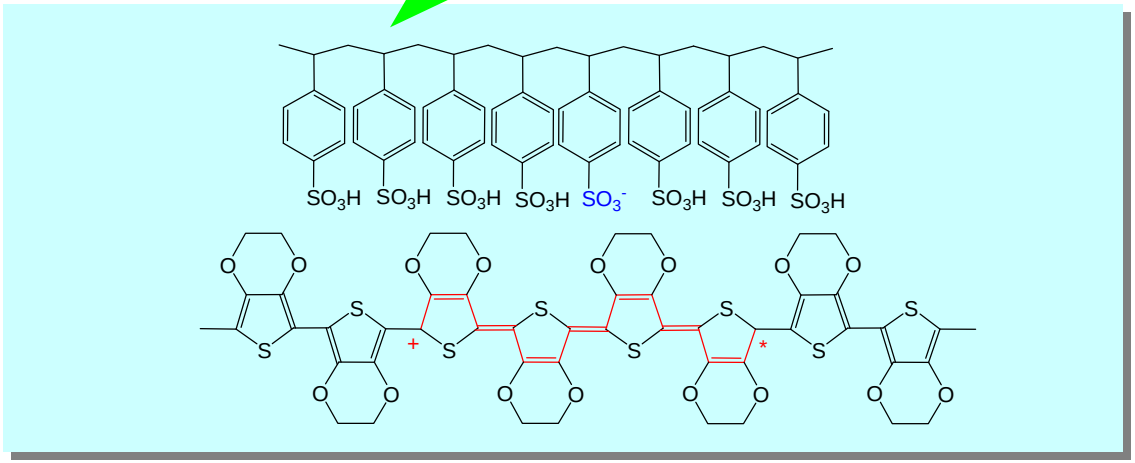


Glass



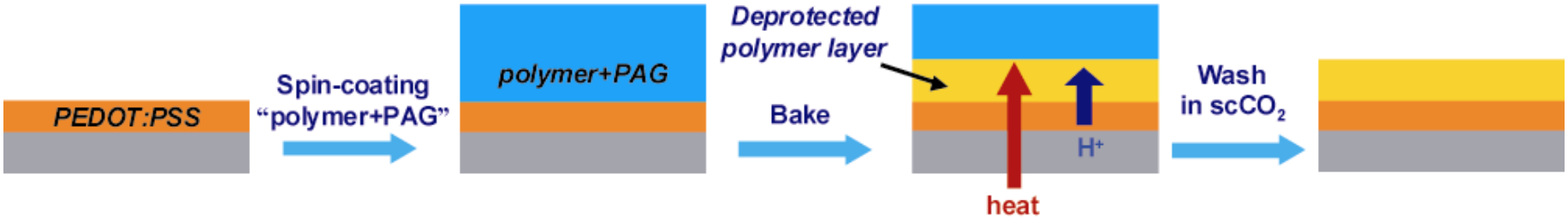


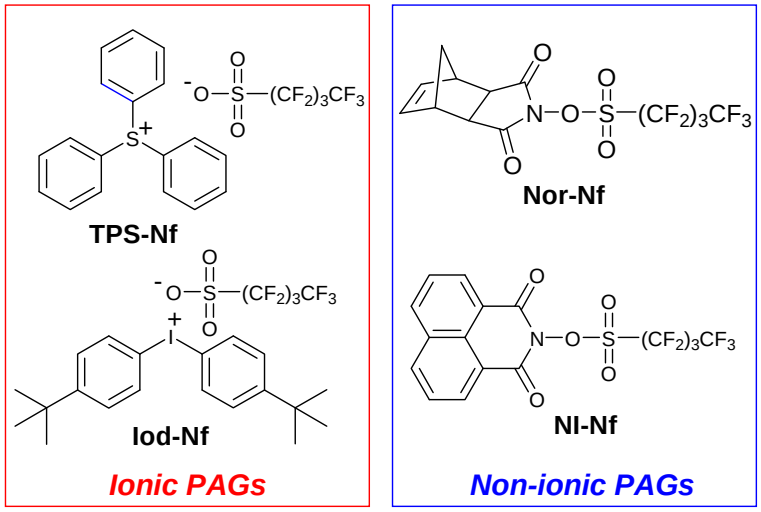
Aluminum

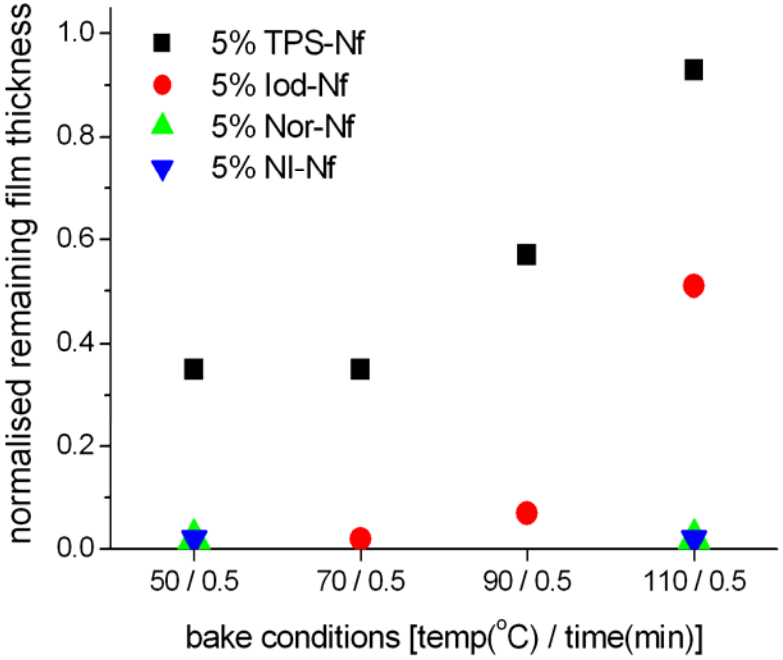


Acid-Diffusion from PEDOT:PSS Film

Unexpected decomposition of acid-labile photoresist was resolved through a careful selection of photoacid generator



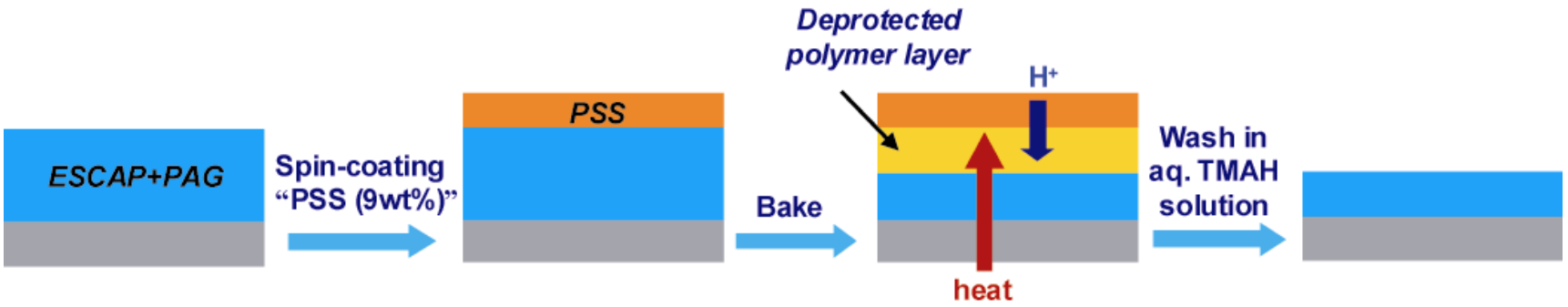


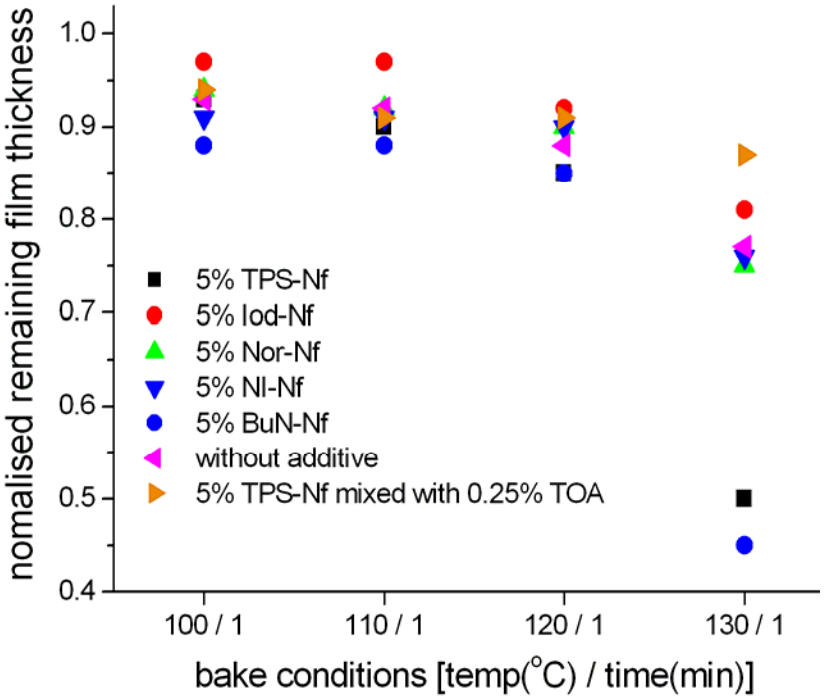


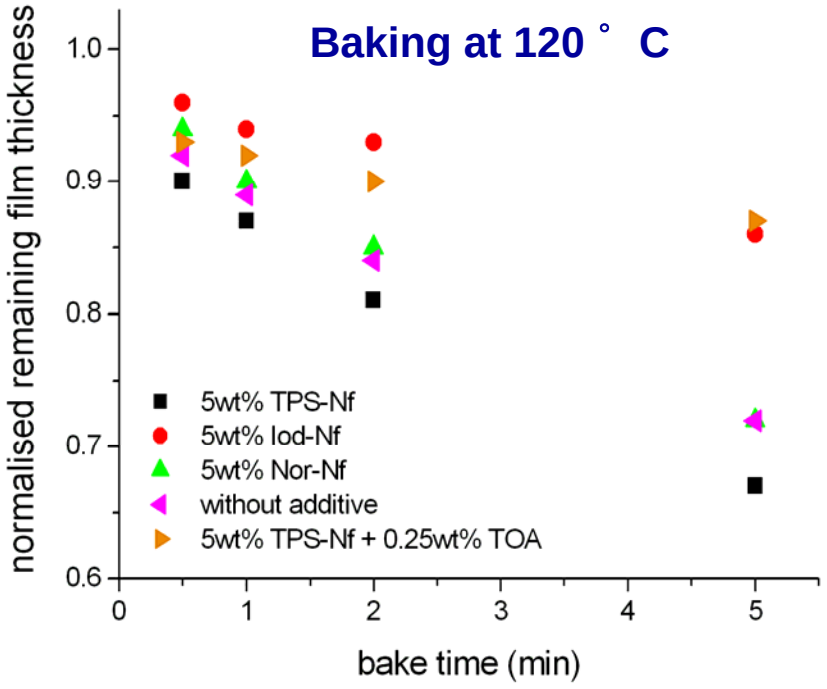
J.-K. Lee, *et al., J. Mater. Chem.*, 2009, 19, 2986.

Acid-Diffusion in Conventional Resist

The same result was observed in case of ESCAP resist

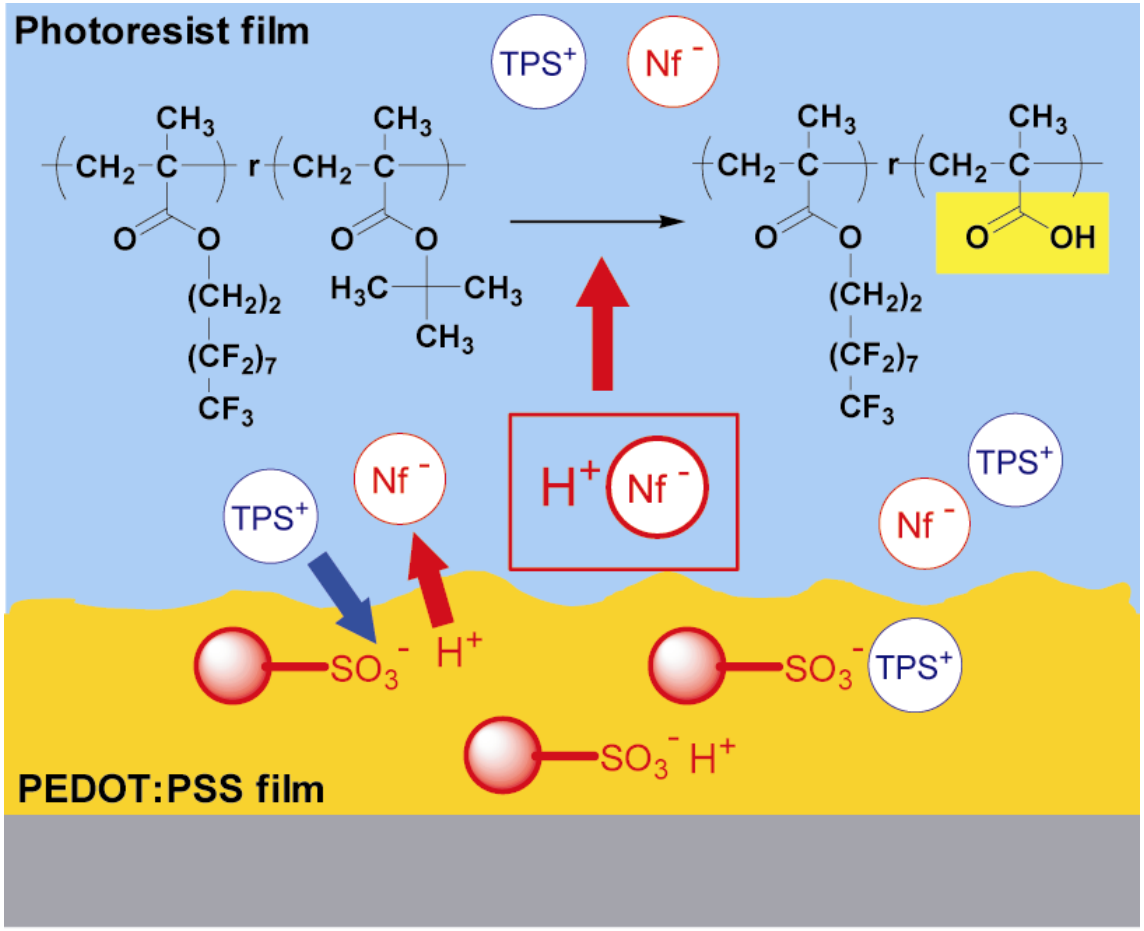






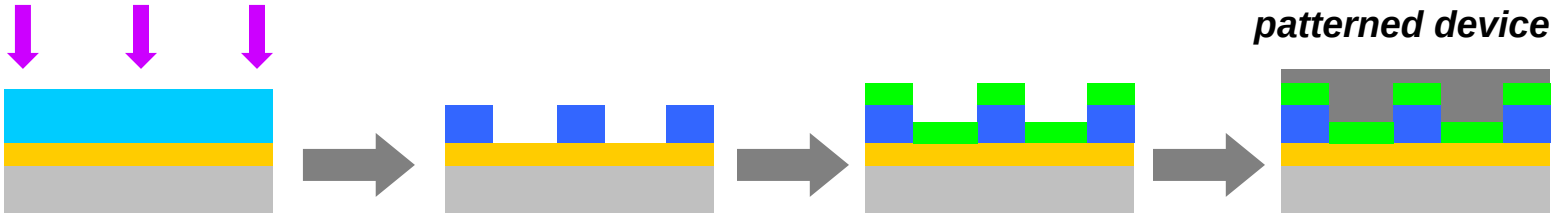
Acid-Diffusion: Proposed mechanism

Ion exchange in the interfacial region has been suspected



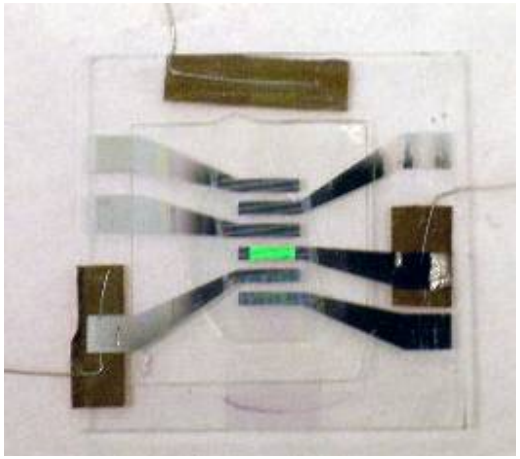
J.-K. Lee, *et al., J. Mater. Chem.*, 2009, 19, 2986.

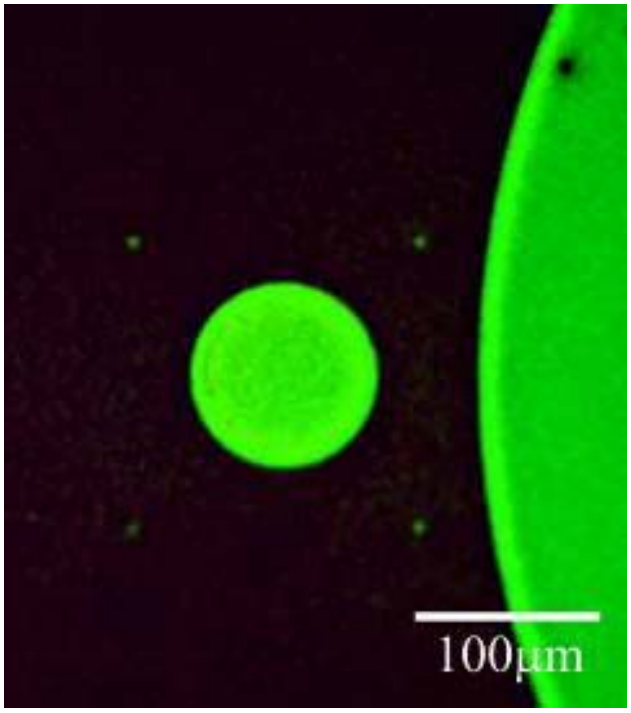
Patterning OLED in $scCO_2$



UV exposure & development in $scCO_2$ | LEP deposition | cathode deposition

- CsF/Al cathode
- light emitting polymer
- exposed resist
- unexposed resist
- PEDOT:PSS
- ITO glass

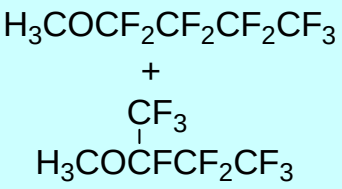




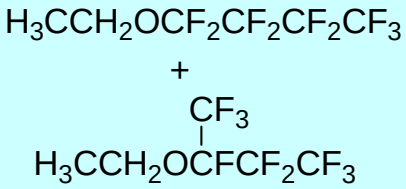
- 5 μm fine features were realized
- luminous efficiency of *ca.* 22 cd/A

H. S. Hwang, *et al., J. Mater. Chem.*, 2008, 18, 3087.

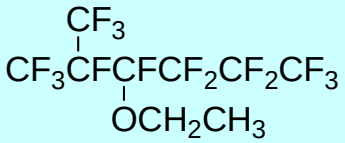
Hydrofluoroethers (HFEs)



HFE-7100 (bp 61 °C)



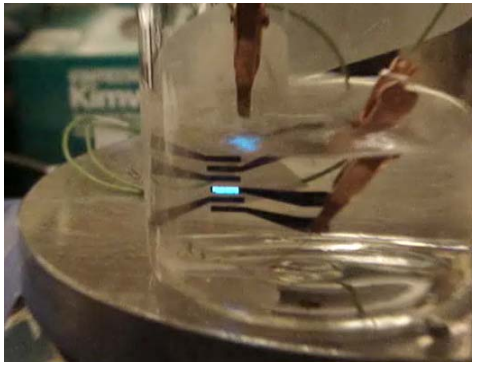
HFE-7200 (bp 76 °C)



HFE-7500 (bp 130 °C)

- Commercialized by 3M
- Benign to non-fluorinated organic electronic materials
- Environmentally safe (zero-ozone depletion potential)
- Facile recycling

EL device with $Ru(bpy)_3(PF_6)_2$



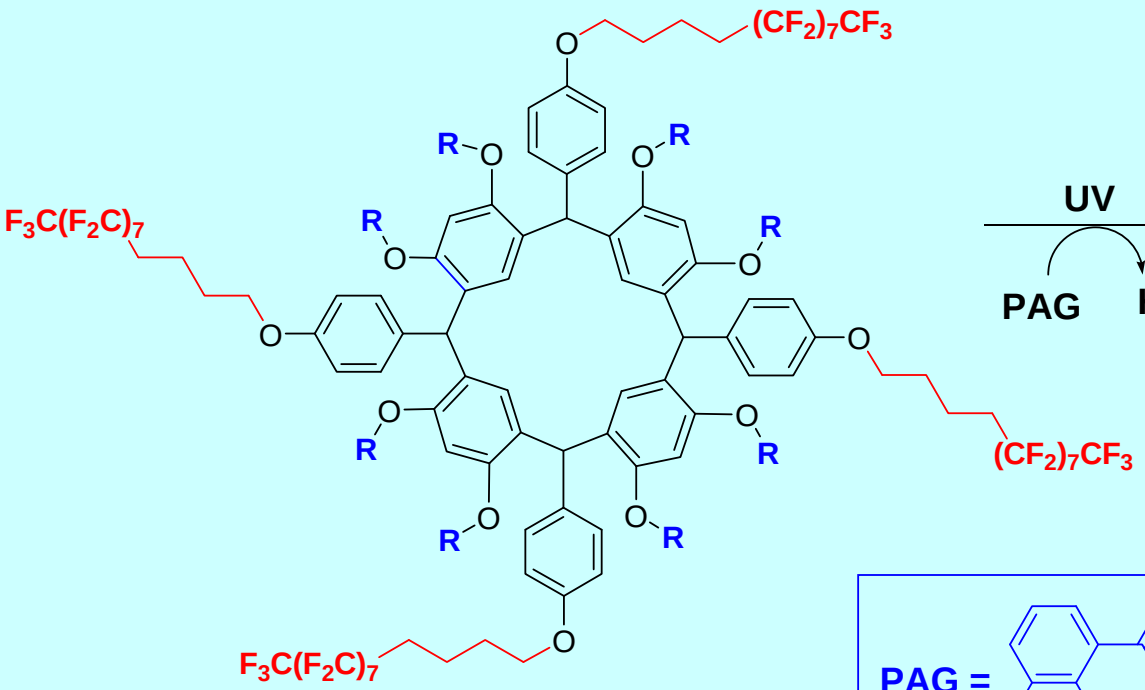
EL device with poly(dioctylfluorene)

HFEs are *orthogonal solvents* for organic electronic devices

A. A. Zakhidov, J.-K. Lee, H. H. Fong *et al., Adv. Mater.,* 2008, 20, 3481.

Molecular Resist Processable in HFEs

Chemically amplified molecular resist processable in HFEs



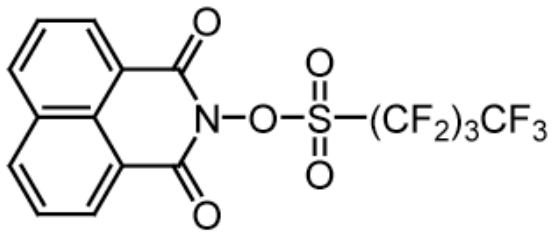
J.-K. Lee, *et al., J. Am. Chem. Soc.*, 2008, 130, 11564.

Lithographic Performance Evaluation

Spin-coated from HFE-7500 (4 parts) + PGMEA (1 part) mixture

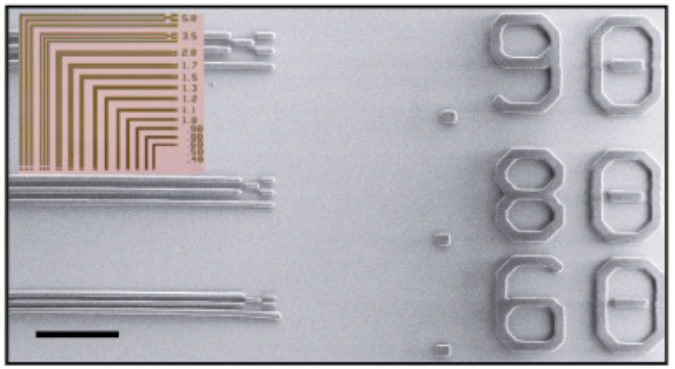
Pattern developed in HFE-7200

(a)

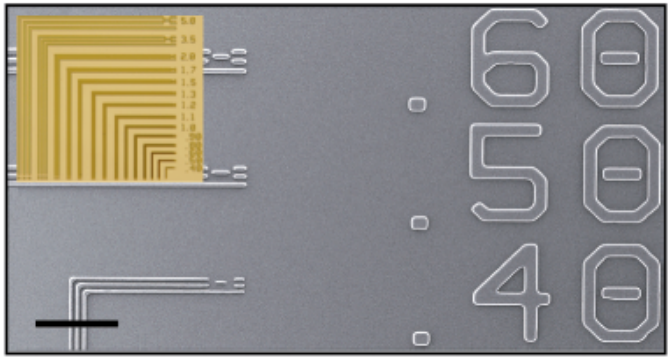


J. Photopolym. Sci. Technol., 2003, *16*, 91.

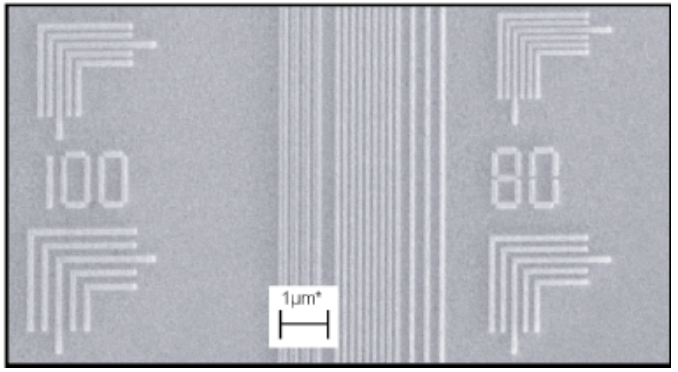
(b)



(c)



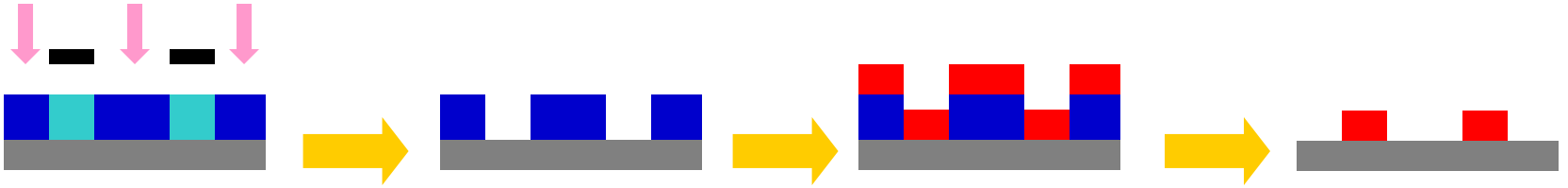
(d)



(a) Structure of a PAG. (b) Glass. (c) Polyimide-coated wafer (scale bars are 10 μm). (d) SEM image on Si under e-beam exposure (80 nm features).

Patterning Materials by Lift-off

Patterning of various electronic materials was successful

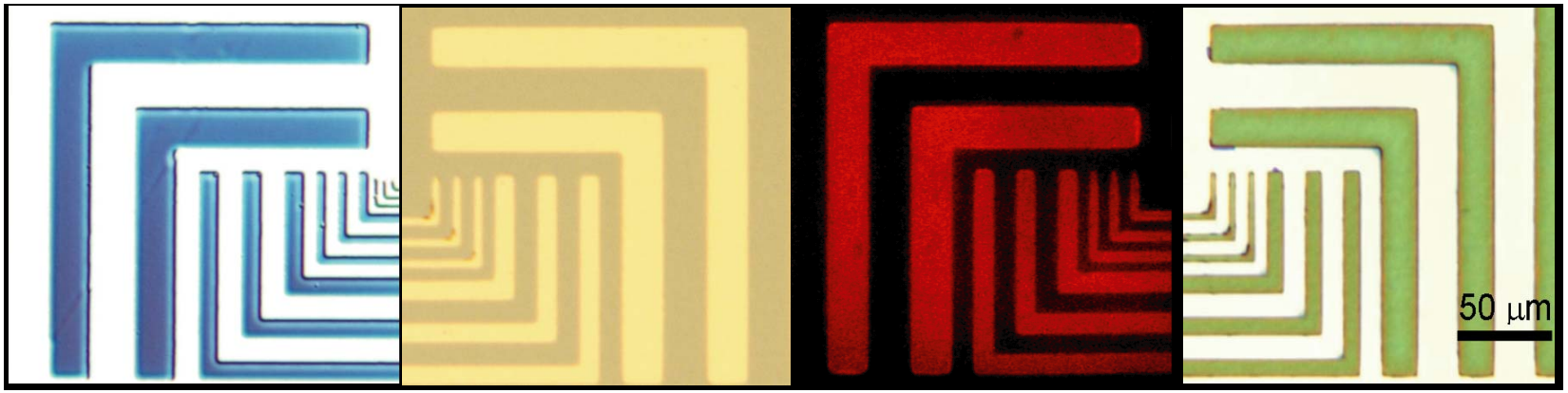


i-line UV exposure

Development In HFE-7200

Active material deposition

Lift-off resist in HFE-7200+IPA (5wt%)



PEDOT:PSS (80 nm)

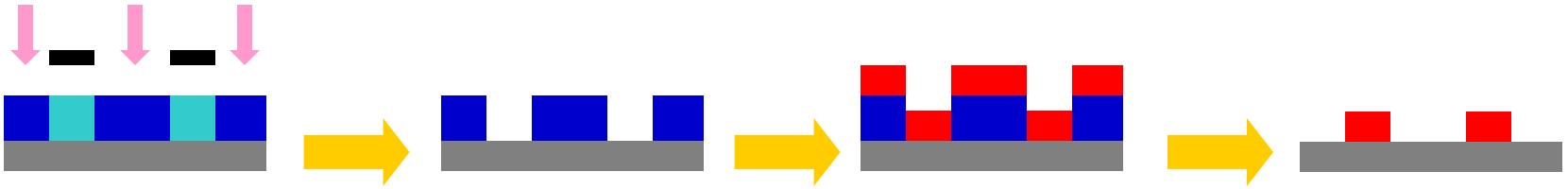
Gold (30 nm)

$Ru(bpy)_3(PF_6)_2$ (100 nm)

P3HT (30 nm)

Patterning Materials by Lift-off

Patterning of various electronic materials was successful



i-line UV exposure

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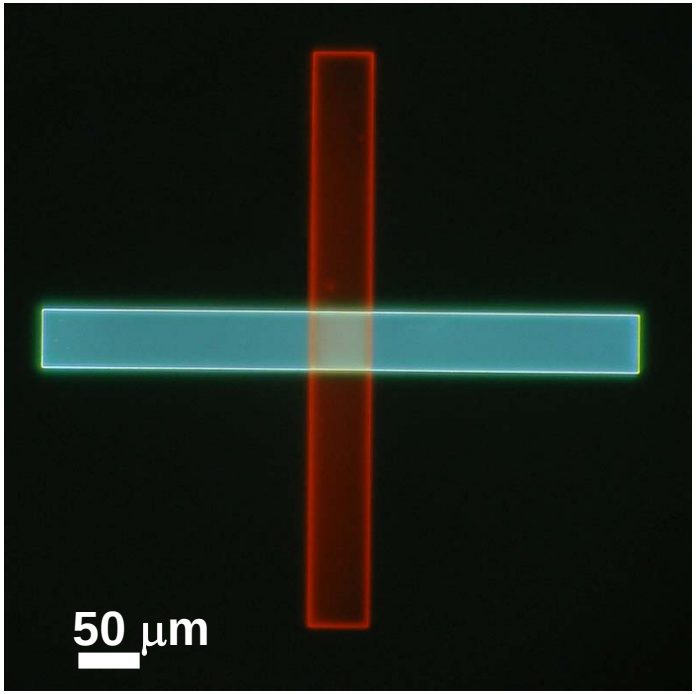
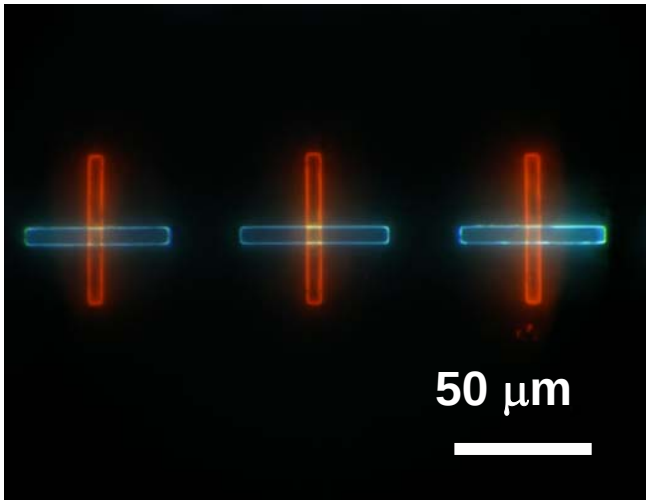
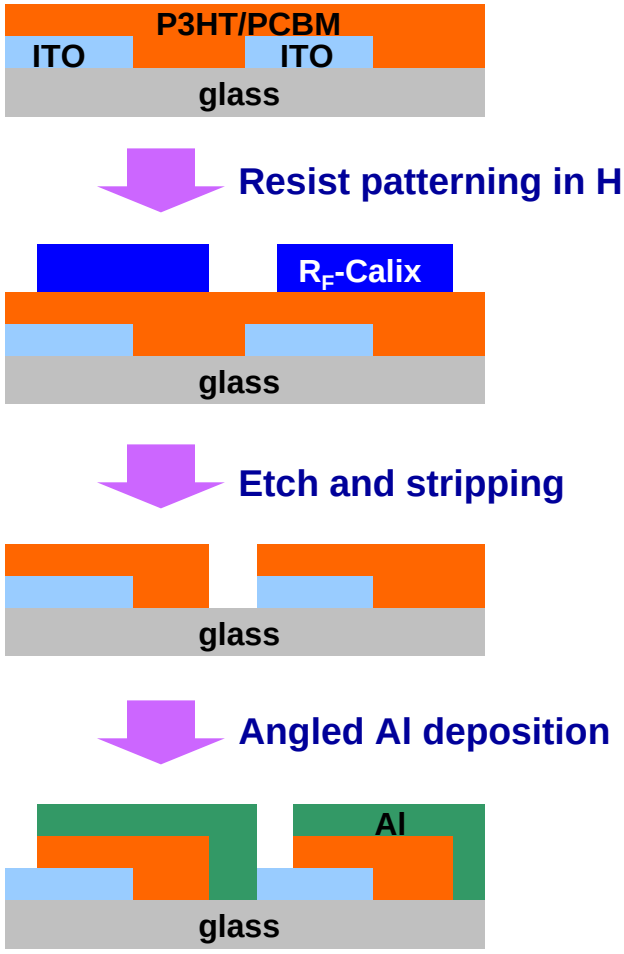


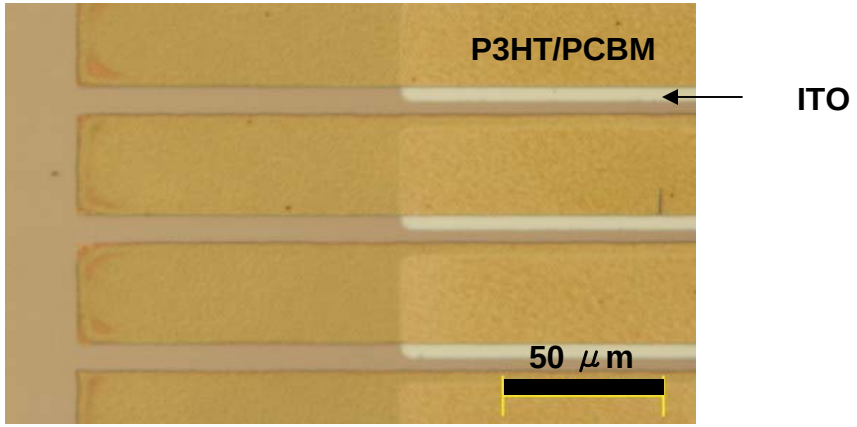
1st layer: polyfluorene (PF8)
2nd layer: $Ru(bpy)_3(PF_6)_2$



High Voltage Polymer Solar Cell

P3HT/PCBM solar cell patterned by orthogonal patterning





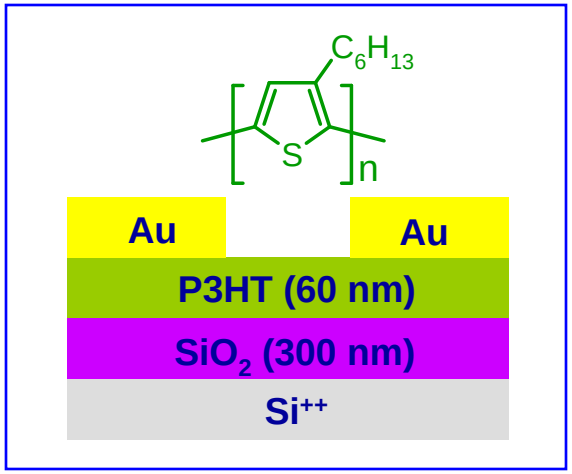
	Ours	Lit.[1]
Voc (V)	89.6	880
# cells	300	24,000
Voc/cell (V)	0.3	0.04
Jsc/cell (mA/cm^2)	4.2	0.34
FF	0.24	0.25
PCE (%)	0.31	0.008

1. M. Niggemann *et al.*, *Adv. Mater.*, 2008, 20, 4055.

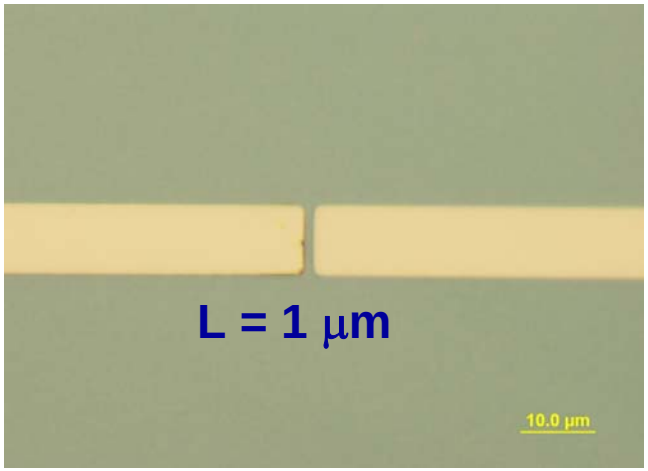
Y.-F. Lim, *et. al.*, *J. Mater. Chem.*, 2009, 19, 5394.

Application to Device Fabrication

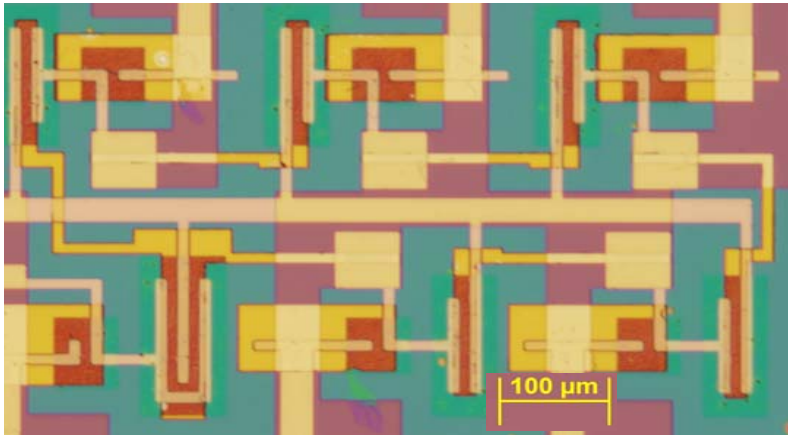
Organic FETs having top-contact source-drain geometry

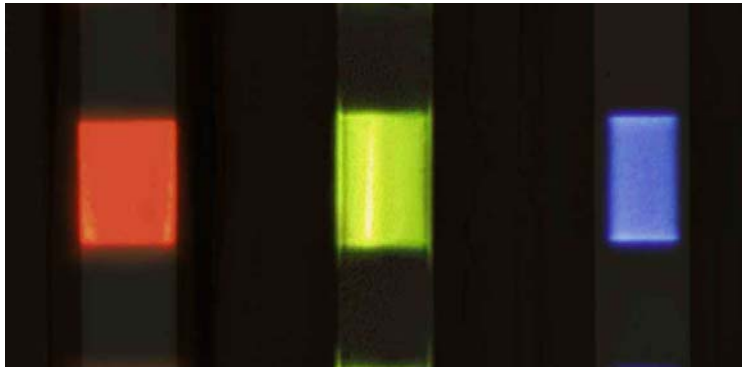


Deposit Au contacts without using shadow masks



Mobility: μ_{SAT} = 0.01 $cm^2V^{-1}s^{-1}$ (0.45 for pentacene)

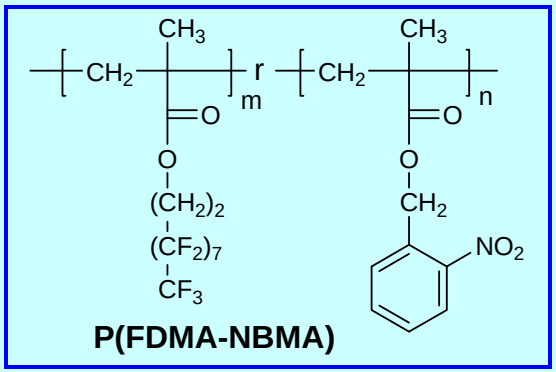




unpublished result

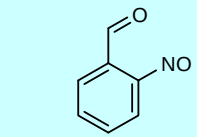
Orthogonal Patterning of PEDOT:PSS

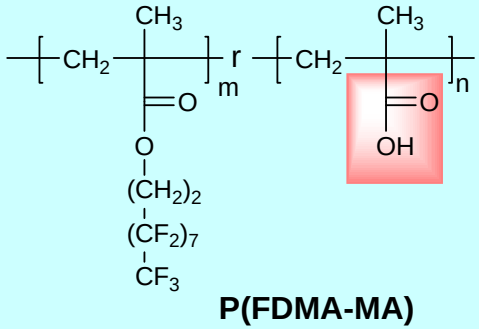
Synthesis of acid-inert photoresist system specially designed for PEDOT:PSS patterning



P(FDMA-NBMA)

soluble in HFEs



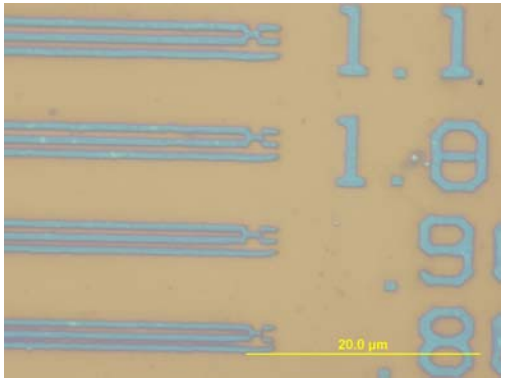


P(FDMA-MA)

insoluble in HFEs

SEM image of P(FDMA-MA) on top of PEDOT:PSS film

O_2 plasma etch

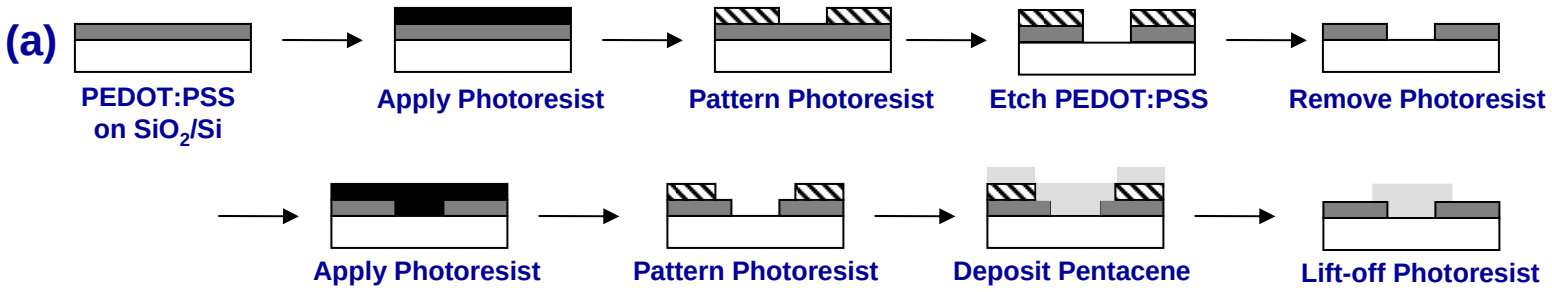


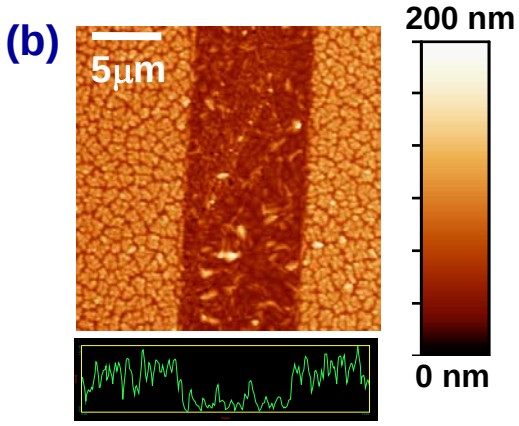
Optical image of patterned PEDOT:PSS film

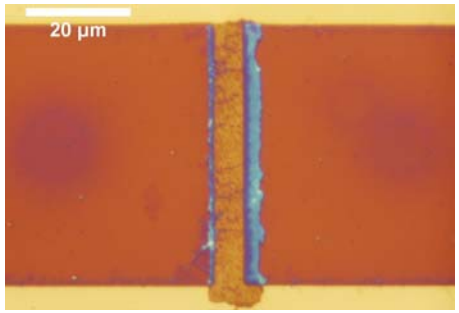
P. G. Taylor, *et al., Adv. Mater.*, 2009, 21, 2314.

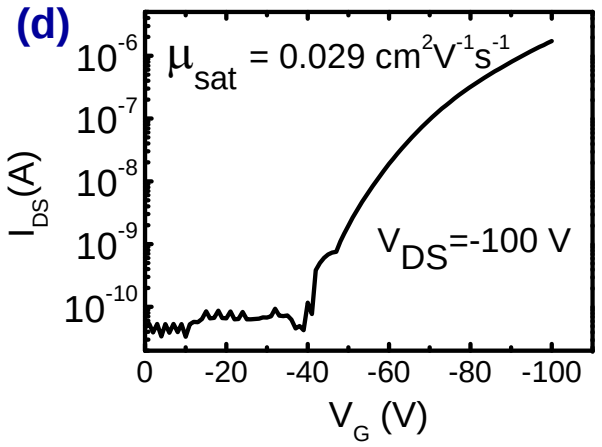
Orthogonal Patterning of PEDOT:PSS

Application to OTFT fabrication: PEDOT:PSS electrodes and pentacene active layer were patterned photolithographically





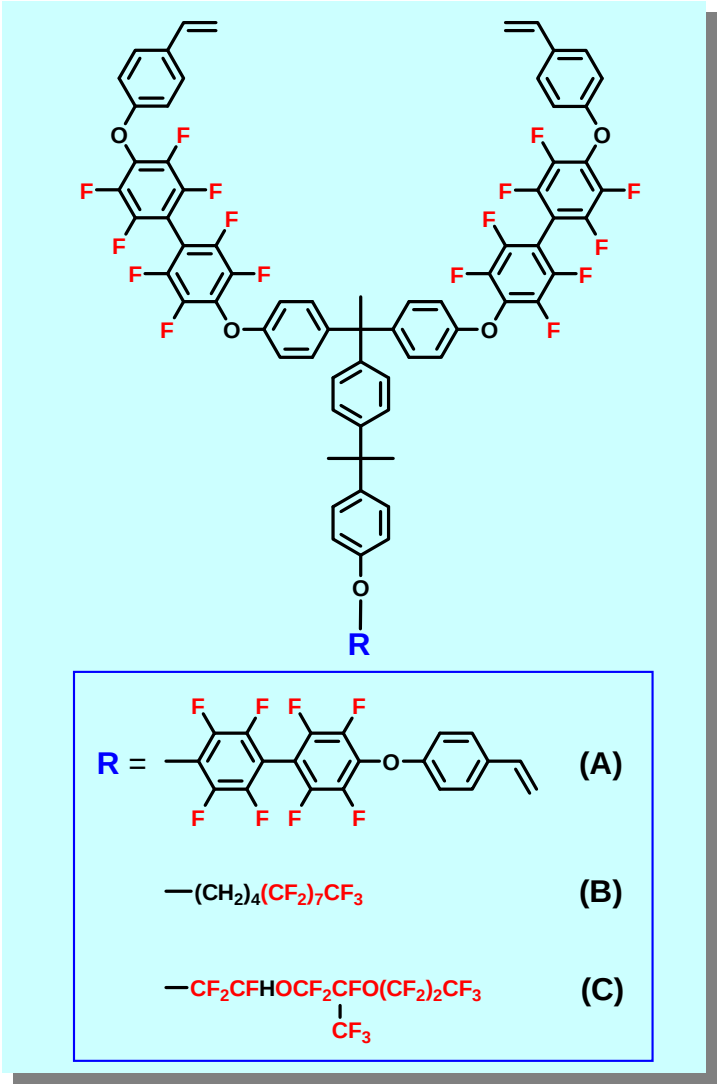




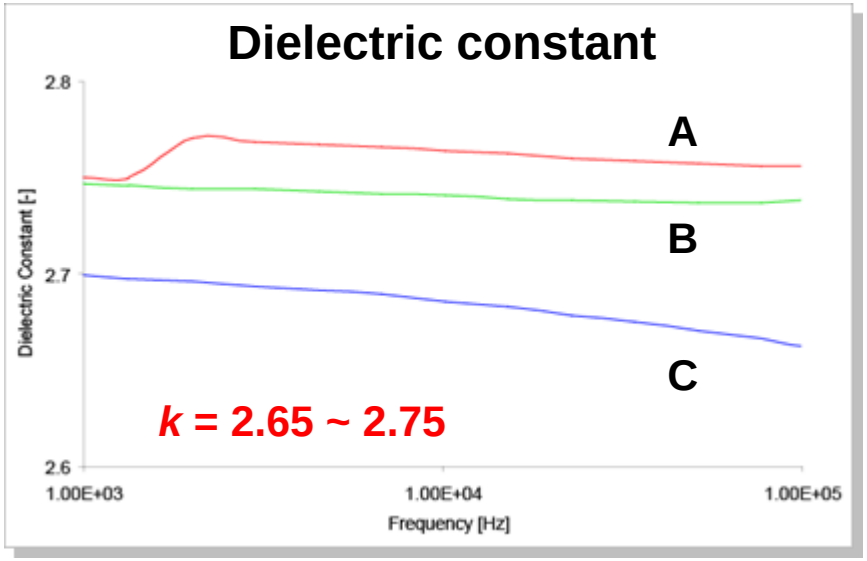
PEDOT:PSS/Pentacene bottom-contact OTFT (a) Schematic illustration of device fabrication, (b) AFM images of a 5 μm (width) x 50 μm (length) Pentacene channel between PEDOT:PSS electrodes (c) optical image of OTFT, (d) device performance plots

Patternable Low-*k* Materials in HFEs

Molecular precursors for low-*k* Materials processable in HFEs



- Solution processable
- Thermally stable (>400 °C by TGA)
- Cross-linkable by H^+
- Low dielectric constant



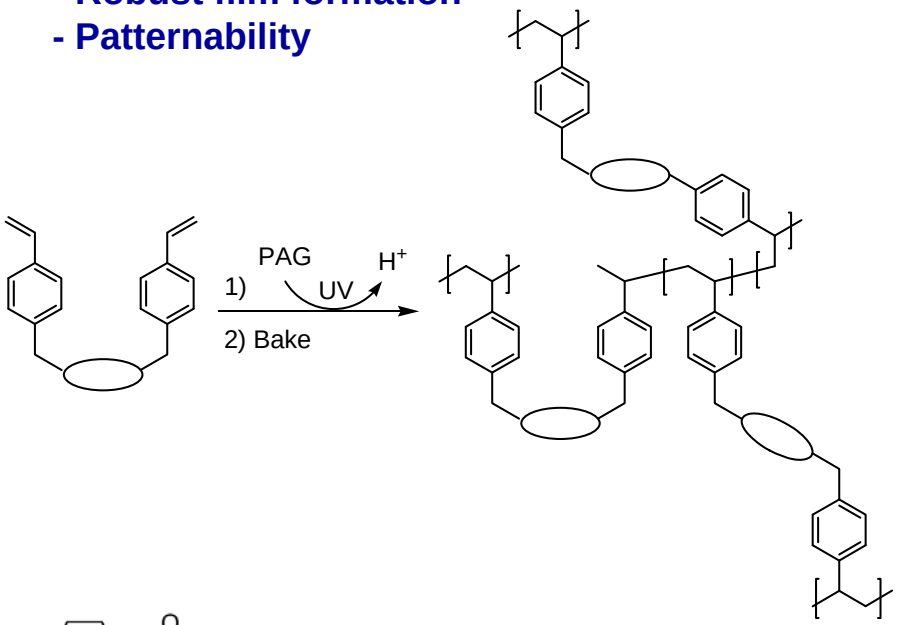
E. Murotani, *et al., ACS Appl. Mater. Interfaces,* 2009, *Accepted.*

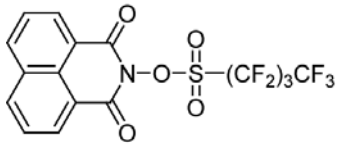
Patternable Low-*k* Materials in HFEs

Photolithographic Patterning in HFEs

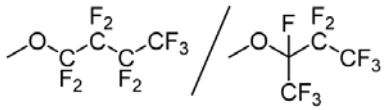
Crosslinking reaction

- Robust film formation
- Patternability



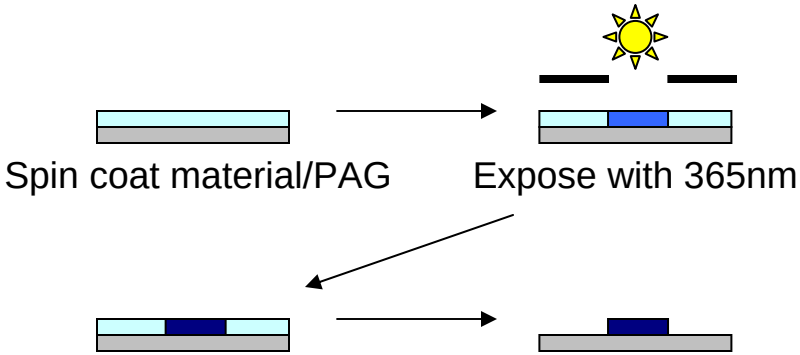


PAG

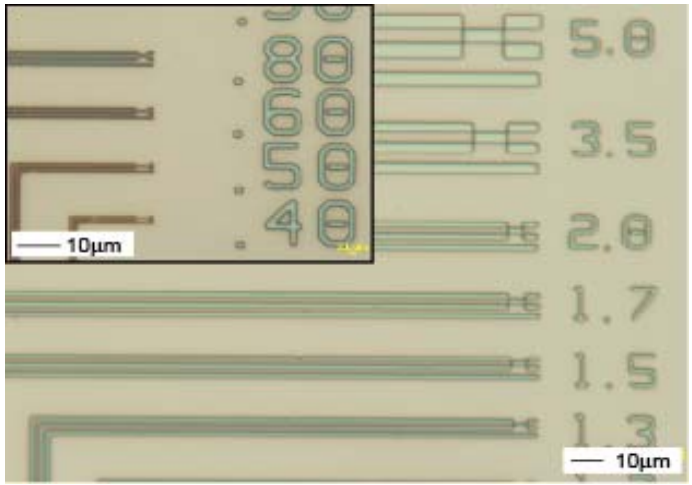


HFE-7100 (b.p. 61°C)

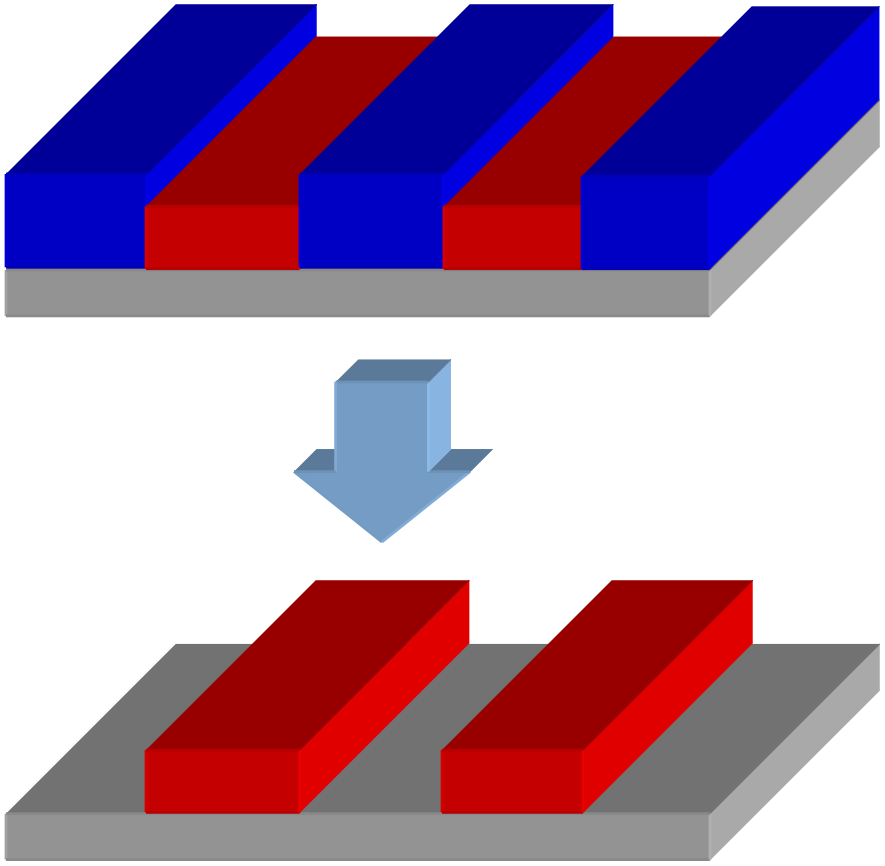
To prove patternability in HFEs



Successful patterning in HFE-7100

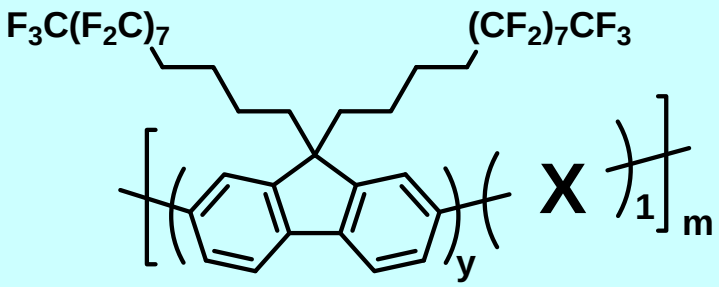


- ✓ ***Patterning Fluorinated Electronic Materials employing Conventional Photoresists in Organic Solvents***

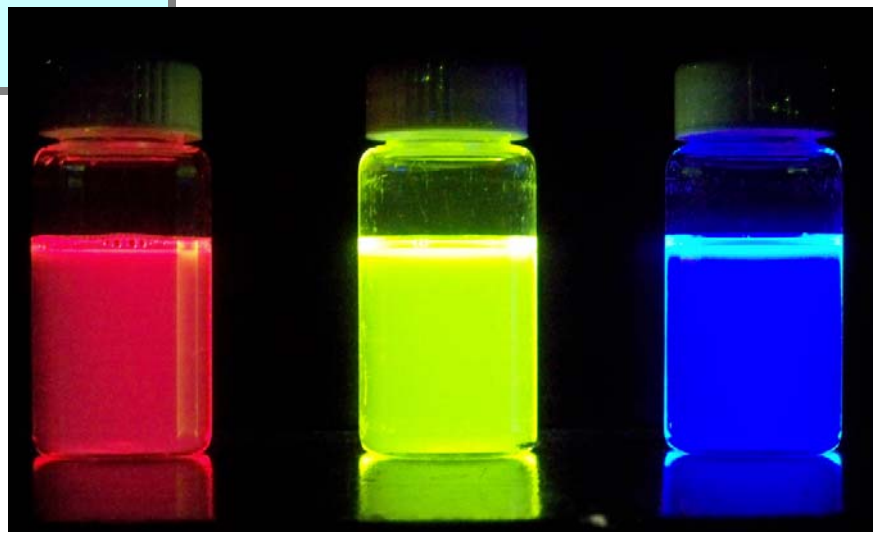


Semi-Perfluoroalkyl Polyfluorenes

Perfluoroalkyl polyfluorenes as blue light-emitting polymers



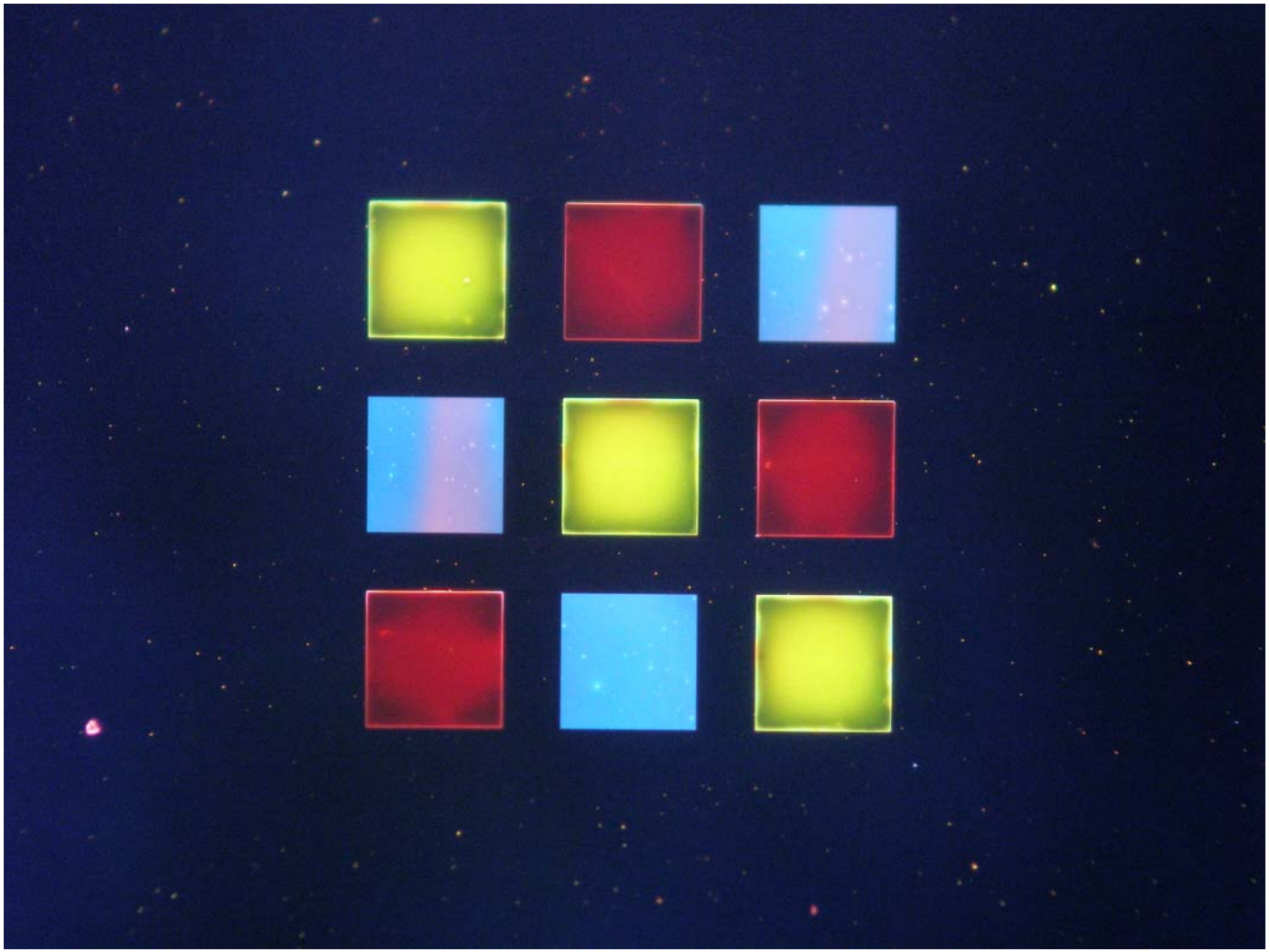
ca. 60% F content by weight



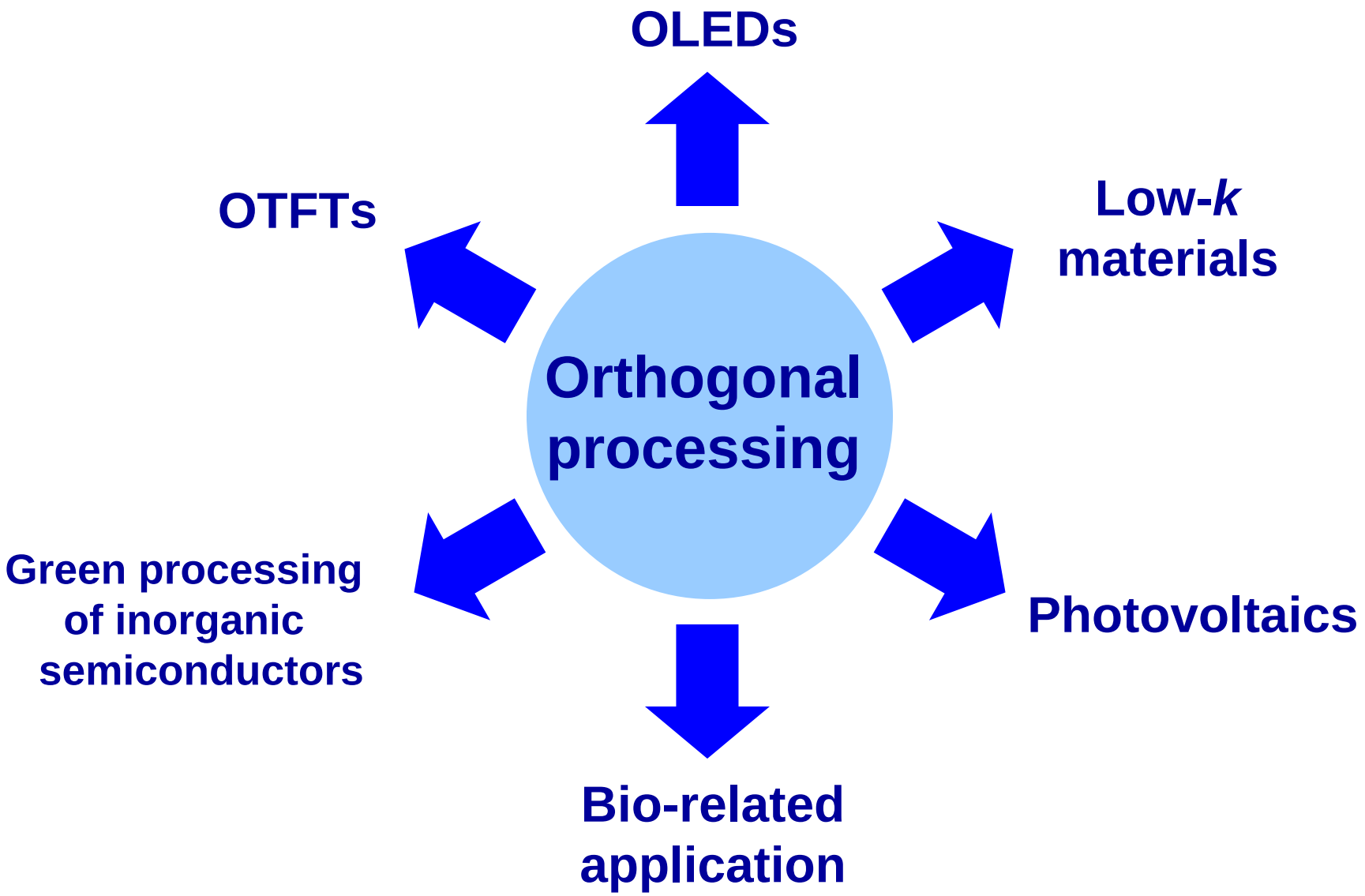
unpublished result

Application to Patterning

RGB patterning using conventional photoresists and organic solvents

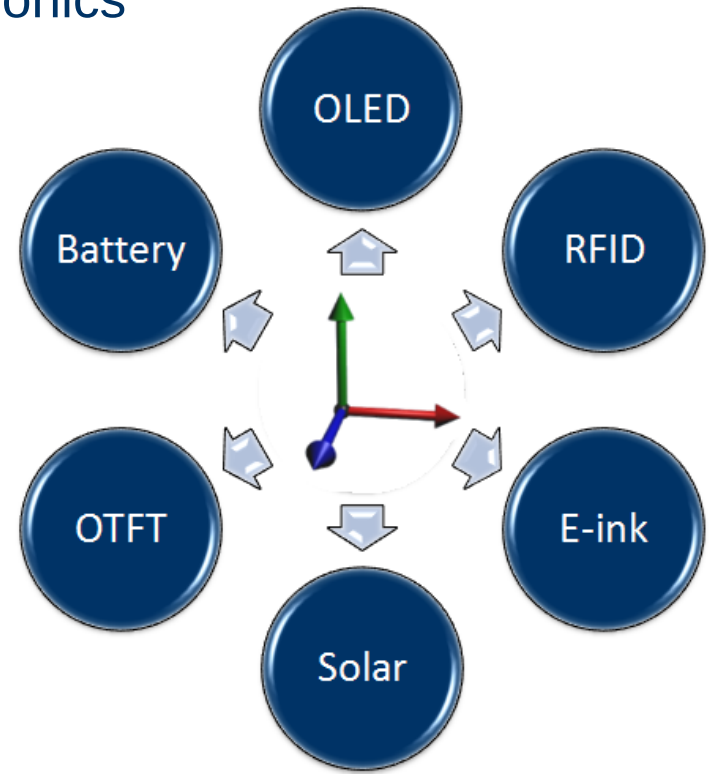


Potential of Orthogonal Processing



The Orthogonal Solution

- Patent-pending photoresist & process to manufacture organic electronics
  - Change photoresist chemistry to be compatible with sensitive organic systems
  - Enabling photolithography infrastructure to produce organic electronics



www.orthogonalinc.com

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Summary

- ✓ **Concept of *Orthogonal Processing* for the patterning of organic electronic materials has been proposed**
- ✓ **HFEs have been identified as environmentally-friendly, chemically non-damaging solvents for *orthogonal processing***
- ✓ **Acid-sensitive perfluoroalkyl resorsinarene has been developed and employed successfully in OTFT and OLED fabrication**
- ✓ **Semi-perfluoroalkyl polyfluorenes have been synthesized and patterned with conventional photoresist and organic solvents**

Acknowledgement

Materials World Network Team at Cornell

Alex Zakhidov, Priscilla Taylor, Hon Hang Fong, Eisuke Murotani, John DeFranco, Margarita Chatzichristidi, Ha Soo Hwang
Prof. George Malliaras

Materials World Network Team at Melbourne, Australia

Georgia McCluskey, Wallace Wong
Prof. Andrew Holmes (Melbourne, Australia)

National Science Foundation/Australian Research Council (Materials World Network, DMR-0602821)
National Science Foundation IGERT program
New York State Foundation for Science, Technology and Innovation (NYSTAR)

Cornell NanoScale Facility (Photolithography)
3M (HFE series solvents)
Asahi Glass (GPC in fluorous solvents)