4th International Conference on Nanotek and Expo
(Nanotek-2014) San Francisco, USA
December 1st, 2014

Nanostructured self-assembled P3HT thin films and their application to enhance organic solar cell efficiency

Varun Vohra[1],Hideyuki Murata[2]

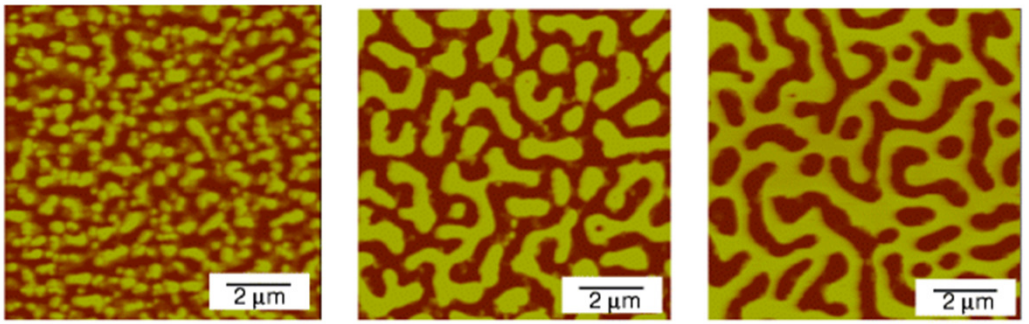
[1]University of Electro-Communications (UEC), Japan

[2]Japan Advanced Institute of Science and Technology (JAIST), Japan

Introduction: Nanostructured films of P3HT

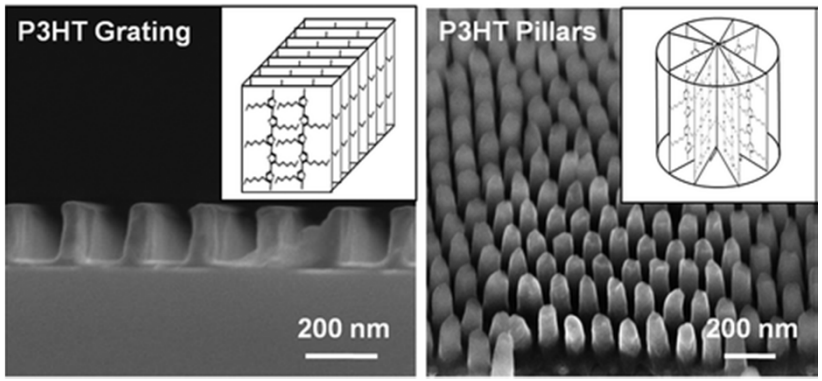
Phase separated polymer blends studied since over a decade

Mostly electronically inactive blends (e.g. PS-PMMA)



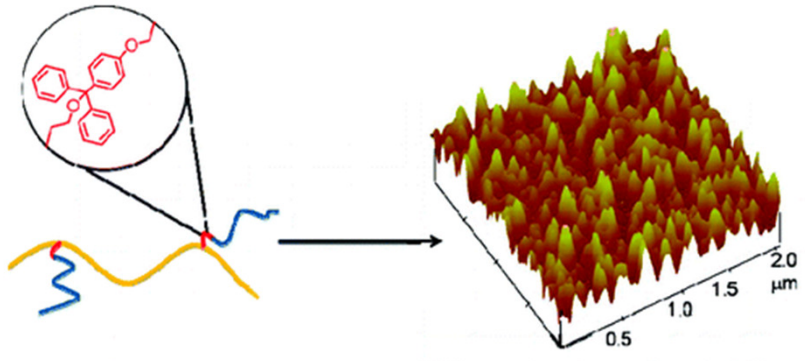
S. Zhu et al. in Nature 400, 49-51(**1999**)

Methods to obtain nanostructured thin films of P3HT:



Nanolithography

M. Aryal et al. in ACS Nano 3, 3085-3090 (**2009**)



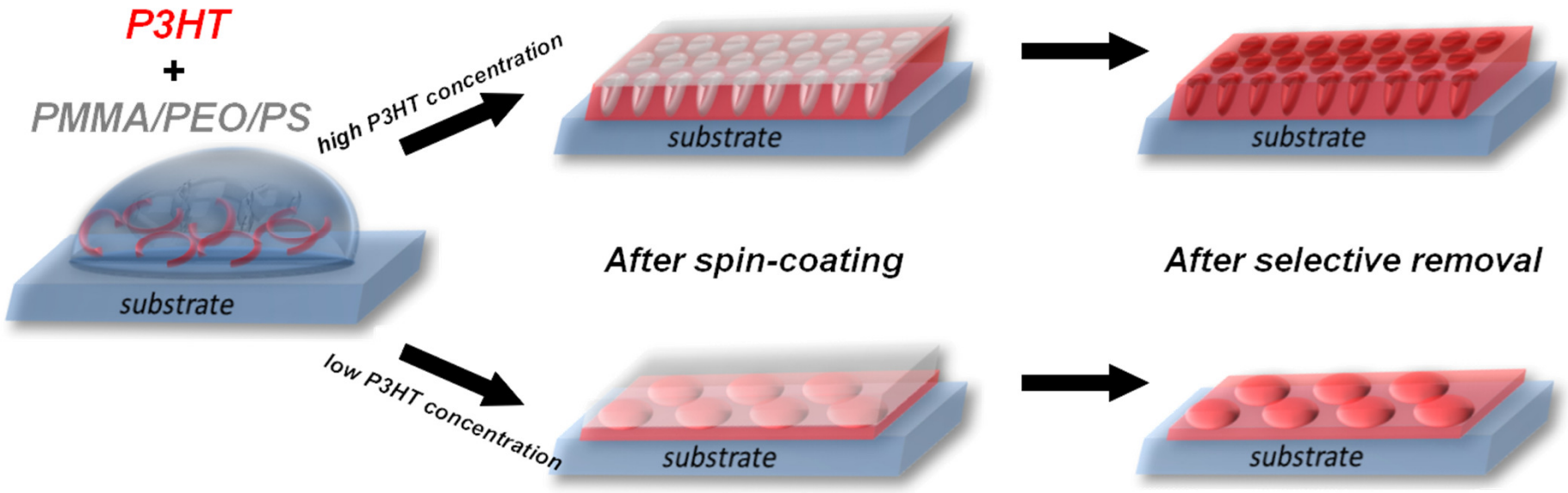
Elaborated chemistry

K. Sivanandan et al. in Macromolec. 43, 233-241 (**2010**)

Can we obtain similar structures using commercially available polymer blends?

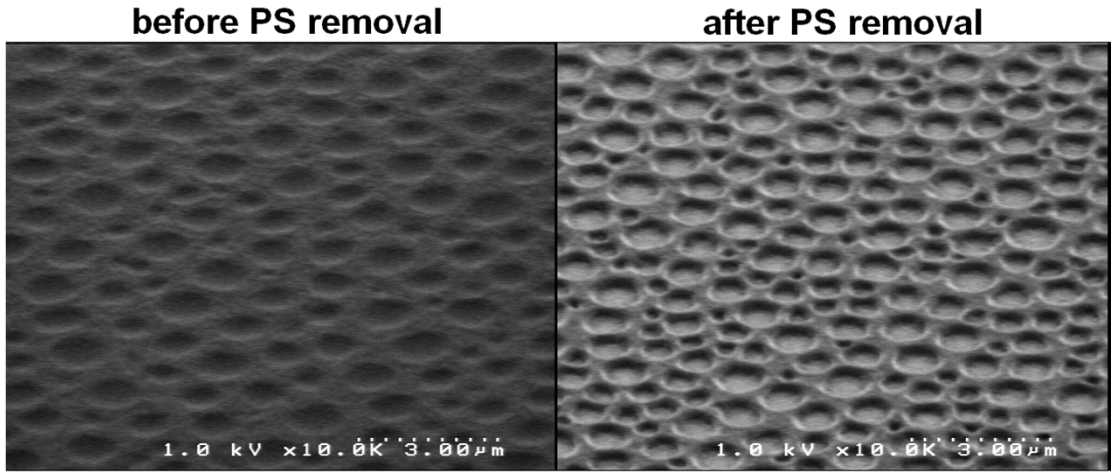
Simple idea to form nanostructured P3HT

Phase separation between P3HT and commercially available polymer materials

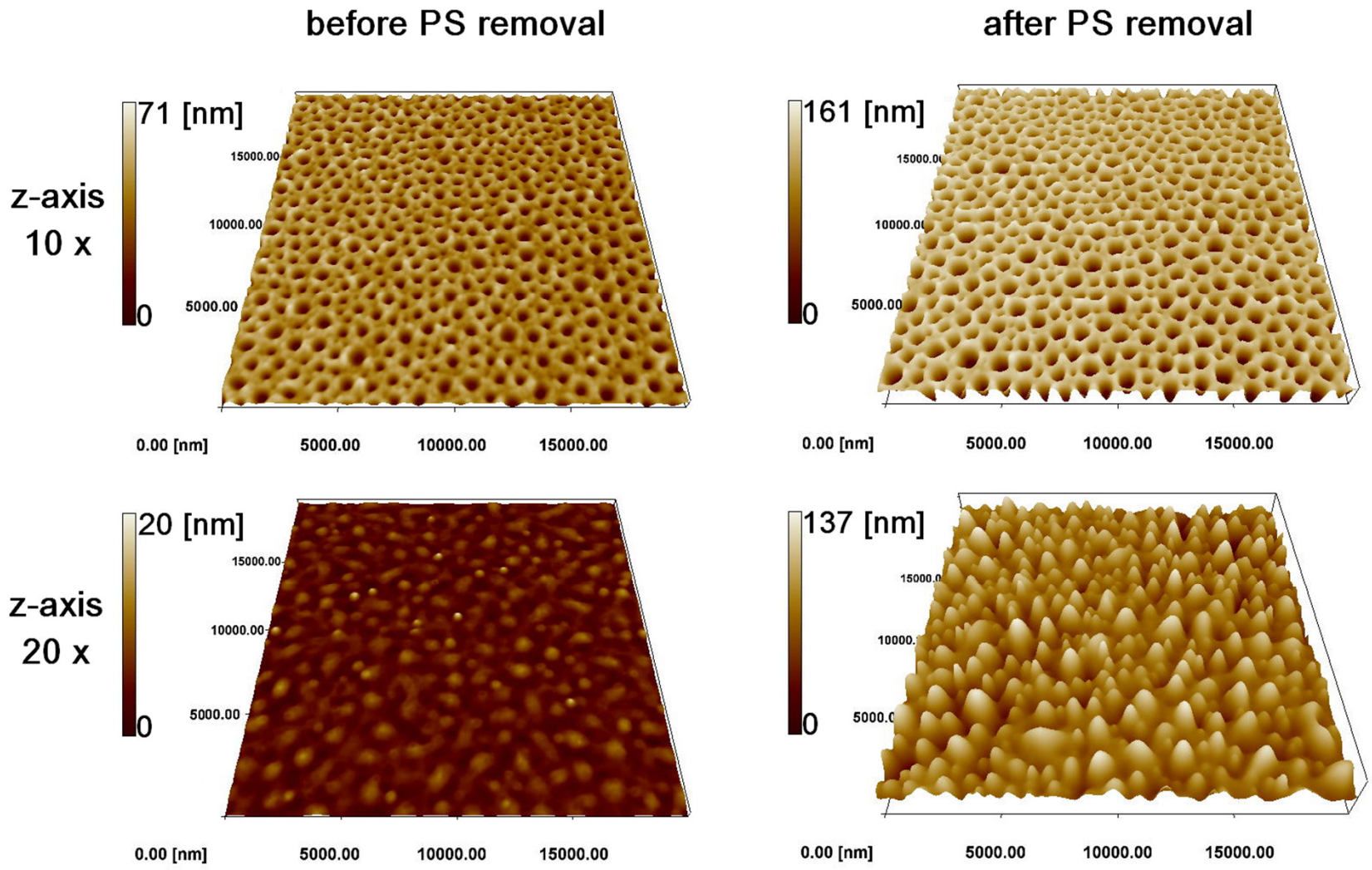


Example of nanoporous structures obtained from P3HT:PS blends before and after selective removal of PS

(structure already formed prior to PS removal)



P3HT nanoporous and nanoisland films



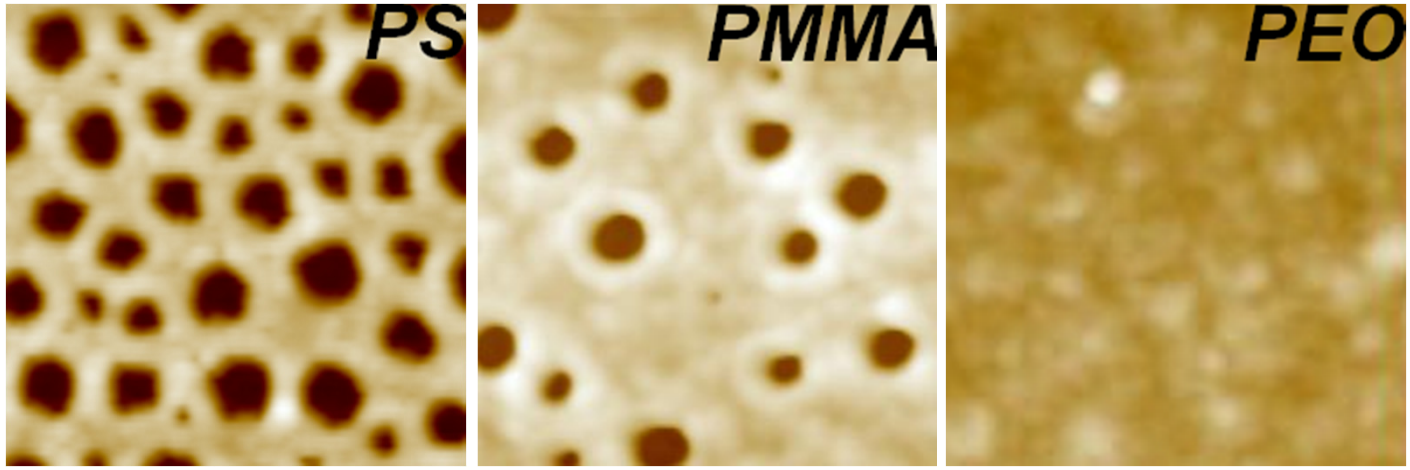
Two types of structure can be fabricated with PS
Focus on nanoporous films

Effect of polymer-polymer miscibility

solubility parameter ($MPa^{1/2}$)	δ_T	δ_d	δ_p	δ_H
P3HT	20.0	18.5	5.3	5.3
PS	22.5	21.3	5.8	4.3
PMMA	22.6	18.6	10.5	7.5
PEO	22.1	17.0	11.0	8.9

Miscibility with P3HT: *PS* > *PMMA* > *PEO*

5µm x 5µm AFM



Adequate polymer miscibility necessary



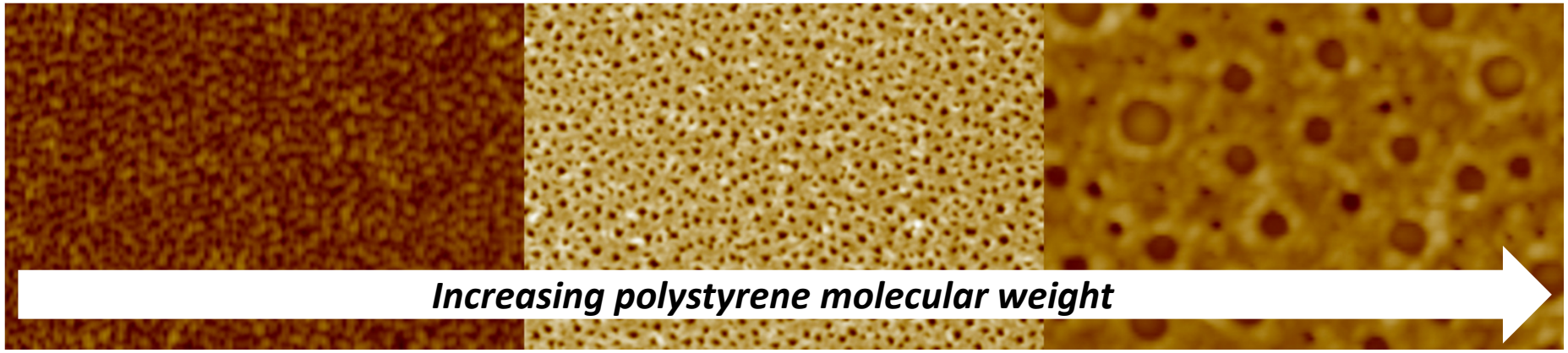
Relatively ordered lateral phase separation

Disordered (low density) lateral phase separation

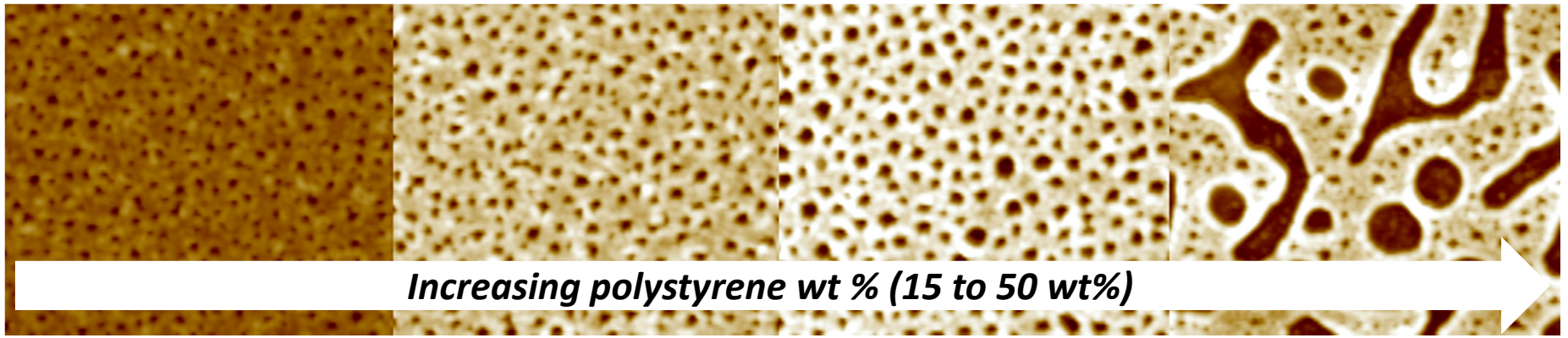
Vertical phase separation

Tuning the pore dimensions / morphology

Method 1: Changing the molecular weight of the polymers

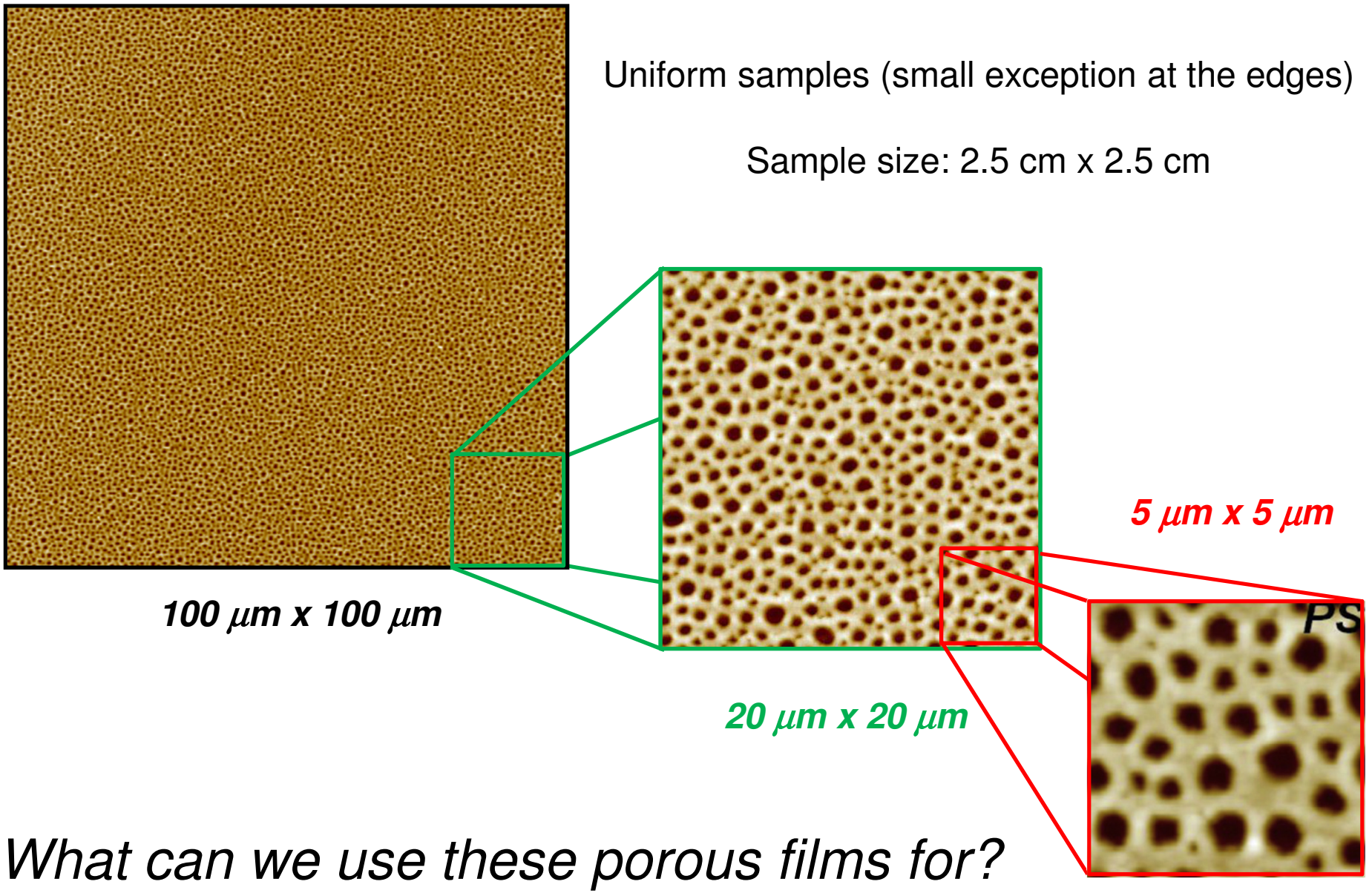


Method 2: Changing the P3HT:PS ratio



Combination of the two methods:
Pore diameters can be tuned from 100 to 650 nm

Large scale nanostructured film formation?



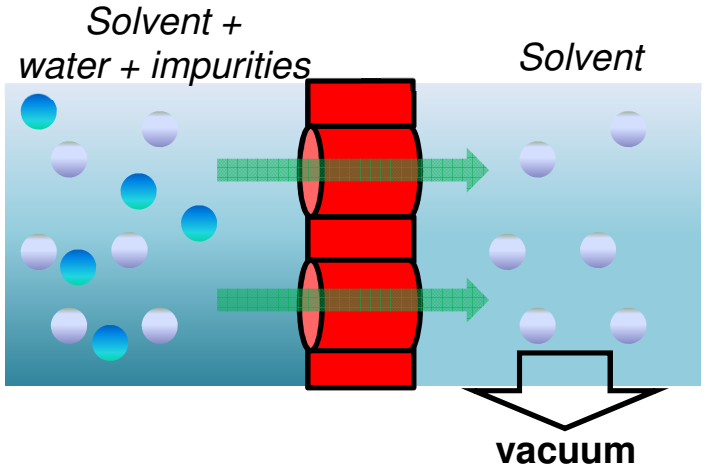
Uniform samples (small exception at the edges)

Sample size: 2.5 cm x 2.5 cm

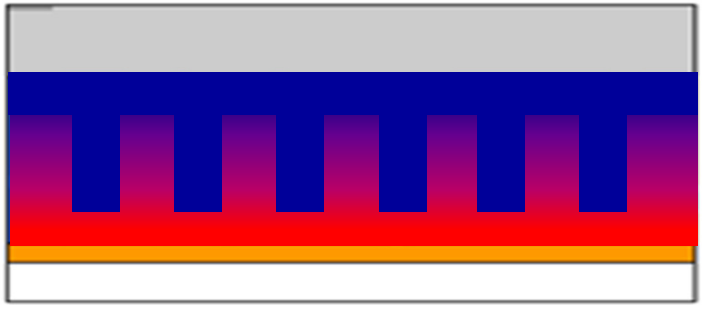
What can we use these porous films for?

Potential applications

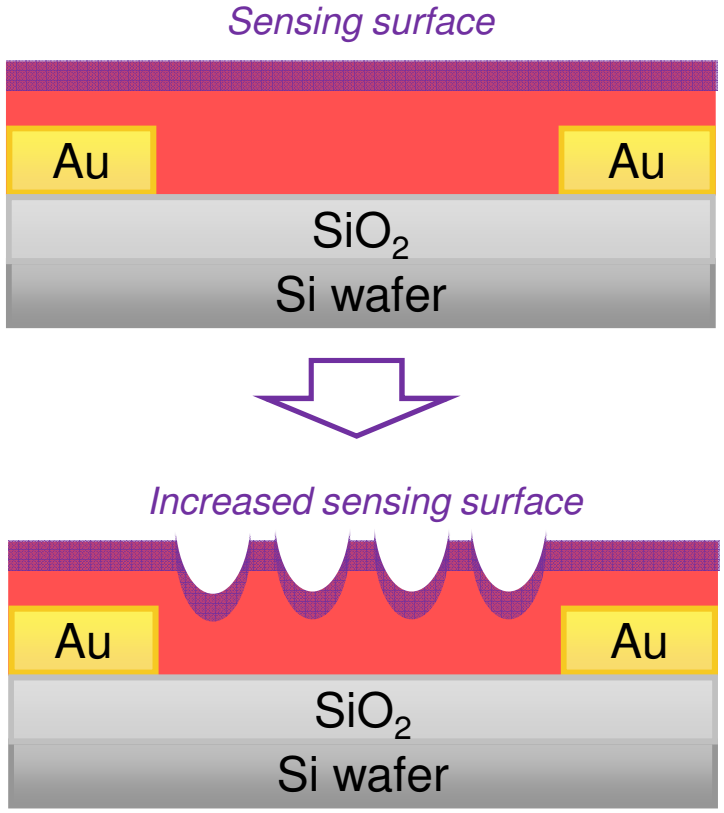
Organic solvent extraction



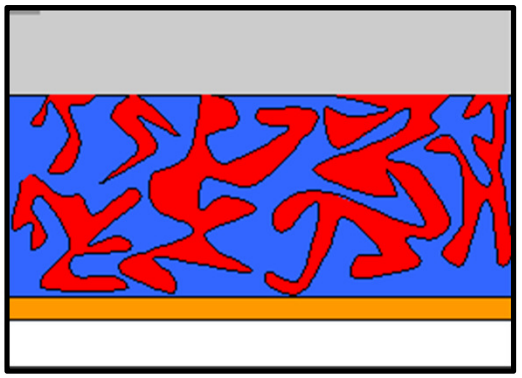
Increased donor-acceptor interface in organic solar cells



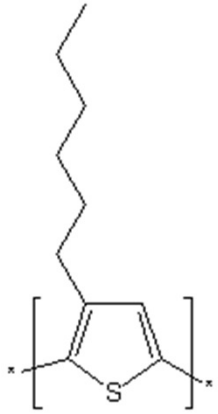
Increased sensitivity of P3HT based OFET sensors



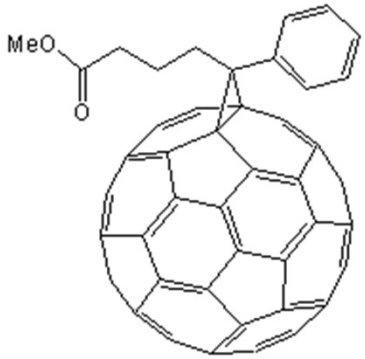
Ideal morphology for polymer solar cells



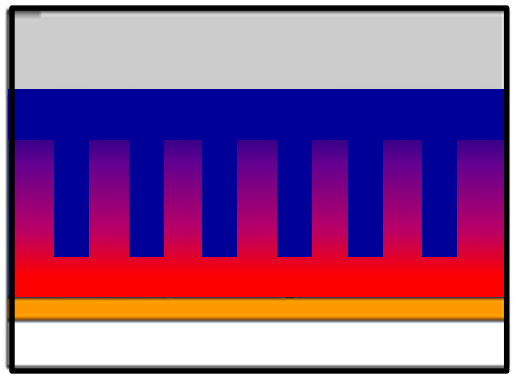
Bulk Heterojunction by Mixture



P3HT



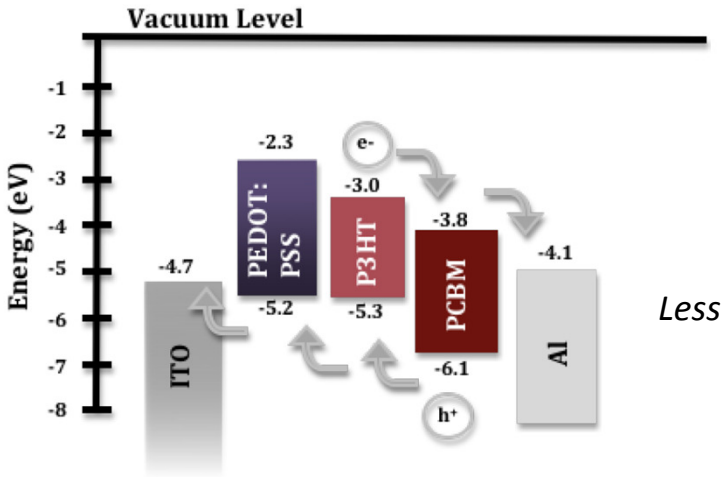
PCBM



Interdigitated Diffusive Bilayer by Sequential deposition

Efficient charge generation

Unefficient charge collection

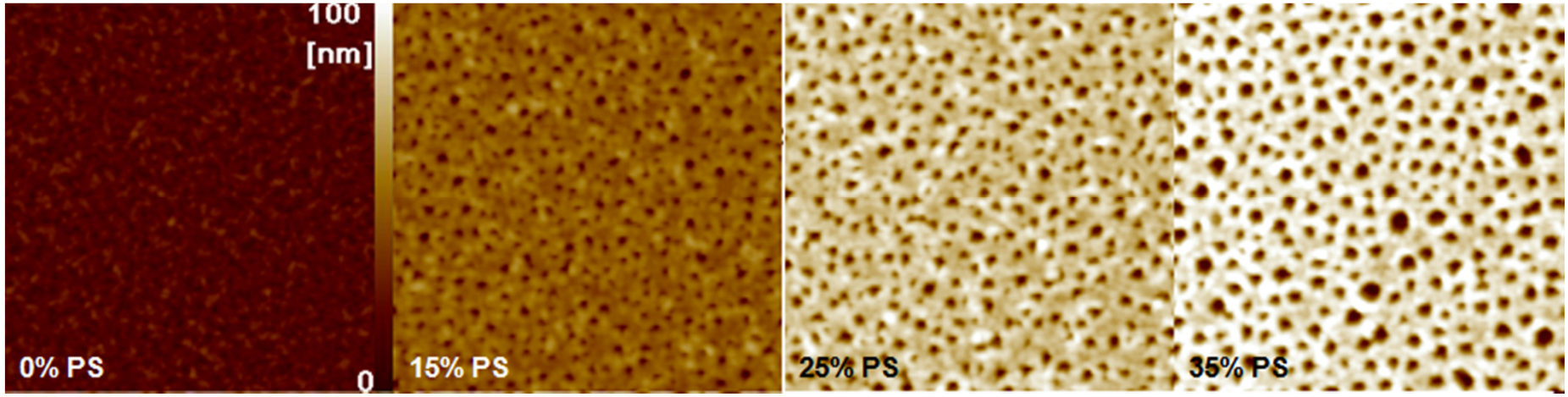


Efficient charge transport to their respective electrodes

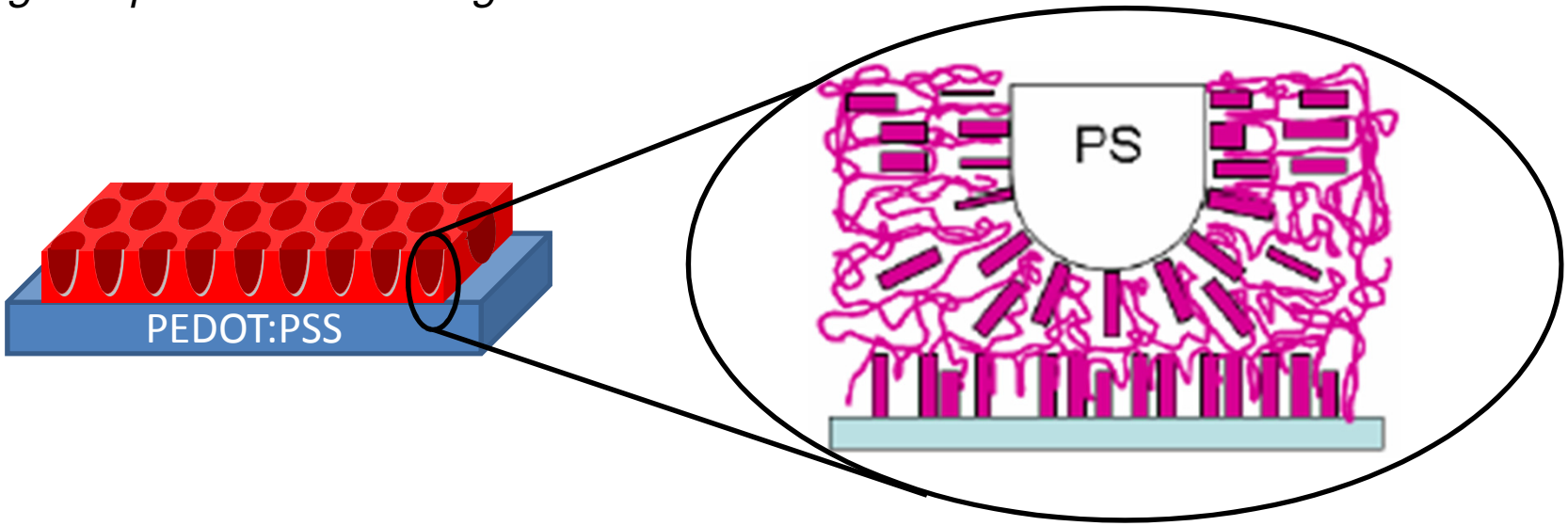
Less charge generation in planar bilayers

Can we increase the charge generation through nanostructured donor-acceptor interfaces?

Morphology of the nanoporous films

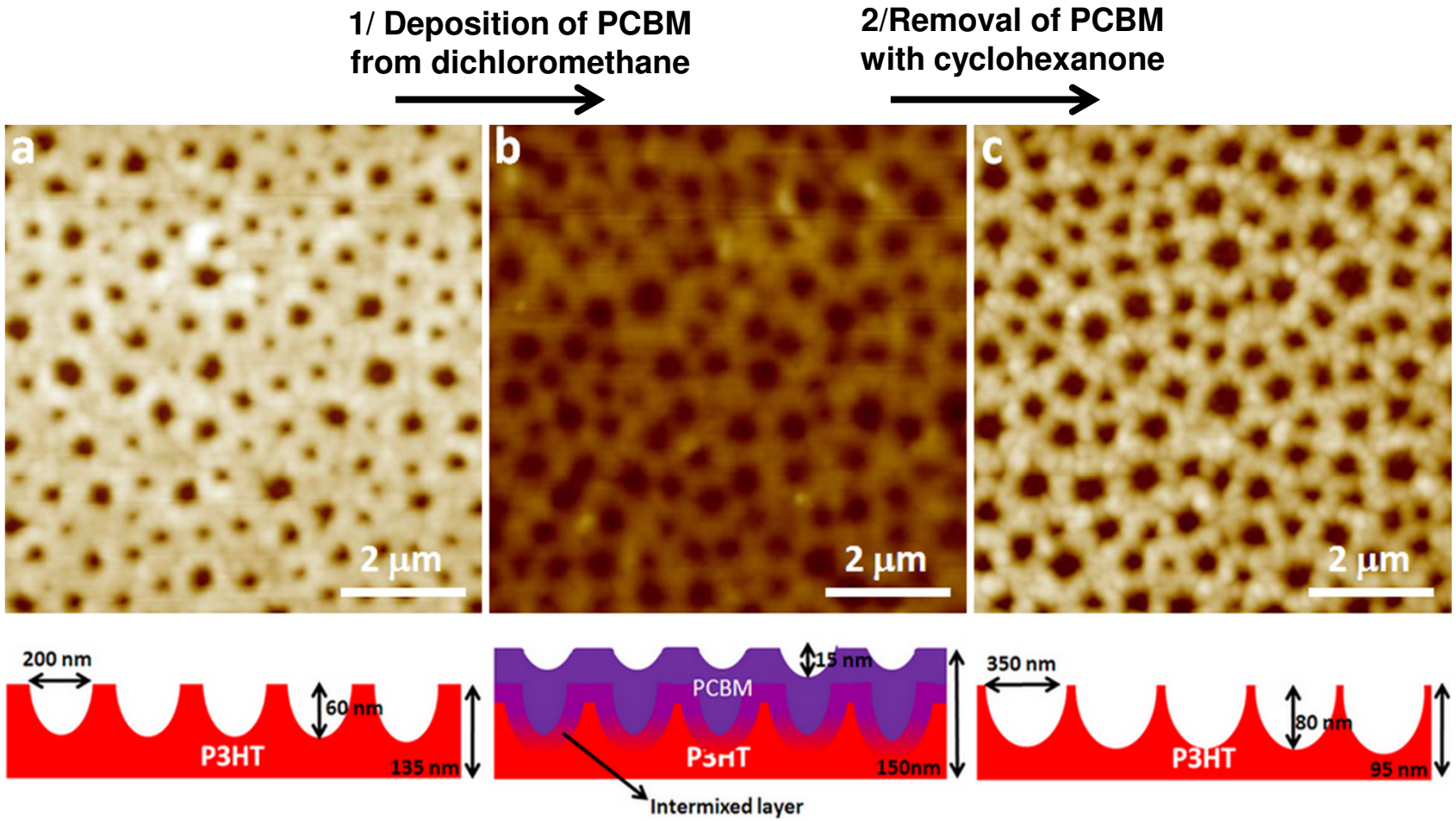


AFM measurements: underlying non structured P3HT buffer layer
Angle dependent FTIR: organization of the P3HT chains at the P3HT-PS interface



In addition to increased Jsc, we should observe increased FF

Different orientations in the bulk and the surface



1/ filling the pores with PCBM and allowing diffusion of PCBM into P3HT

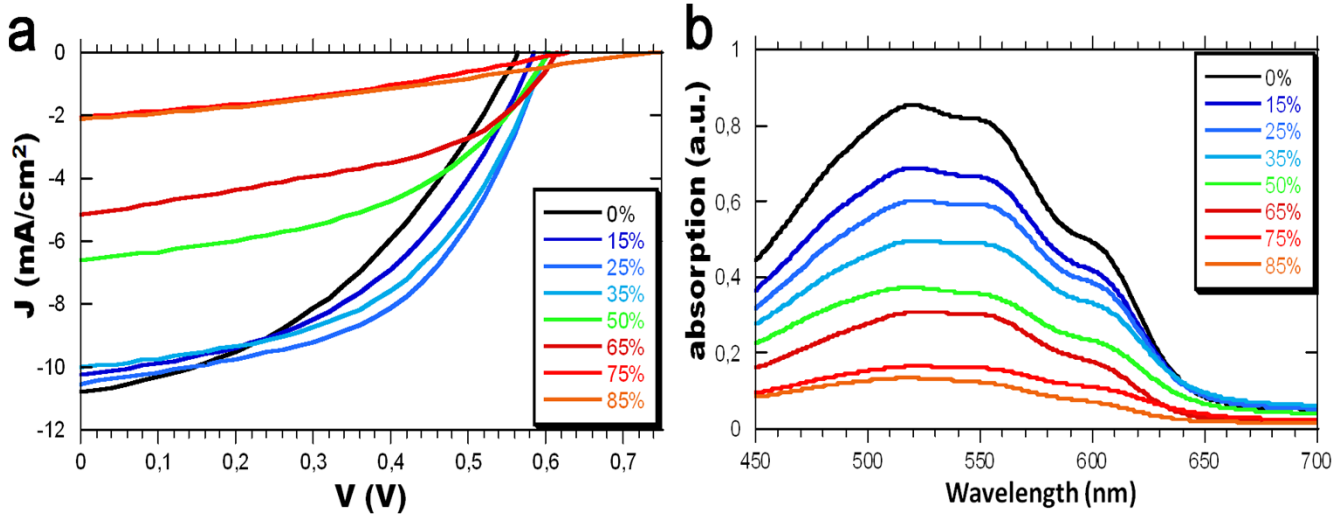
➔pore depth decreases from 60 to 15 nm (PS 25wt% after PS removal)

2/ removing the PCBM and the parts of P3HT containing a high concentration of (diffused) PCBM

➔ widening : +75 nm on each sides deepening: +60 nm

Lateral diffusion > Vertical diffusion: Confirms the different orientations!

Photovoltaic parameters



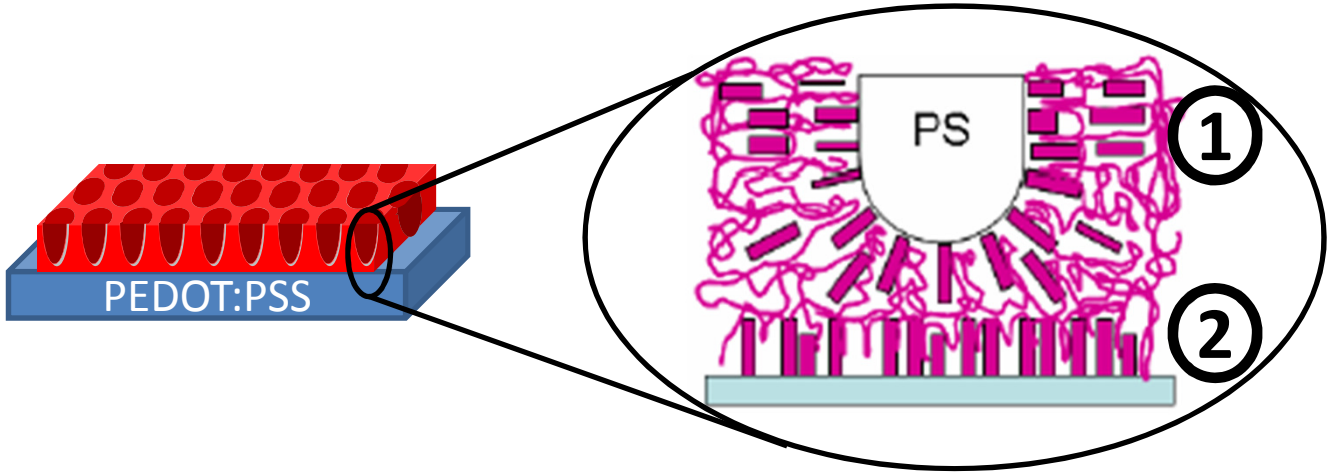
PS (wt%)	Jsc* (mA/cm²)	Voc (V)	FF (%)	η (%)	Rs (Ω/cm²)	Wetting layer	Absorption ratio (A/A_0)
0	10.8 10.8	0.57	41	2.51	7.04	130 nm	1
15	10.2 12.3	0.60	46	2.77	8.27	104 nm	0.832
25	10.5 14.1	0.61	51	3.25	4.61	76 nm	0.745
35	10.0 15.6	0.61	49	3.02	4.18	63 nm	0.640

**Jsc* corresponds to the measured Jsc divided by the absorption ratio*

Increase in corrected Jsc, Voc, FF and consequently PCE

Origins of the increase in device performances

PS (wt%)	Jsc* (mA/cm^2)	Voc (V)	FF (%)	η (%)	Rs (Ω/cm^2)	Wetting layer	Absorption ratio (A/A_0)
0	10.8 10.8	0.57	41	2.51	7.04	130 nm	1
25	10.5 14.1	0.61	51	3.25	4.61	76 nm	0.745



① Planar bilayer ➔ nanostructured bilayer:
P3HT crystallite reorientation :

increase in donor-acceptor interface
better hole transport properties
reduced Rs → increased Voc and FF

② Thin P3HT buffer layer (no PCBM):

nanostructured p-i-n junction
➔ *further increases FF*

Summary

- Easy and cost effective method to prepare spin-coated nanostructured P3HT films from blends of commercially available polymers (P3HT + PS)
- Tuning of pore dimensions can be controlled by wt% and Mw
- Nanoscale phase separation induces reorientation of the polymer crystallites at the P3HT/PS interface
- Nanostructured diffusive bilayer solar cells have an average PCE of upto 3.25% (30% increase with respect to the planar equivalent)
- A deeper analysis of the active layer morphology is necessary to understand the increase in PV performances

The nanostructured thin films have potential for various applications

Feel free to come and exchange ideas

An international collaboration



On-going and future collaborations:



JAIST
JAPAN ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY
1990

Hideyuki Murata
Masayuki Yamaguchi
Osamu Notoya
Tong Huang

Mariano Campoy-Quiles
Miguel Garriga

ICMAB



UEC TOKYO

Varun Vohra





Xiaojun Guo
(future projects)



Very open to new collaboration and projects

Organic solar cells based on nanoporous P3HT obtained from self-assembled P3HT:PS templates
V. Vohra, M. Campoy-Quiles, M. Garriga, H. Murata, *J. Mater. Chem.,* **2012**,*22,* 20017-20025

Nanostructured P3HT films with tunable dimensions through self-assembly with PS
V. Vohra, O. Notoya, T. Huang, M. Yamaguchi, H. Murata, *Polymer*, **2014**, *55*, 2213-2219

Thank you for your attention!!!

Email: varun.vohra@uec.ac.jp

