

# *Microstructured Conducting Polymers On-Chip*

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Dublin City University**

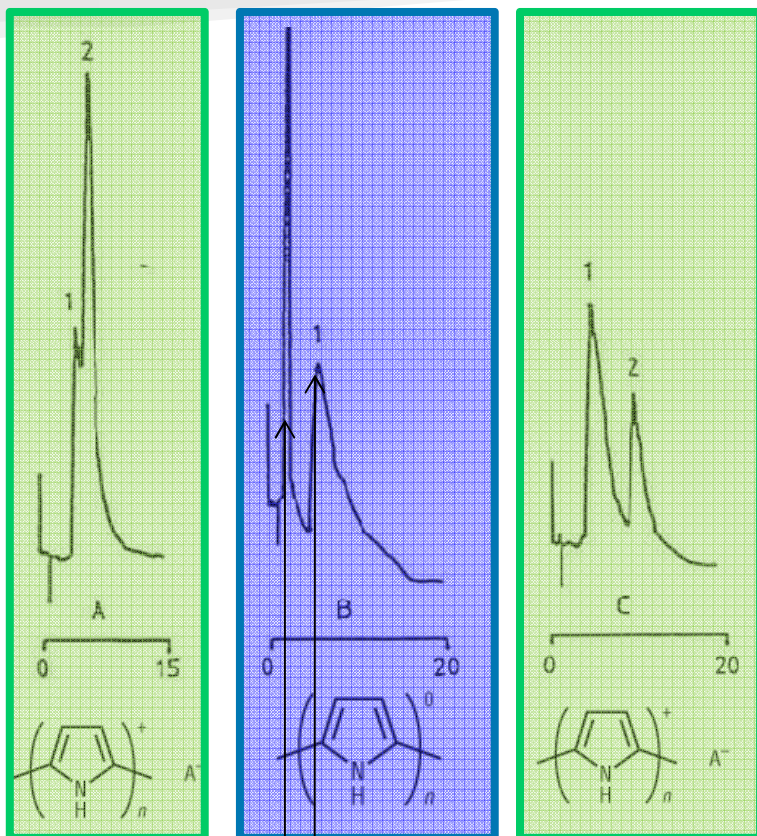


# Outline

- Conducting polymers in chromatography
- Fabrication of conducting polymer monoliths on-chip
- $\mu$ Chip electrochemical cell design
- Electrochemistry on-chip
- Applications



# Electroactive polymers as coatings on separation phases: Early work



- Particulate packing: Ppy-coated silica particles
- Chemical switching of Ppy states

Chriswanto & Wallace, J. Liq. Chrom. & Rel Technol., 19:2457 (1996)

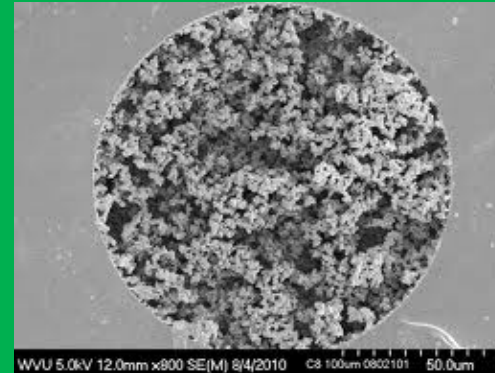
**15 YEARS ON.....  
TIME TO REVISIT!**



Caffeine  
Theophylline

# From particulates to monoliths in chromatography

Passive, inert structures comprised of rigid polymer rods  
UV or thermally curable monomers, e.g., methacrylates, styrenes etc.

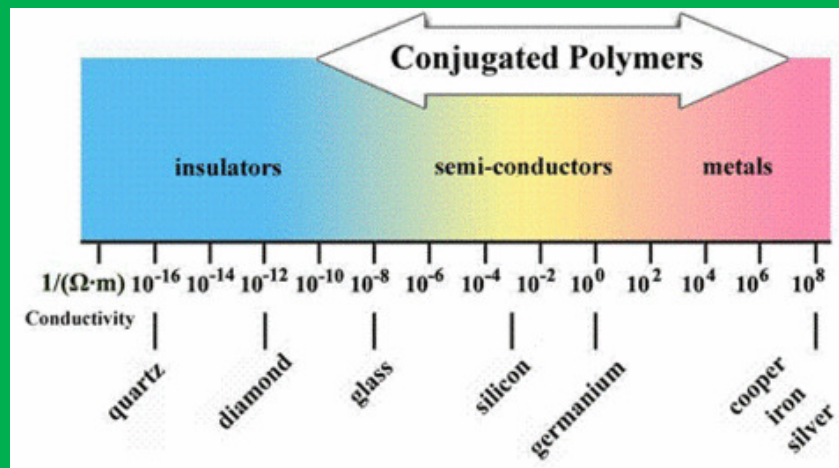


Do functional materials offer a viable alternative???

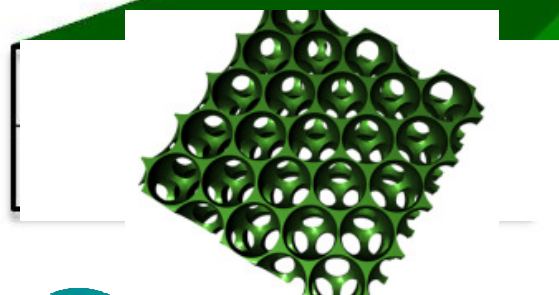
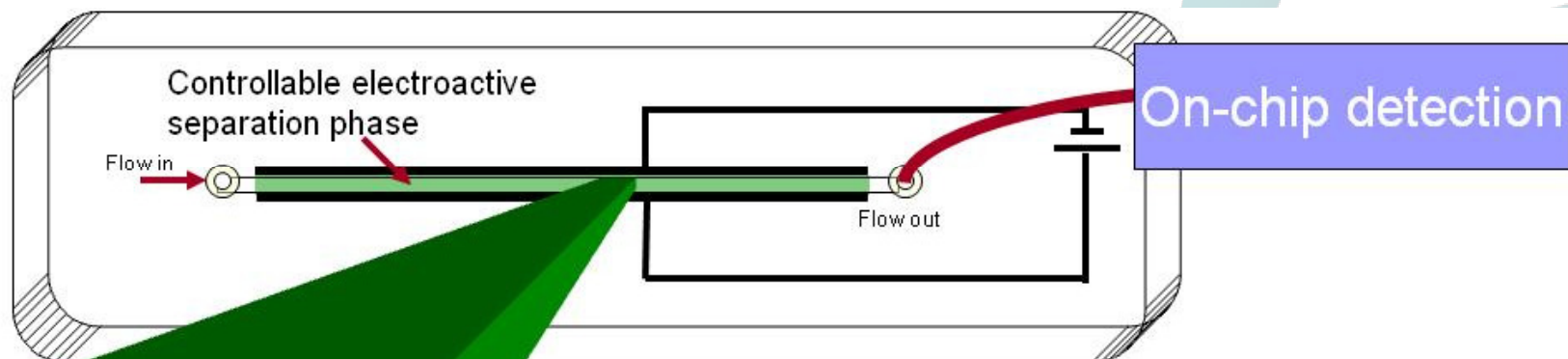
## Conducting polymers as

**monoliths** could provide:

- A new fabrication method
- Conducting stationary phases
- Dynamic separations (active)



# Electroactive Monolith $\mu$ Chip (EM $\mu$ )

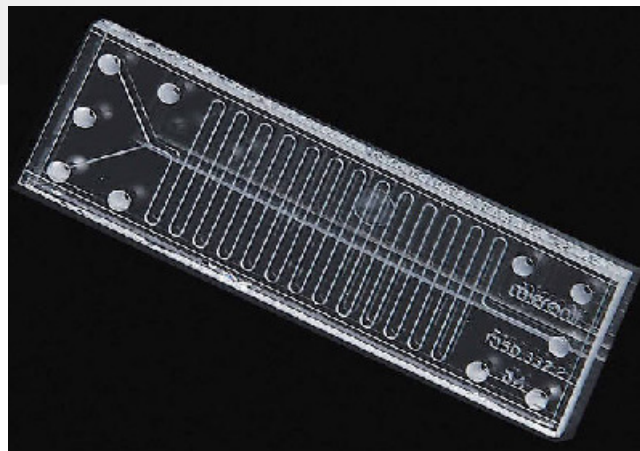


# EM<sub>μ</sub> credentials

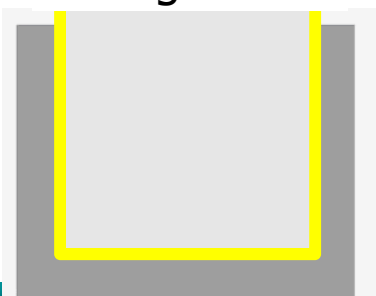
- Electrochemical growth of **uniformly templated** monolithic stationary phases
- Precise control over stationary phase fabrication enabling high reproducibility
- Micro-structuring of the monolithic stationary phase enabling:
  - Further decrease of the A-term in Van Deemter
  - Large flow through pores
  - Small skeleton size
- Precise electrochemical tuning of stationary phase before & during separation to affect:
  - Retention factors
  - Hydrophobicity/hydrophilicity
  - Pore size
  - Ionic capacity



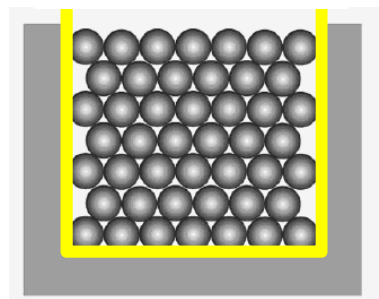
# Conducting polymer monoliths – fabrication on-chip



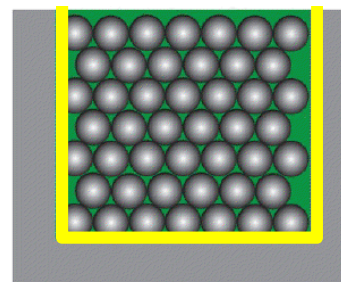
Working  
Electrode  
Integration



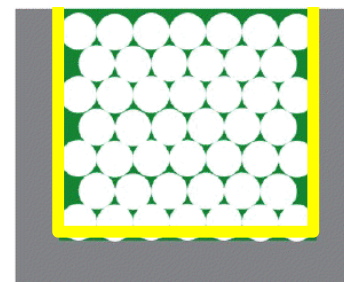
Template  
Deposition



Electrochemical  
Polymer  
Growth



Dissolution of  
Template



Channel Width: 110 micron

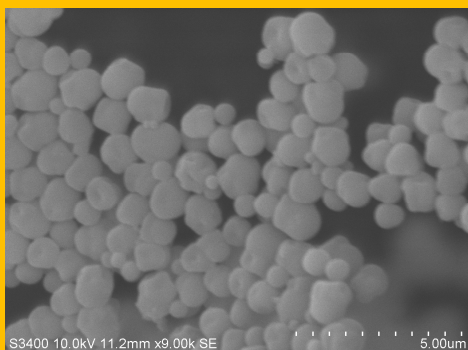
75th Prague Meeting on  
Macromolecules 2011



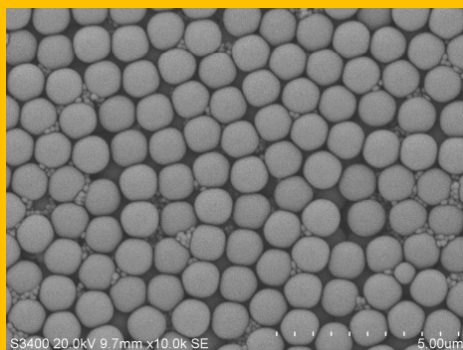
# Dissolvable PS template

## PS bead synthesis

Two Critical Factors:  
Appropriate cross-linker  
concentration to give uniformity and  
permit dissolution

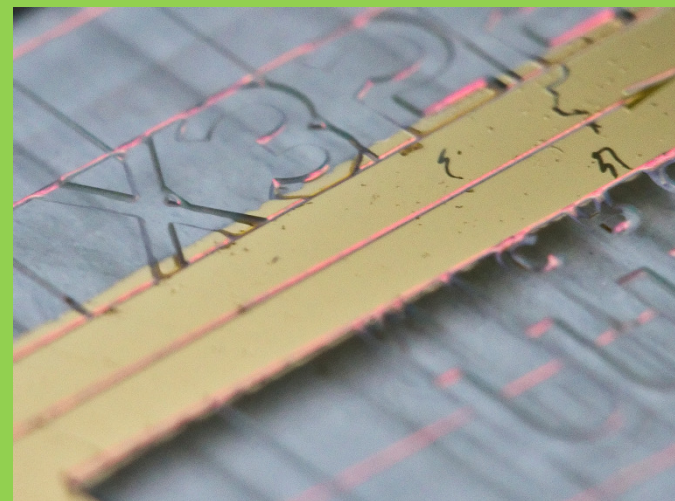


vs.



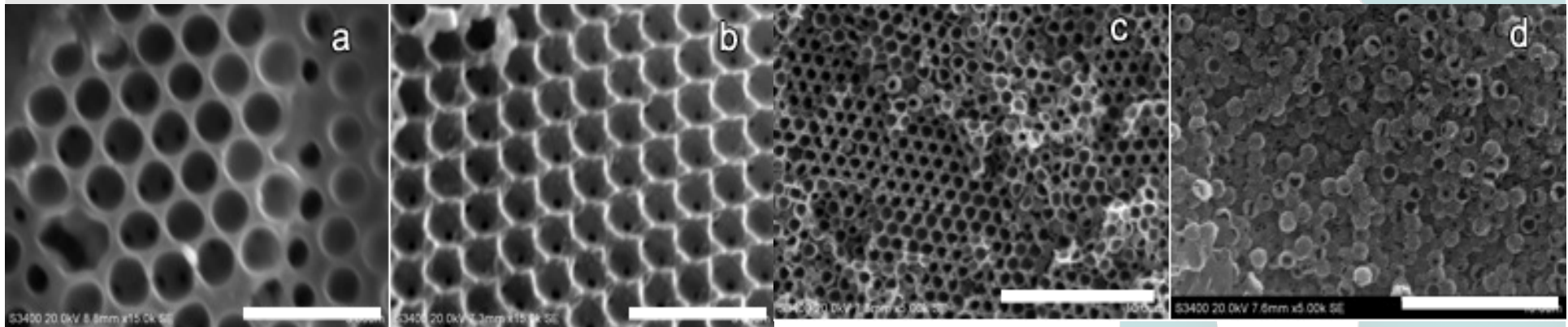
Surfactant content of dispersions

## PS crystal in $\mu$ fluidic channel





# Surfactant levels in PS dispersions – resulting PANI structures



Deionised Water

0.01 % w/v SDS

0.1 % w/v SDS

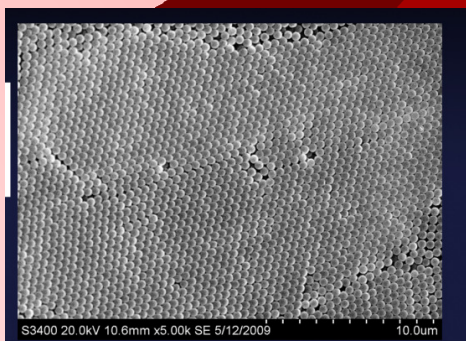
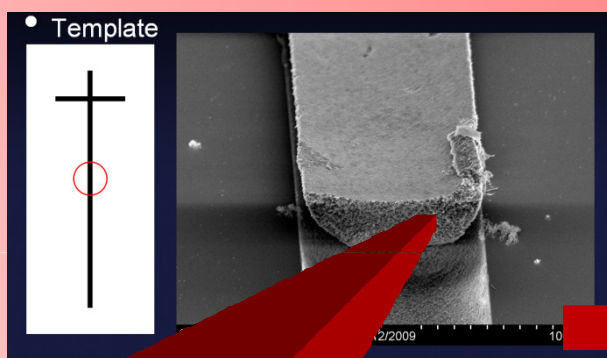
1 % w/v SDS

***Increasing %w/v surfactant in dispersions -  
Order in resulting structures changes***

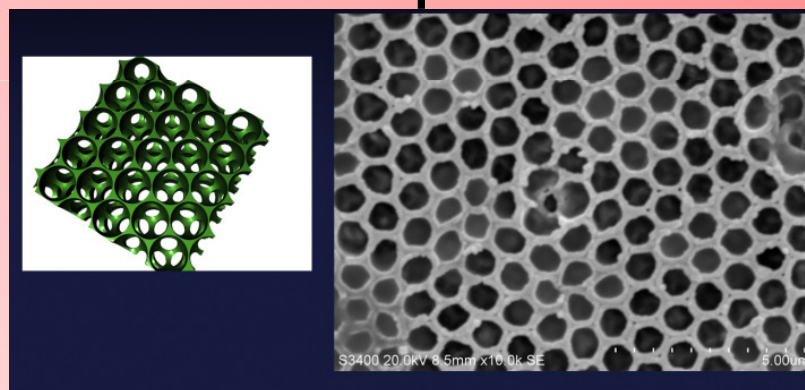


# On-chip conducting polymer monolith

## PS Template

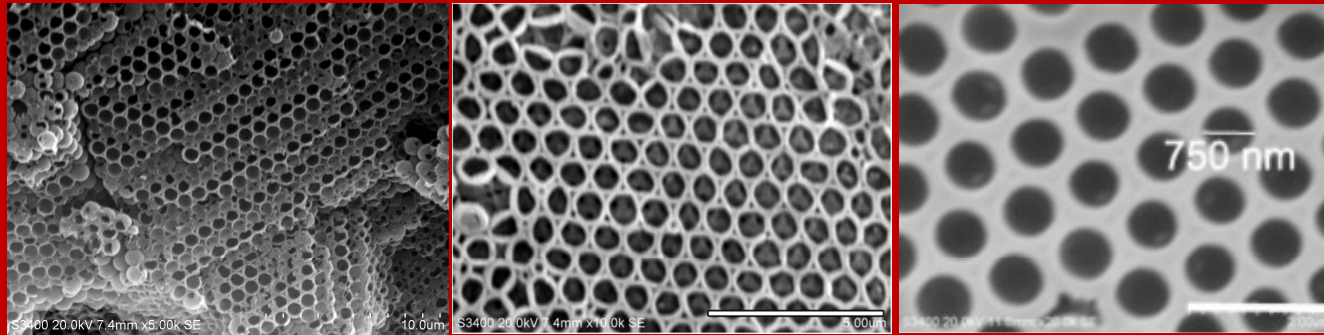


## Polyaniline Inverse Opal

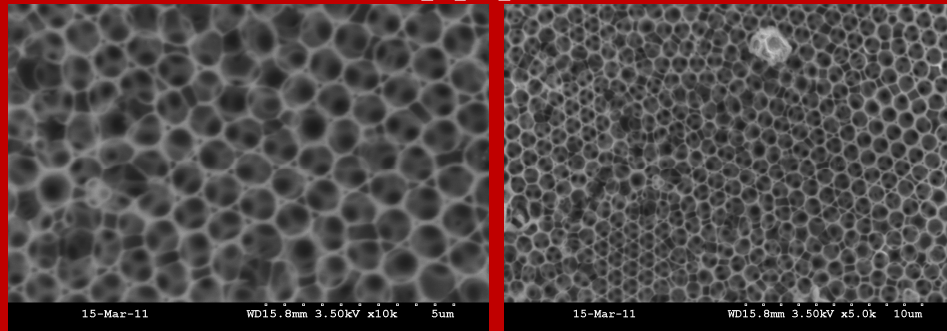


# Micro-structured conducting polymers on-chip - unimodal

## Polyaniline



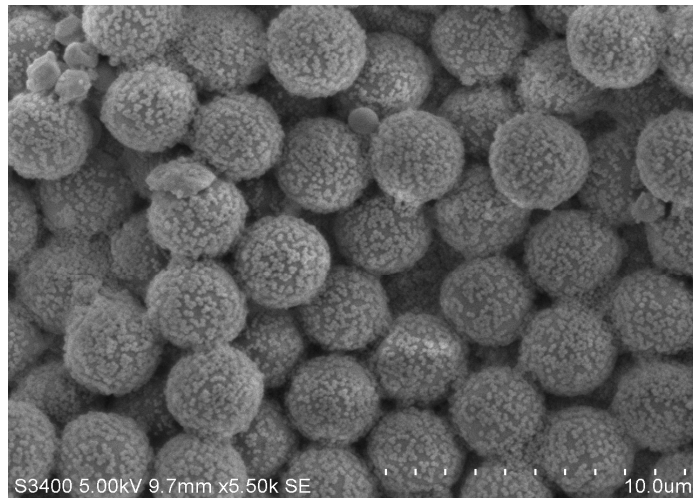
## Polypyrrole



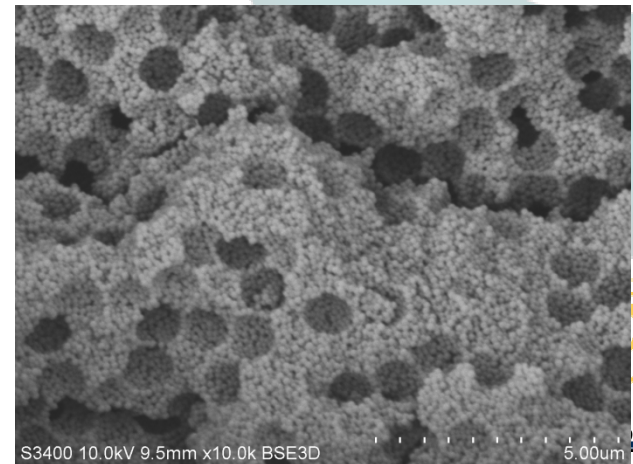
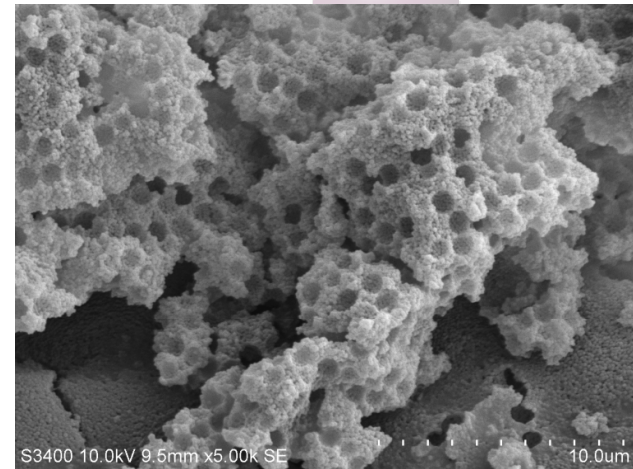
**Order in 3-D**  
A new way for  
improving chip-to-chip  
reproducibility of  
monolithic stationary  
phases

# Bimodal Structures

PS template  
comprising 3 micron &  
300 nm beads

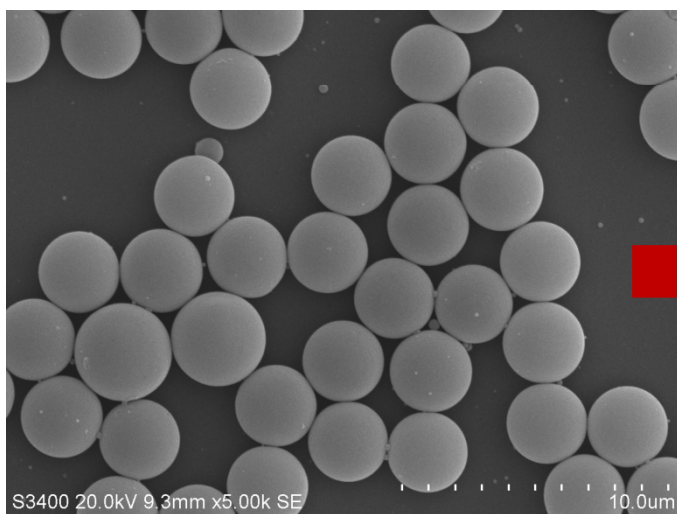


## Bimodal Ppy Monolith

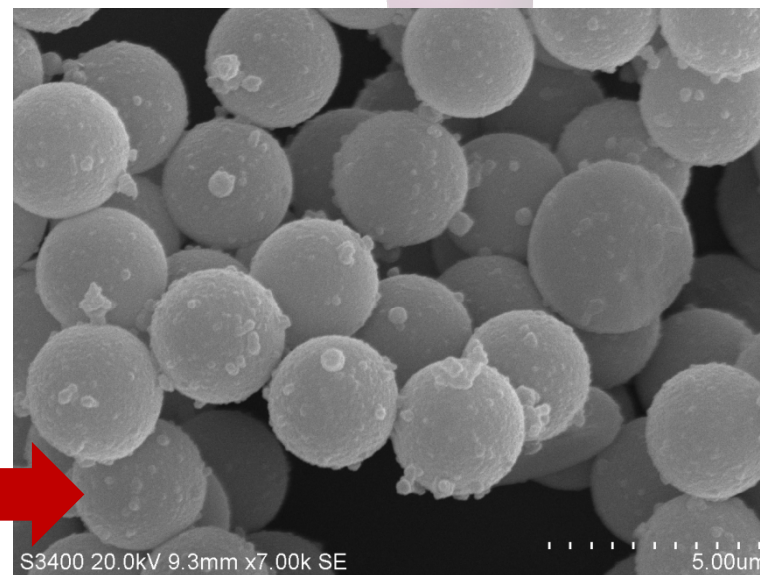


# Composite structures for chip packings

PS template (3  $\mu\text{m}$  beads)



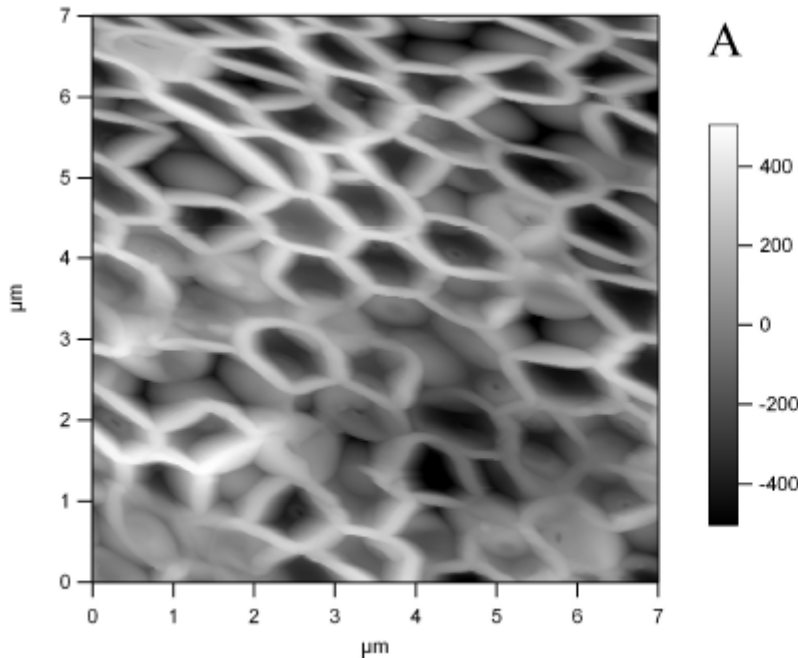
Ppy coated PS beads



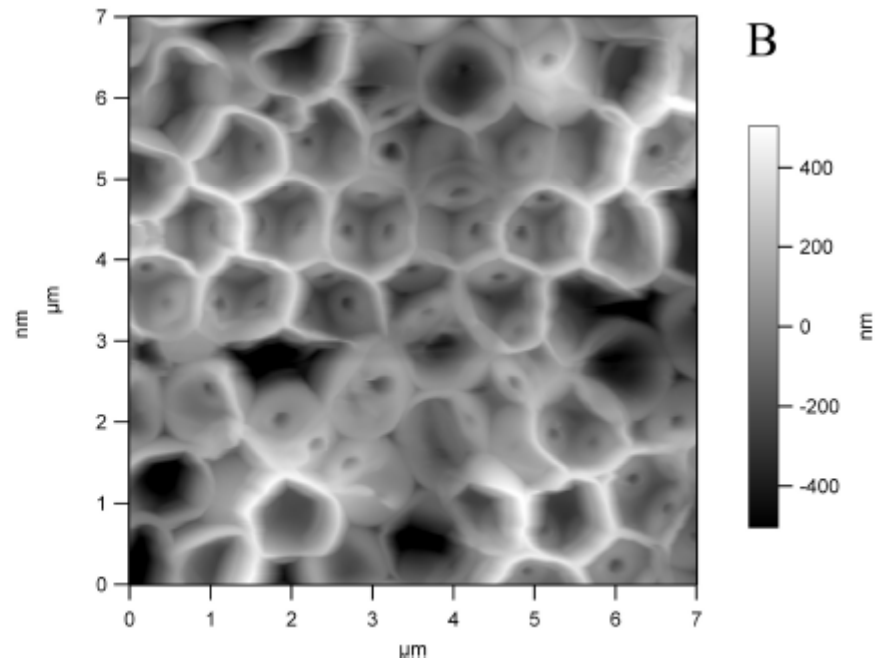
# Dry and wetted states of inverse opals

Electrochemically grown micro-structured Ppy doped with DBS

Dry State

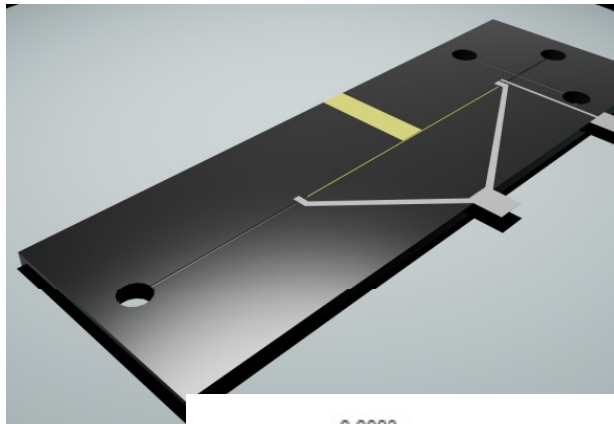


In Electrolyte

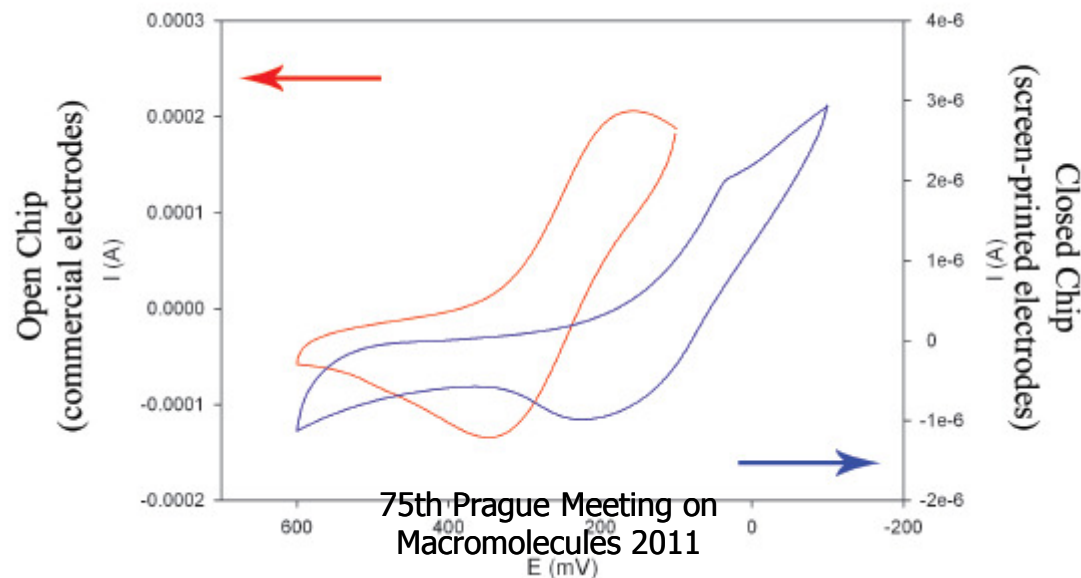
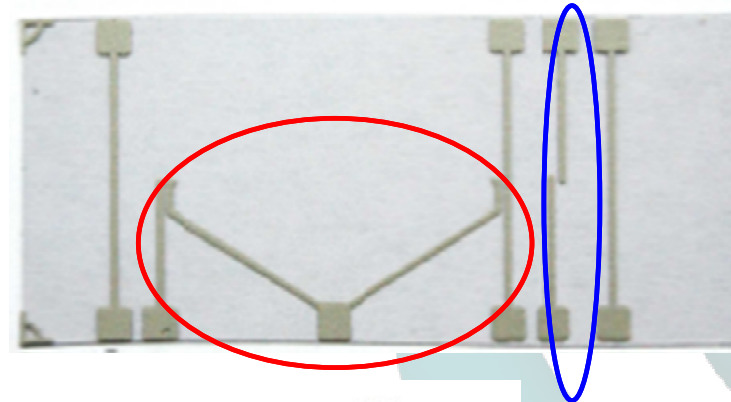


# On-chip electrochemical cell

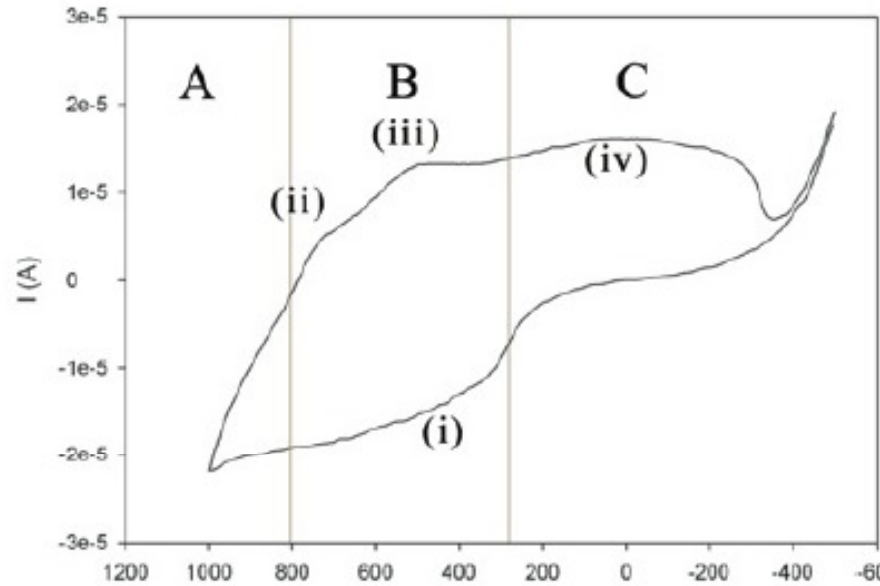
Glass Base Chip



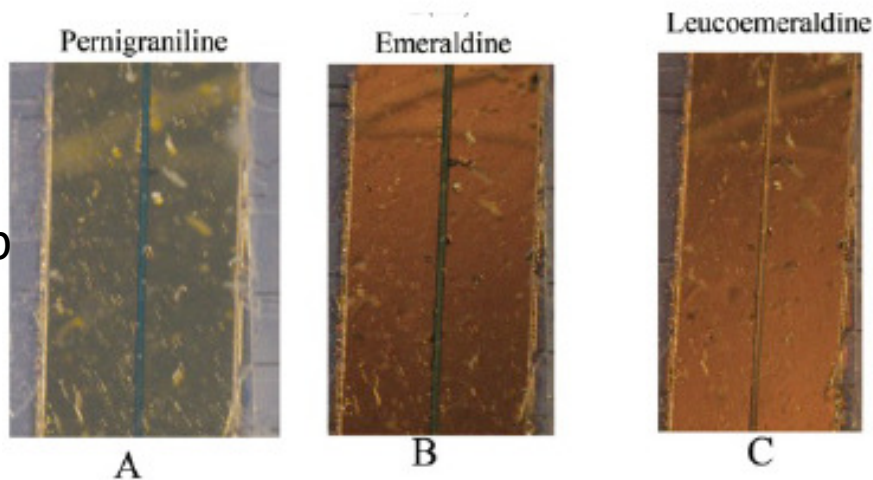
PET lid with silver paste screen-printed cell electrodes



# PANI electrochemistry on-chip

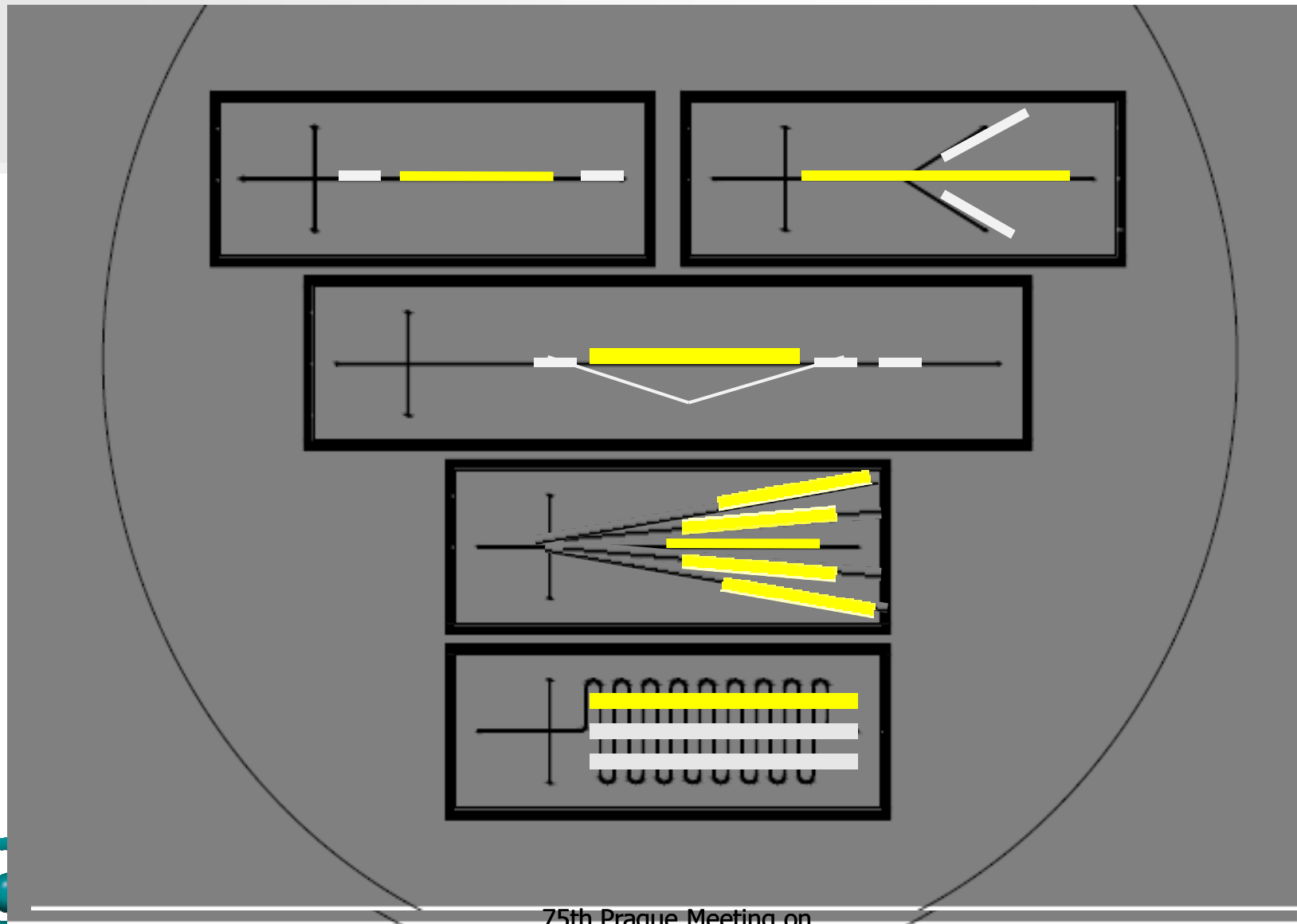


Corresponding colour change on-chip





# Improving chip design



# Target applications

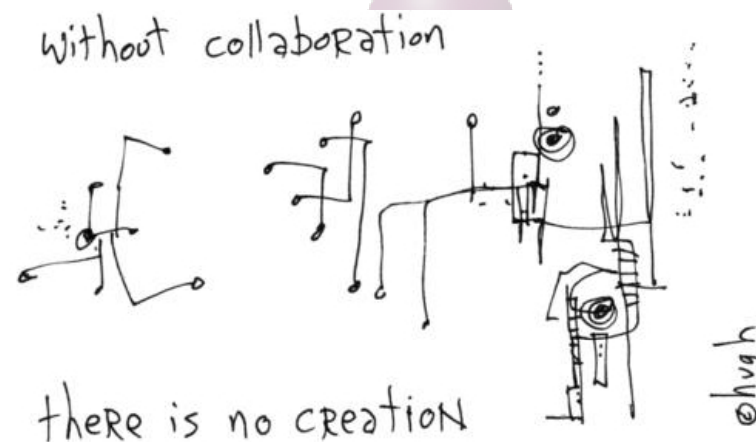
- HPLC
  - Highly reproducible micro-structured polymer monolithic stationary phase for nanoLC, HPLC chip, and electrochromatography
  - EMLC: Precise tuning of stationary phase properties before & during separations (by application of a voltage)
- Lab-on-a-chip applications
  - Point of care diagnostics e.g., (multi-analyte) electrochemical sensing on-chip
  - Fluidic control



# Thanks!

- The organisers and audience at Prague Meeting on Macromolecules 2011

- Dr. Blánaid White
- Prof. Malcolm Smyth
- Prof. Gordon Wallace
- Prof. Tony Killard
- Dr. Damian Connolly
- Dr. Jeremy Galineau
- Brian Gorey
- Dr. Courtney Collins
- Orla Gaffney
- Dr. Fuqiang Nie



# Printed Functional Materials 2011

Dublin City University and The National Centre for Sensor Research  
12<sup>th</sup> September 2011 (preceding the OE-A working group meeting)

*“Showcasing academic and industry based research in the area of functional materials for printed electronics”*

REGISTRATION AND ABSTRACT SUBMISSION EXTENDED  
TO 30 JULY

## Call for papers

Abstracts submissions are invited for Poster presentations.

All abstracts must be submitted electronically to: [aoife.morrin@dcu.ie](mailto:aoife.morrin@dcu.ie).

The deadline for abstract submissions is **10 July 2011**.

## Themes

- Functional nanomaterials
- Processes for device fabrication
- Printed devices including sensors, memory, displays, batteries, energy harvesting
- Component integration challenges

## Scientific Organising Committee

Dr. Aoife Morrin (DCU)

Dr. Karl Crowley (DCU)

Prof. Tony Killard (UWE)

Dr. Sven Breitung (OE-A)

Dr. Mazhar Bari (SolarPrint)

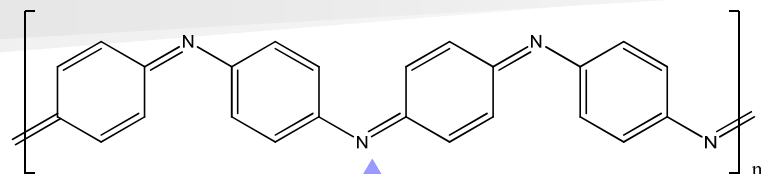
Prof. Donald Lupo (TUT)

Prof. Dermot Diamond (DCU)

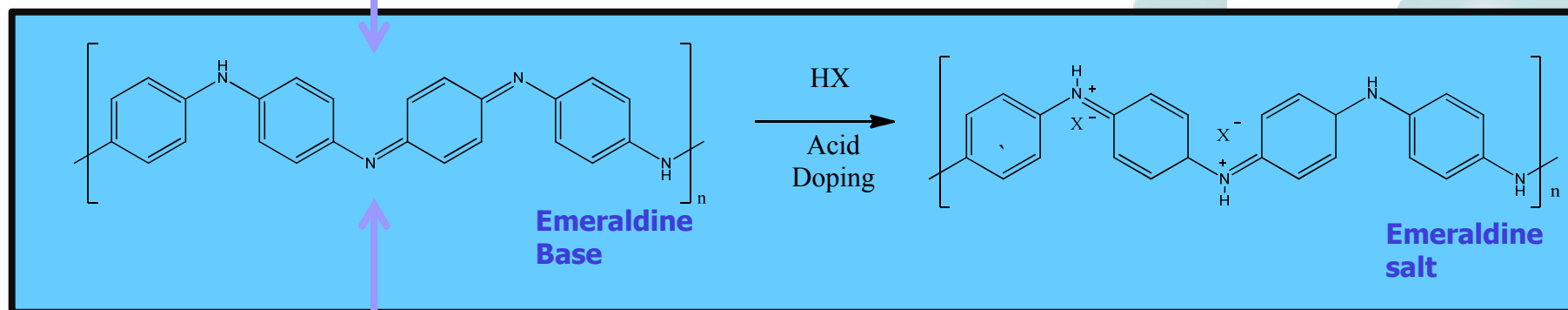
Details are available at

[www.dcu.ie/conferences/pfm2011](http://www.dcu.ie/conferences/pfm2011)

# Electroactive Polymers

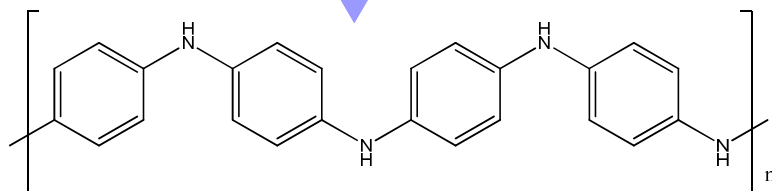


**Pernigraniline**



**Emeraldine Base**

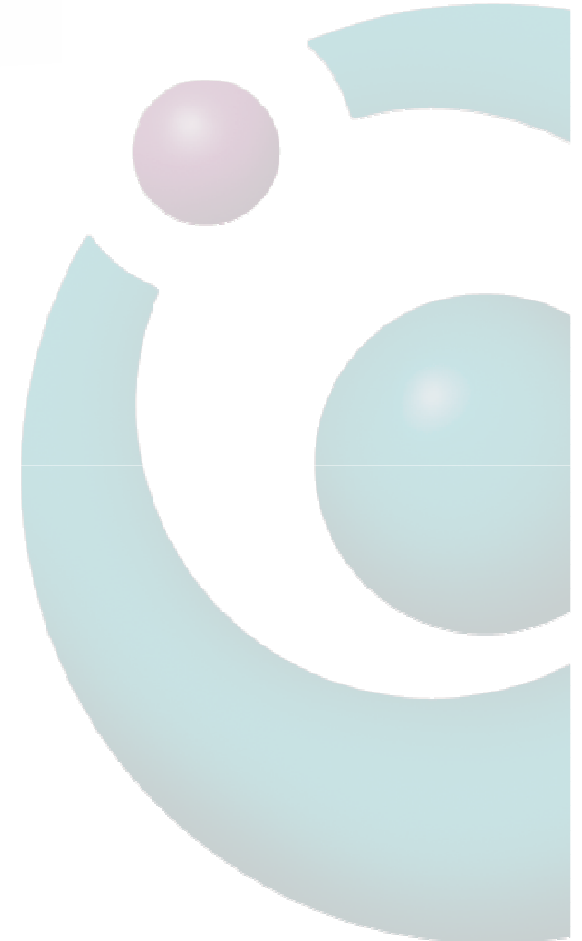
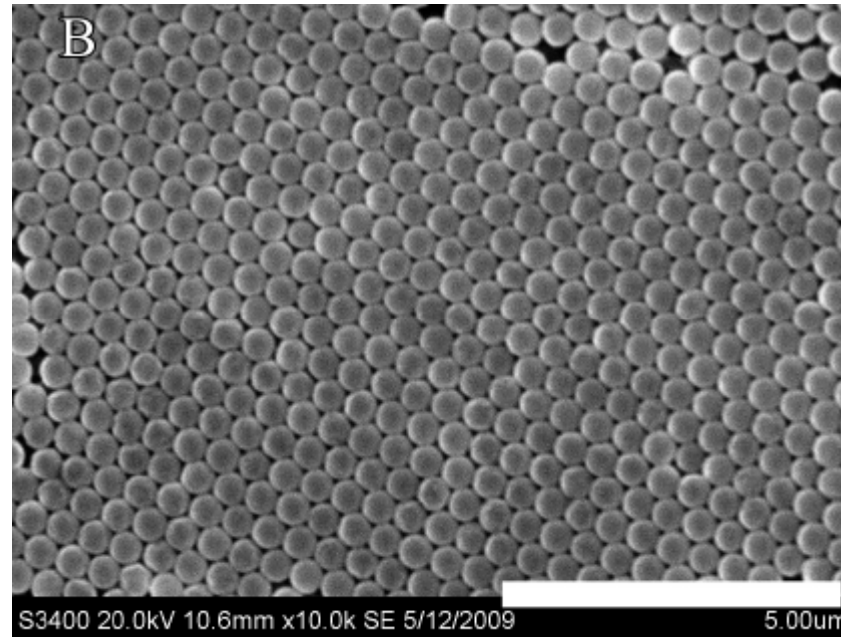
**Emeraldine salt**



**Leucoemeraldine**



# Surfactant Levels in PS Dispersions



# Packing conducting polymers on-chip?

## ■ HPLC

- Highly reproducible micro-structured polymer monolithic stationary phase for nanoLC, HPLC chip, and electrochromatography
- EMLC: Precise tuning of stationary phase properties before & during separations (by application of a voltage)

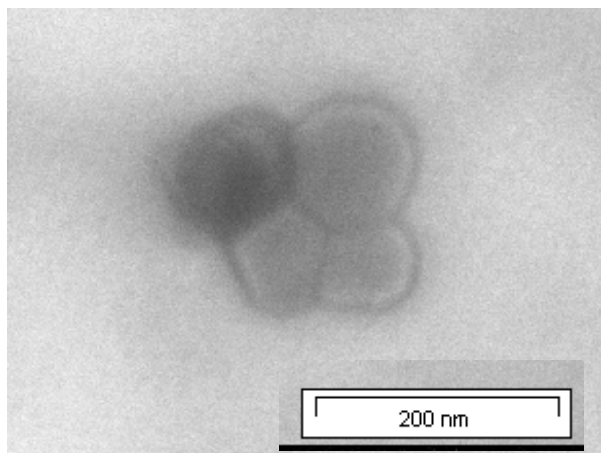
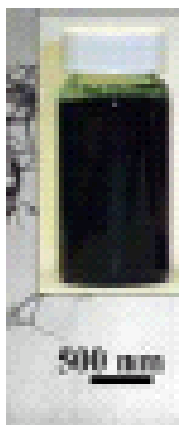
## ■ Lab-on-a-chip applications

- Point of care diagnostics e.g., (multi-analyte) electrochemical sensing on-chip
- Fluidic control



# Packing conducting polymer nanoparticles on chip

PANI nanoparticles:  
80 nm



Pack directly  
on-chip by  
capillary fill?

