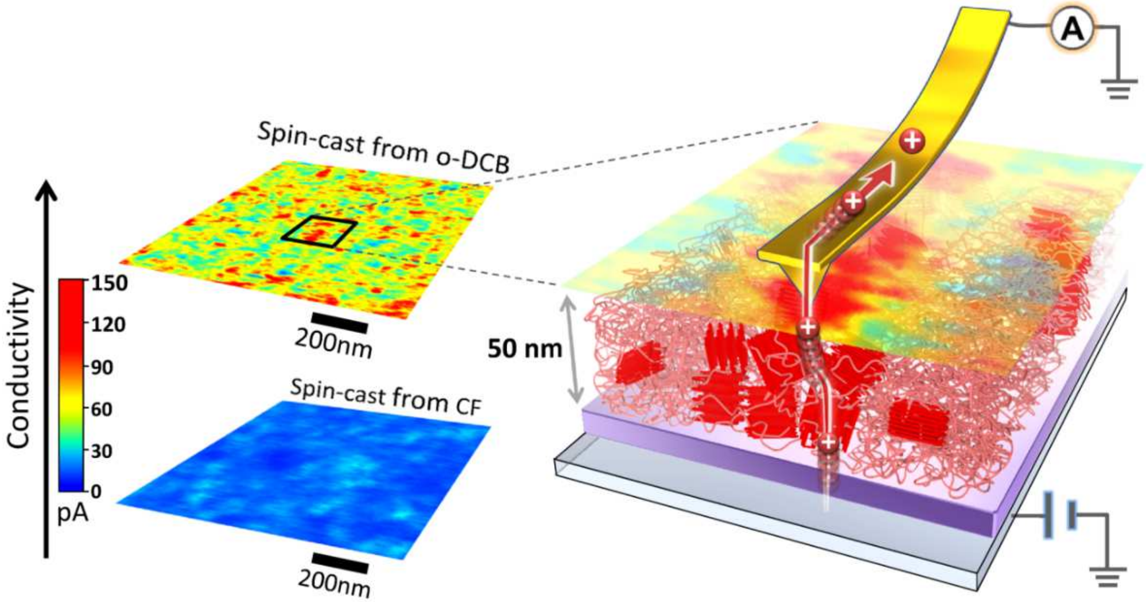
Nano and Giga Challenges in Electronics, Photonics and Renewable Energy
Tomsk, Russia, September 21, 2017

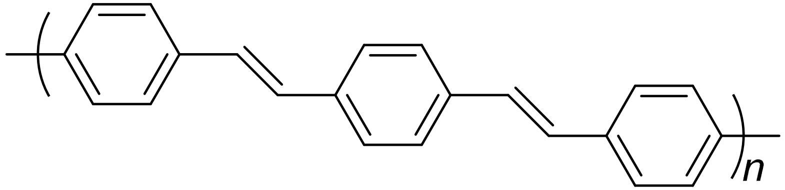
Nanoscale Mapping of Charge Transport Properties of Conjugated Polymer Films by Conducting Atomic Force Microscopy

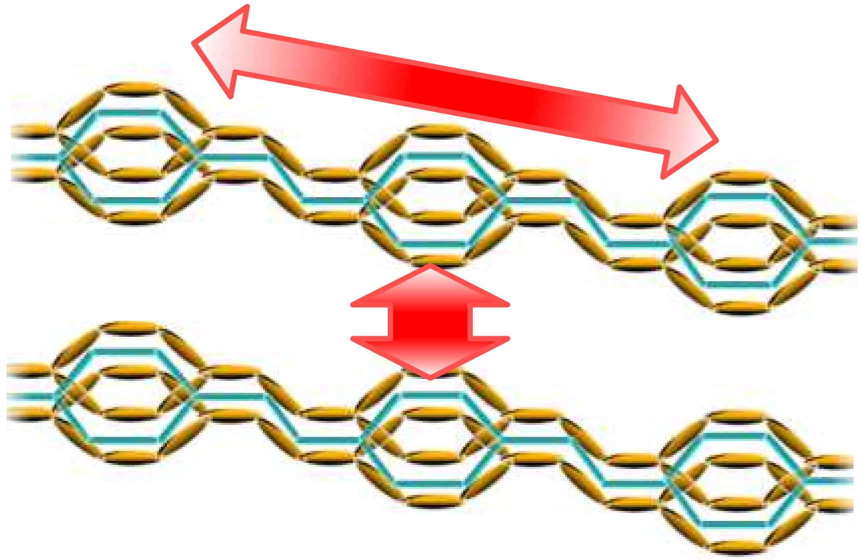


Hiroaki BENTEN

Nara Institute of Science and Technology

Conjugated Polymer: Excellent Organic Semiconductor

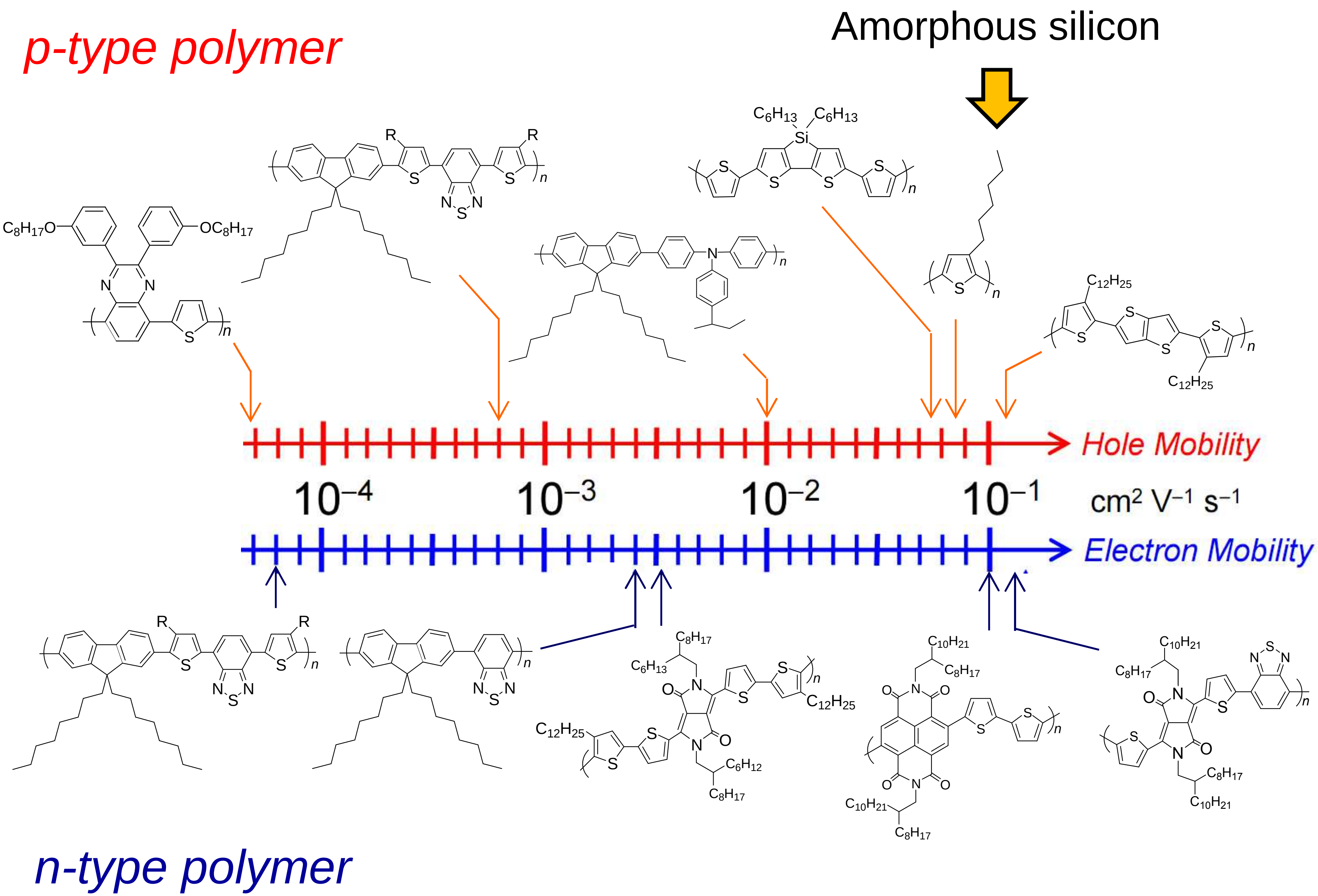




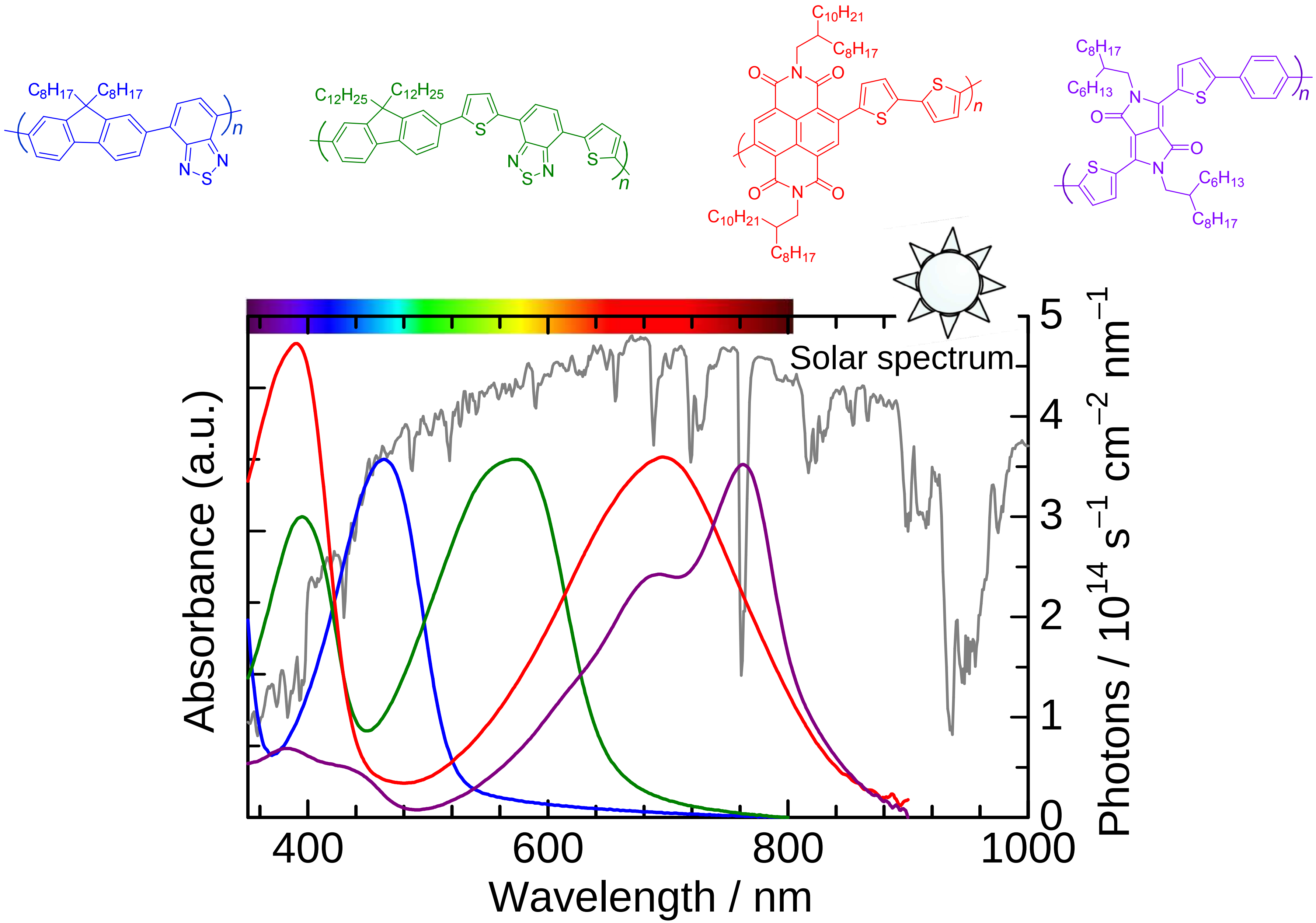
Semiconducting properties are due to the conjugation of π–electrons along the polymer chains and the delocalization of π–electrons between π–π stacking polymer chains.

http://www.chm.bris.ac.uk/webprojects2002/howell/LEPs/chemistry.html#

Charge-Carrier Transport



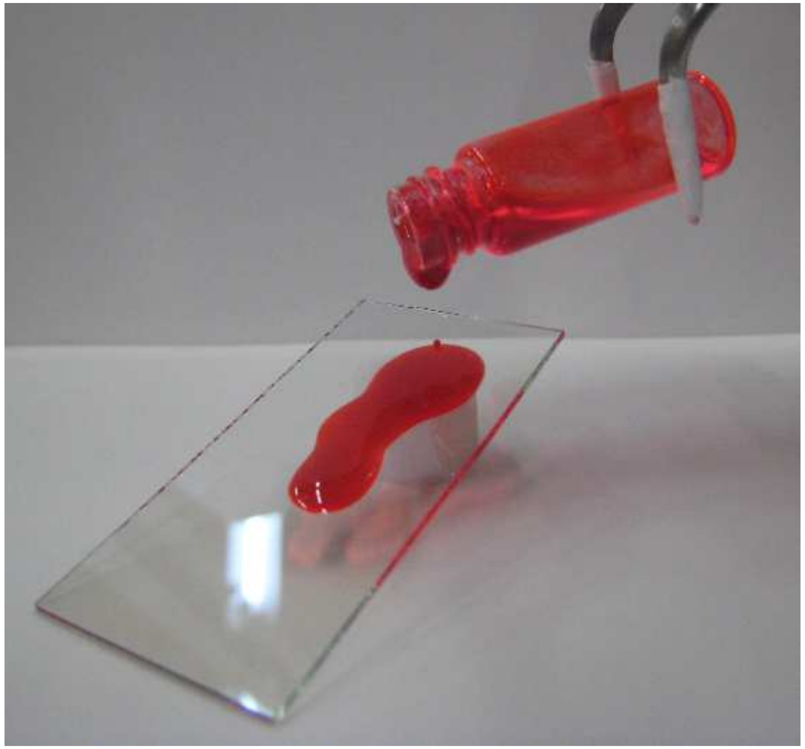
Light-Harvesting



Emission

http://www.shef.ac.uk/polopoly_fs/1.88176!/image/Molecular-materials-1.jpg

From a View Point of Practical Application ･･･



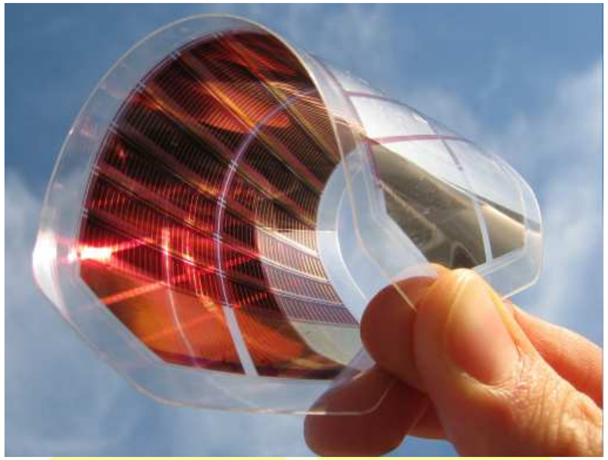
Good solubility in organic solvents and ease of preparation of uniform thin-films of polymer materials are suitable for the low-cost and large-scale device production based on the printing technology.

From a View Points of Practical Application ・・・

http://www.printedelectronicsnow.com/

Good solubility in organic solvents and ease of preparation of uniform thin-films of polymer materials are suitable for the low-cost and large-scale device production based on the printing technology.

Solar cell

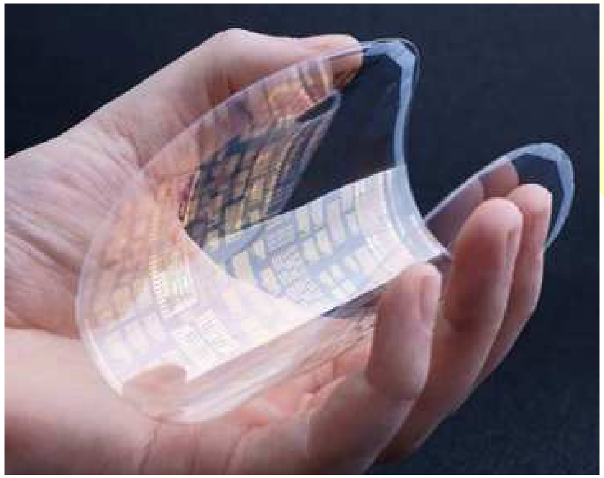


By using these attracting properties of conjugated polymers･･･

http://www.plasticseurope.org/documents/document/20150508114037-expo2015b.jpg

Plastic Electronics

FET



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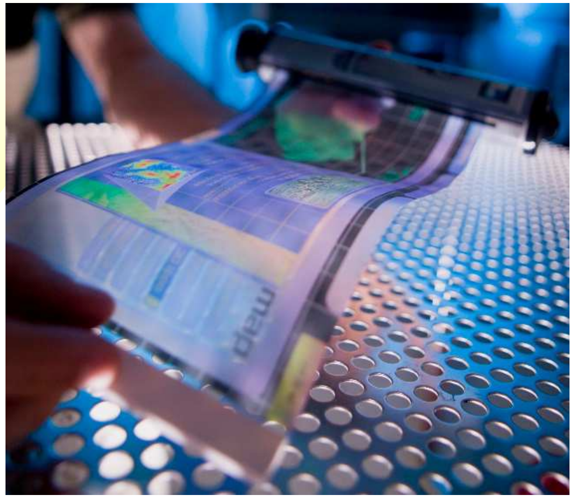
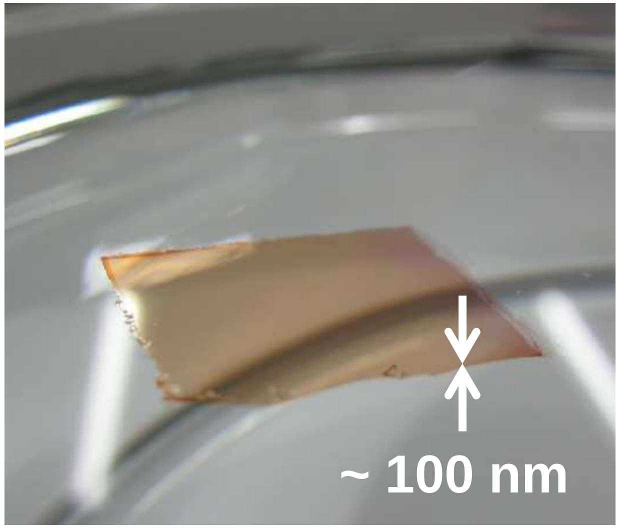
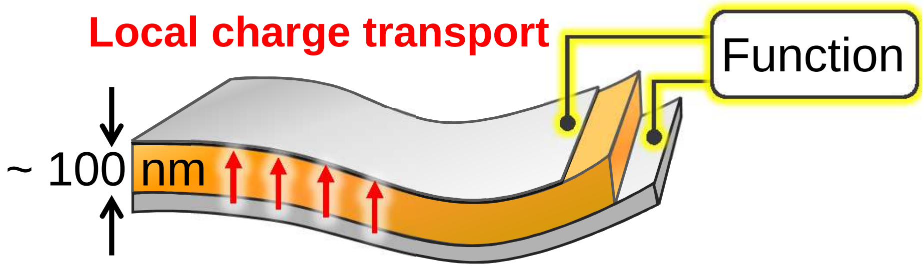


http://www.flickr.com/photos/rdecom/4146880795/

Device Configuration based on Conjugated Polymers

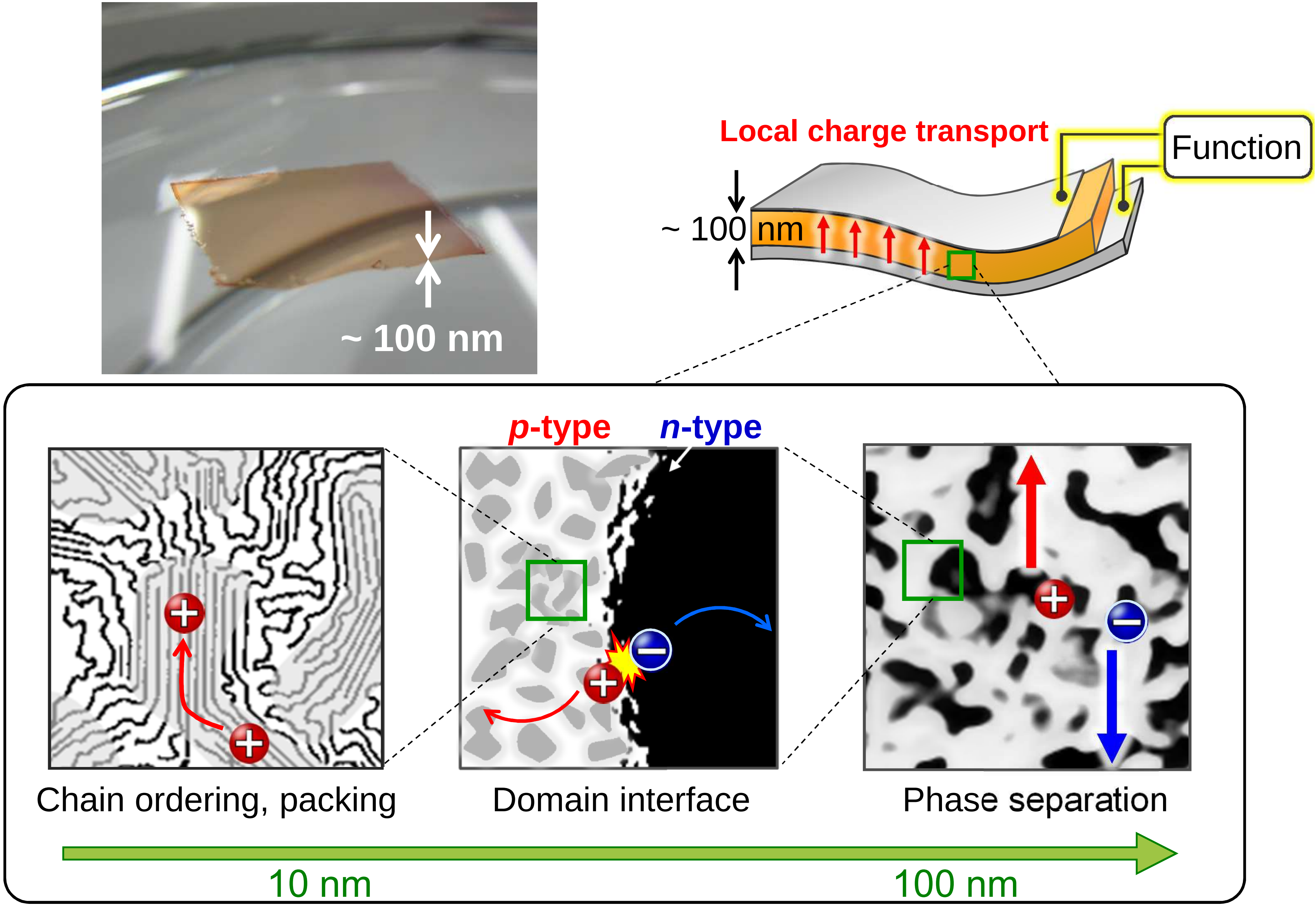




Devices based on the conjugated polymers are usually consist of a thin film of a polymer or polymer blends sandwiched between electrodes with different WF.

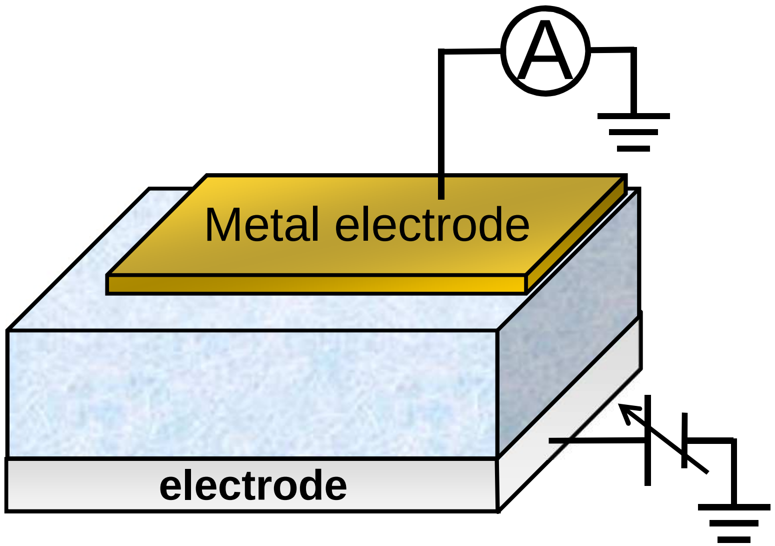
Charge transport is universal and important process for the functionalization in all materials for electronic applications.

Charge Transport through a Hierarchical Nanostructure

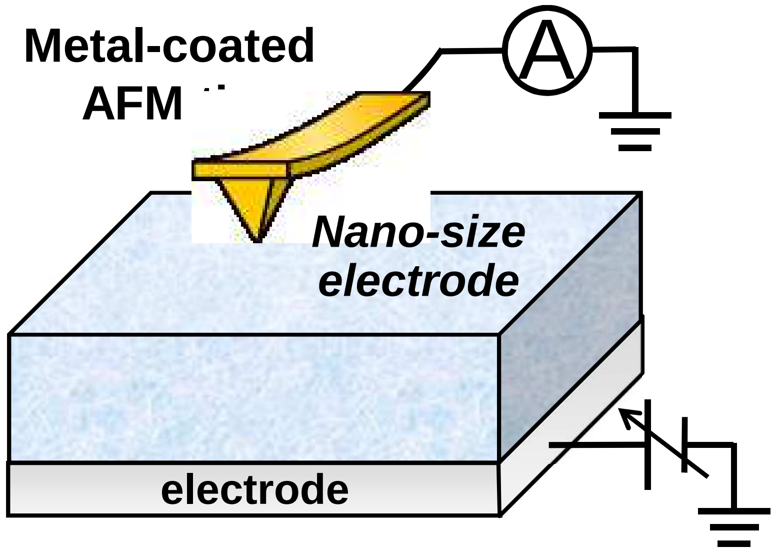


Conductive Atomic Force Microscopy (C-AFM)

Macroscopic information



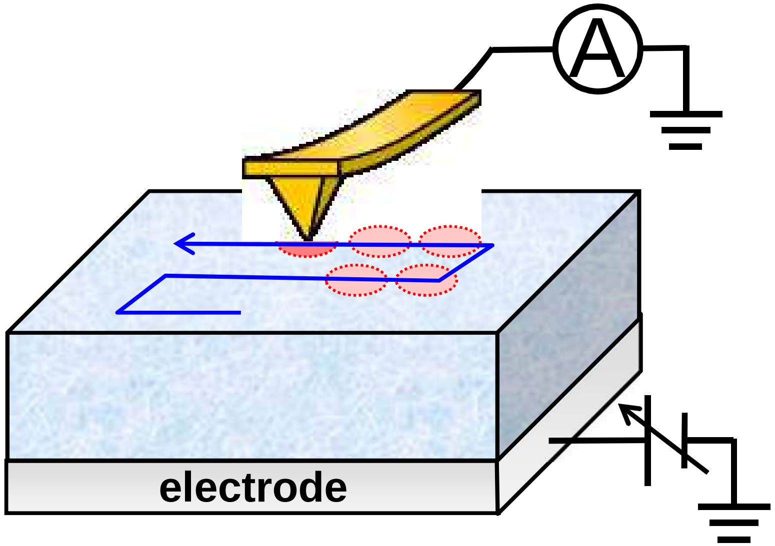
Nanoscale information

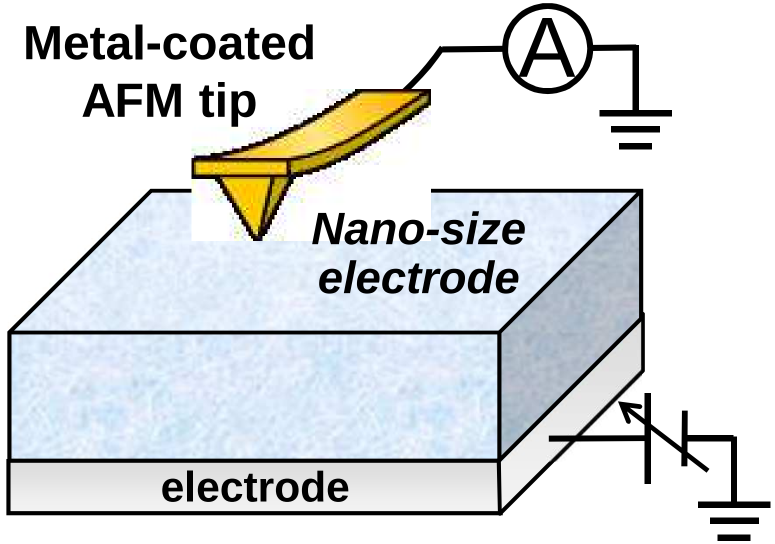


CAFM is a powerful tool for a nanoscale observation of charge transport. Electrical properties, such as conductivity, *I*–*V* characteristics below the AFM tip can be measured at nanometer resolution.

Conductive Atomic Force Microscopy (C-AFM)

Spatial resolution ≤ 20 nm **Detection current ~ 0.3 pA**

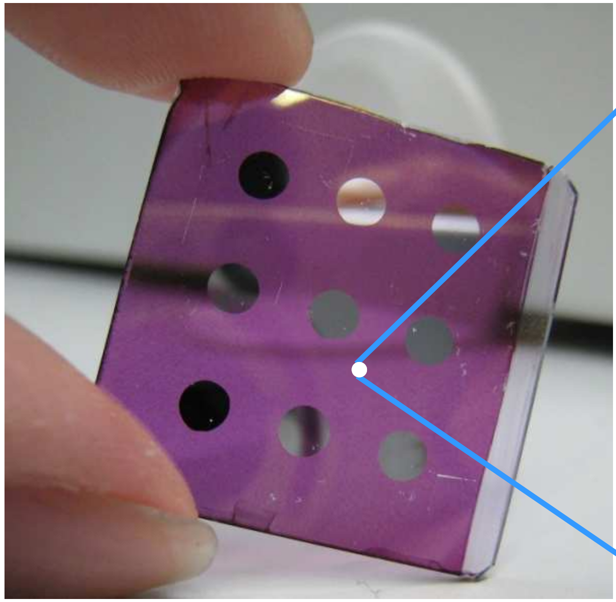


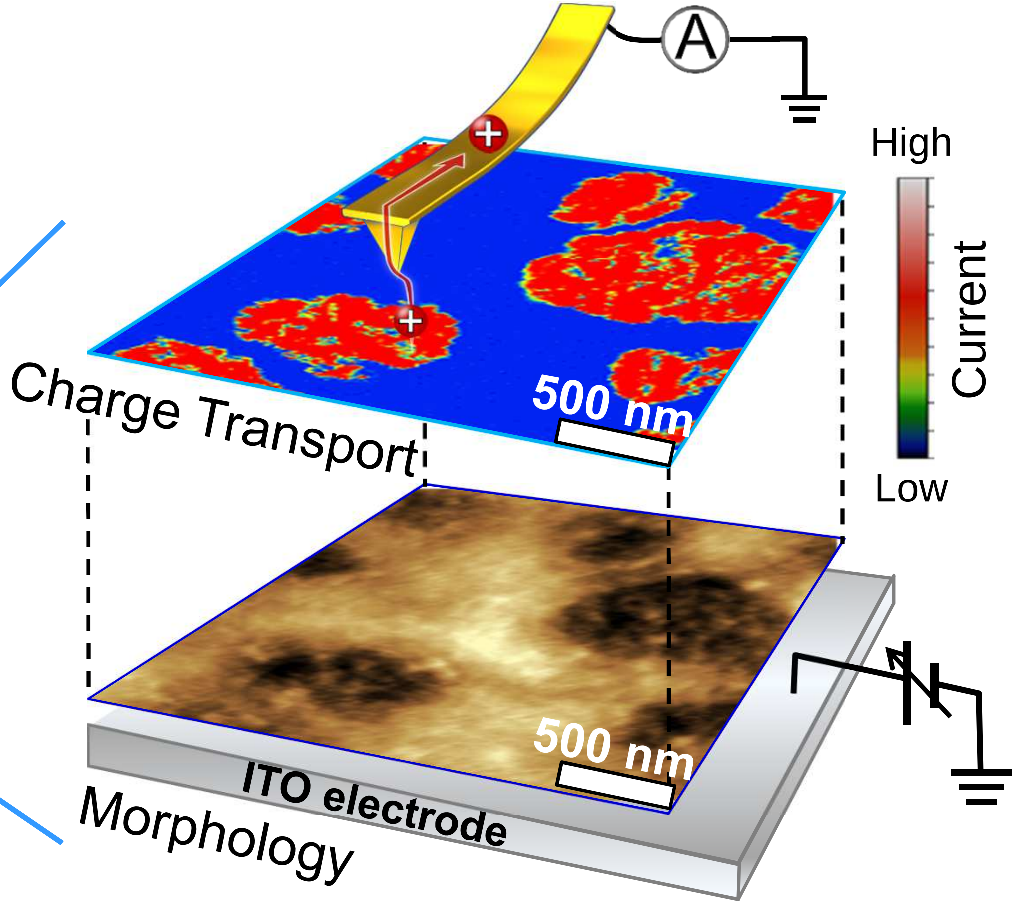


C-AFM can provide the insight into both local charge transport properties and their spatial distribution in the film.

Our Approach

Polymer Solar Cell





Visualize nanostructures for charge carrier transport in the polymer films, which could determine the overall electronic functions of the materials.

Outline

1. Nanostructures for hole transport of *p*-type semicrystalline conjugated polymer films.

M. Osaka et al. *Polymer,* **54** (2013) 3443., *J. Phys. Chem. C* **119**, (2015) 24307.

2. Nanostructures for electron transport of *n*-type conjugated polymer films.

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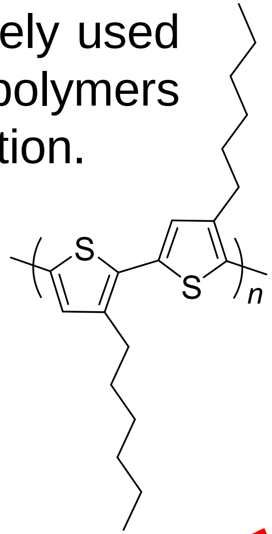
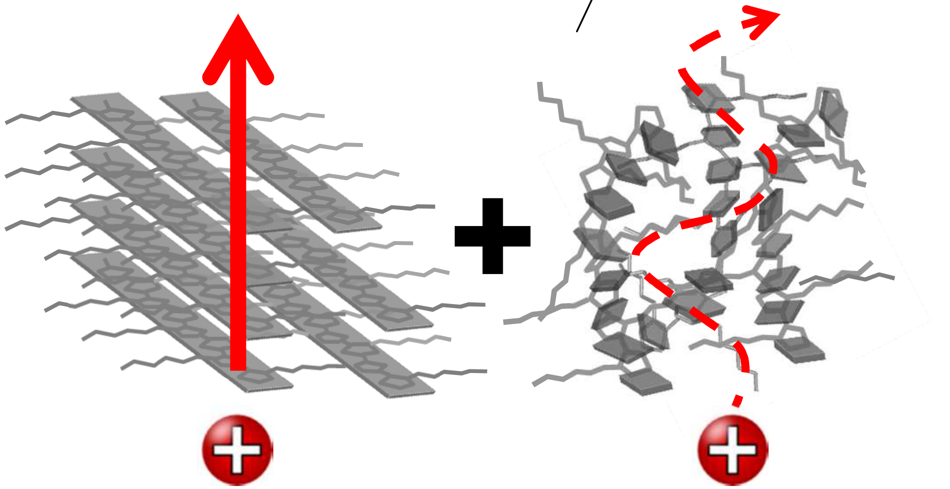
M. Osaka et al. *Macromolecules,* **50** (2017) 1618., *ACS Appl. Mater. Interfaces* **9**, (2017) 15615.

Morphology-Dependent Hole Transport of P3HT Films

Poly(3-hexylthiophene) (P3HT)

One of the most widely used *p*-type conjugated polymers for electronic application.

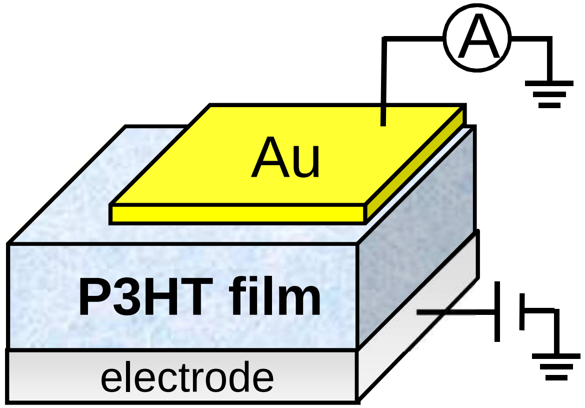


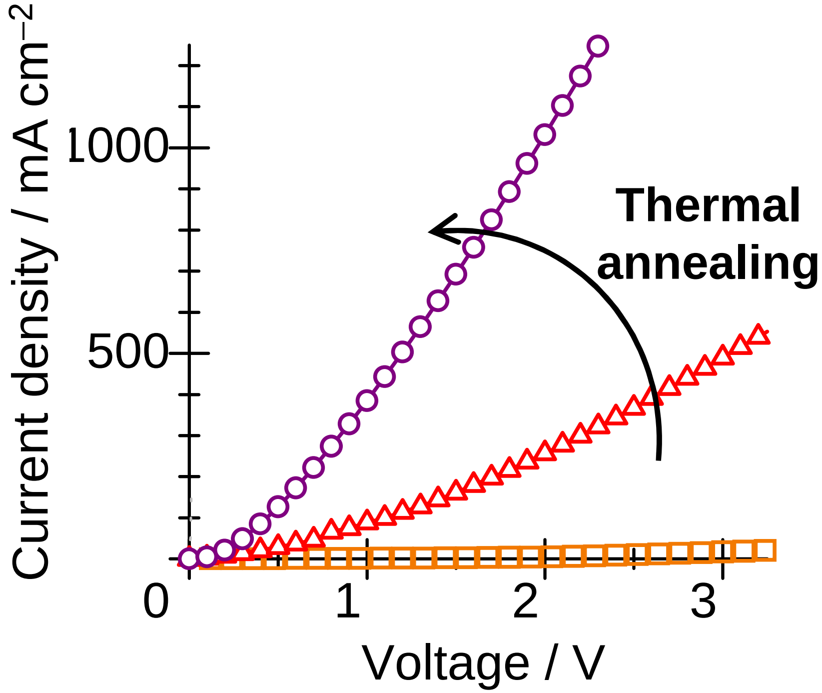


Crystalline phase

Amorphous phase

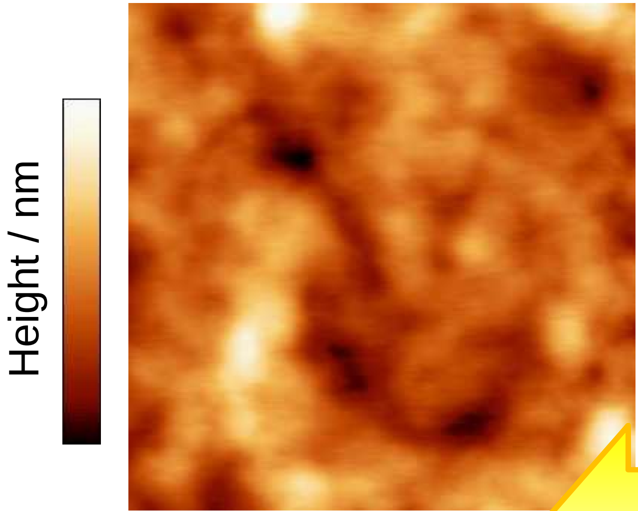
Macroscopic charge transport



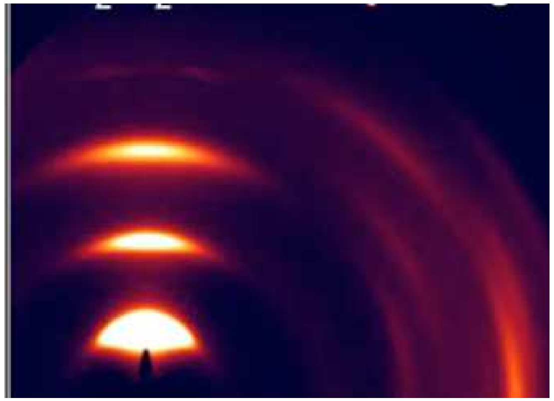


Film Morphology Shows Little about Charge Transport

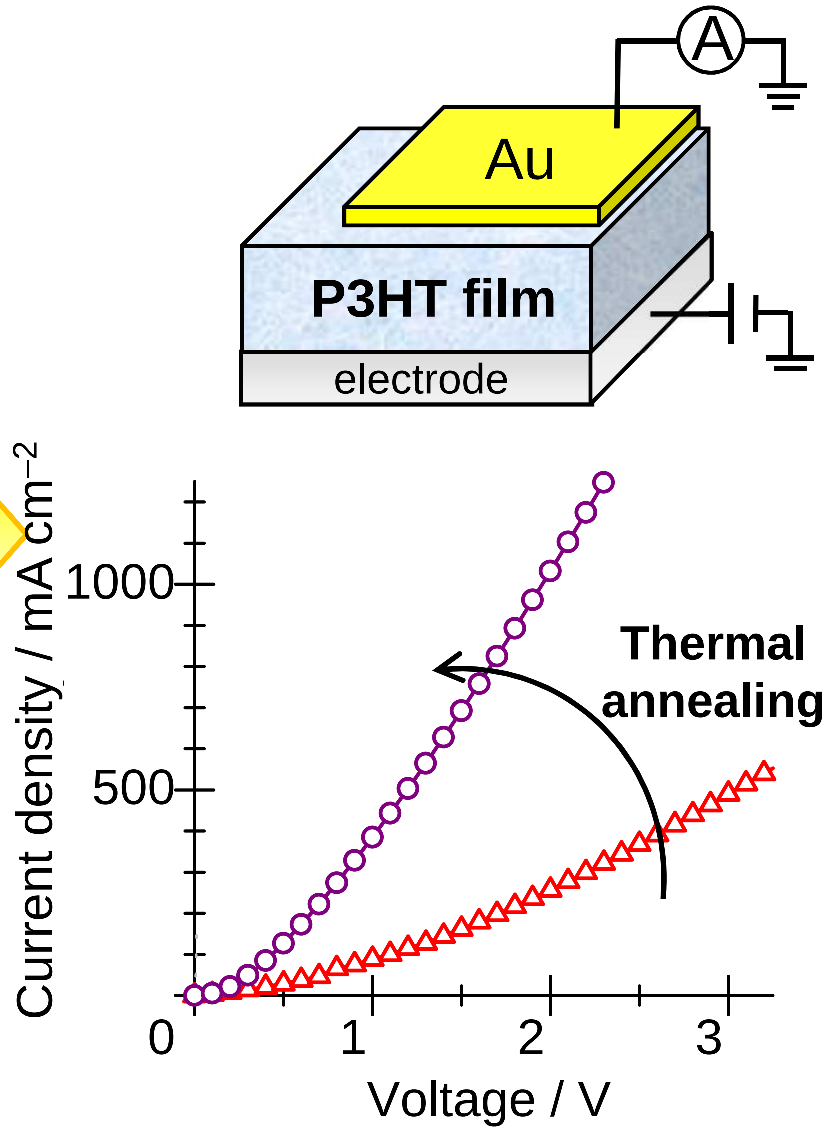
AFM surface topography



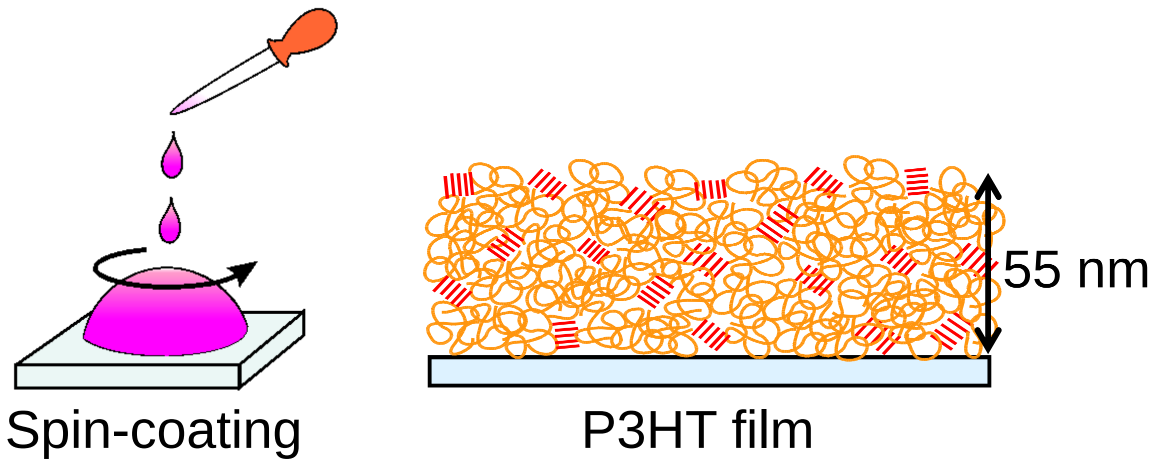
X-ray scattering

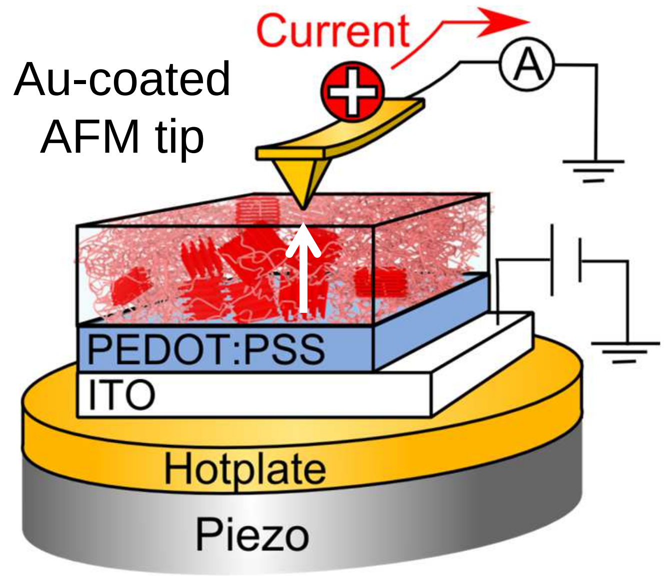


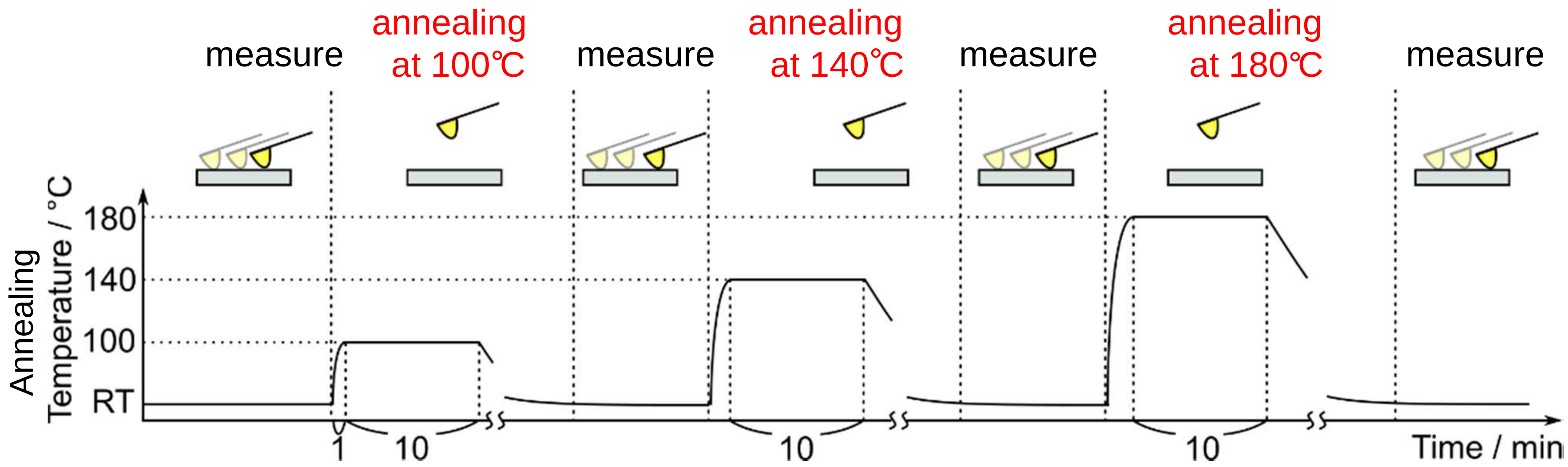
Macroscopic charge transport



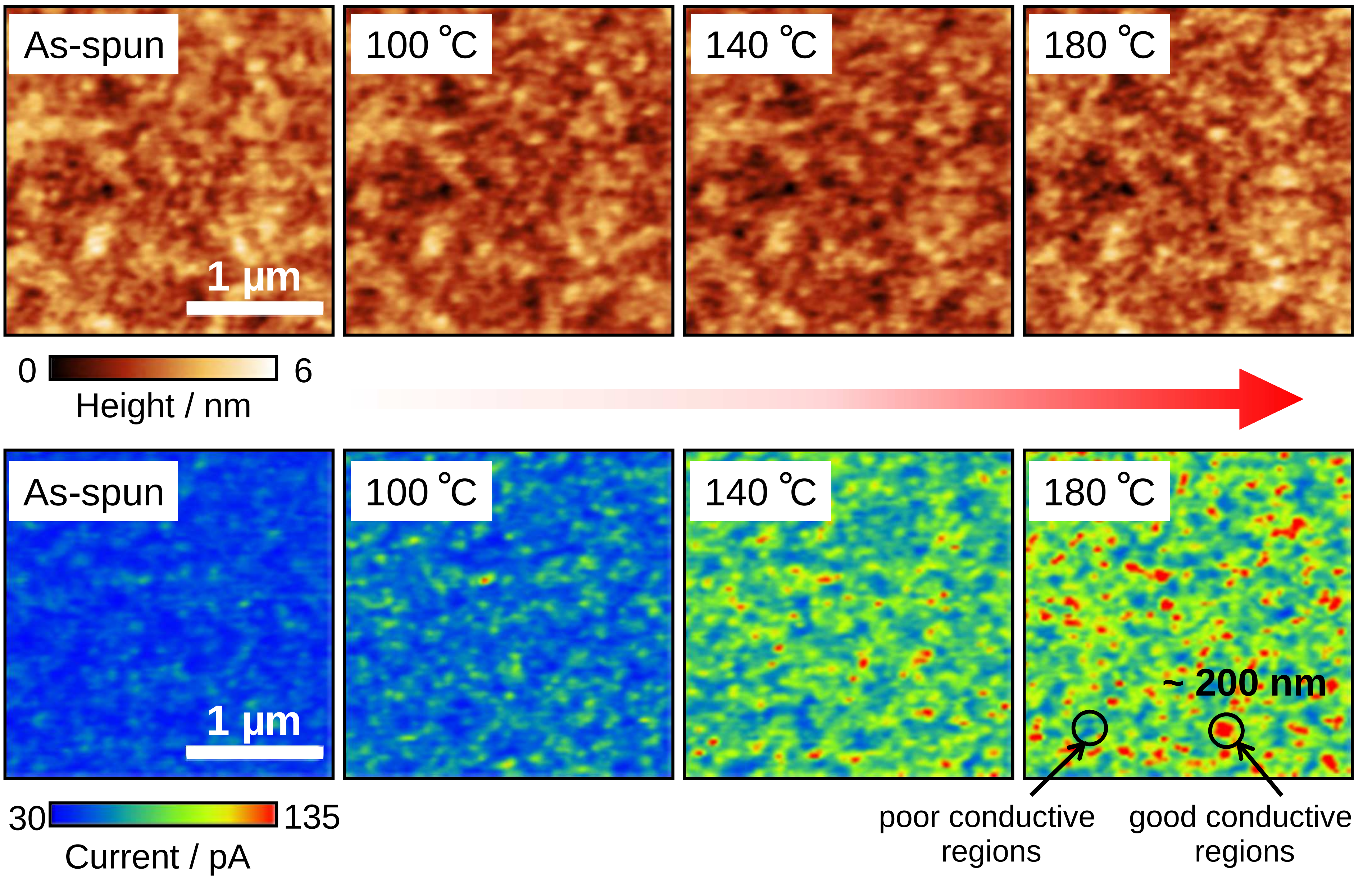
C-AFM Measurements



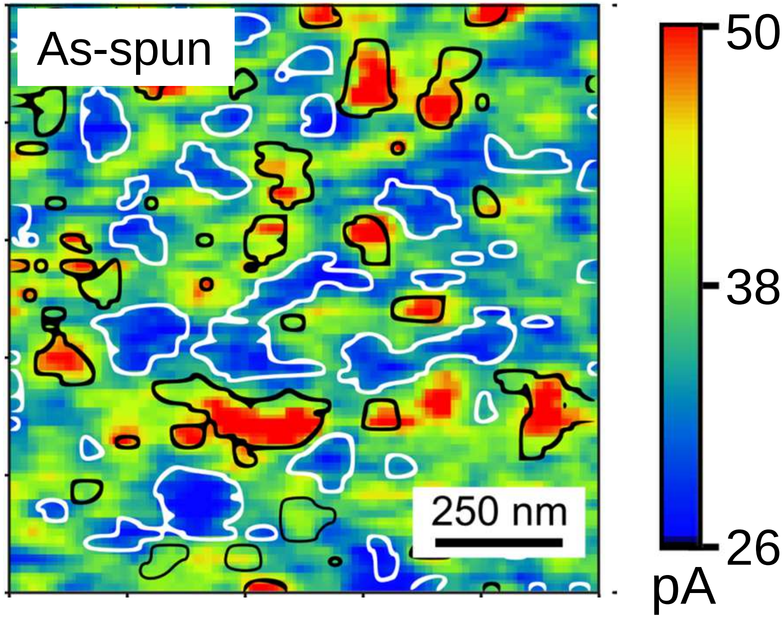


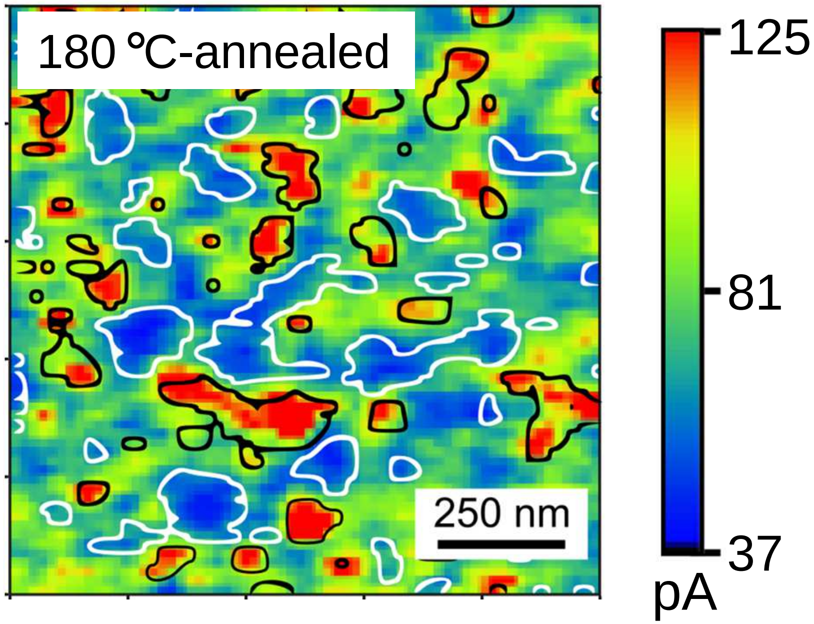


Hole Current Images



Distribution of Good Conductive Regions

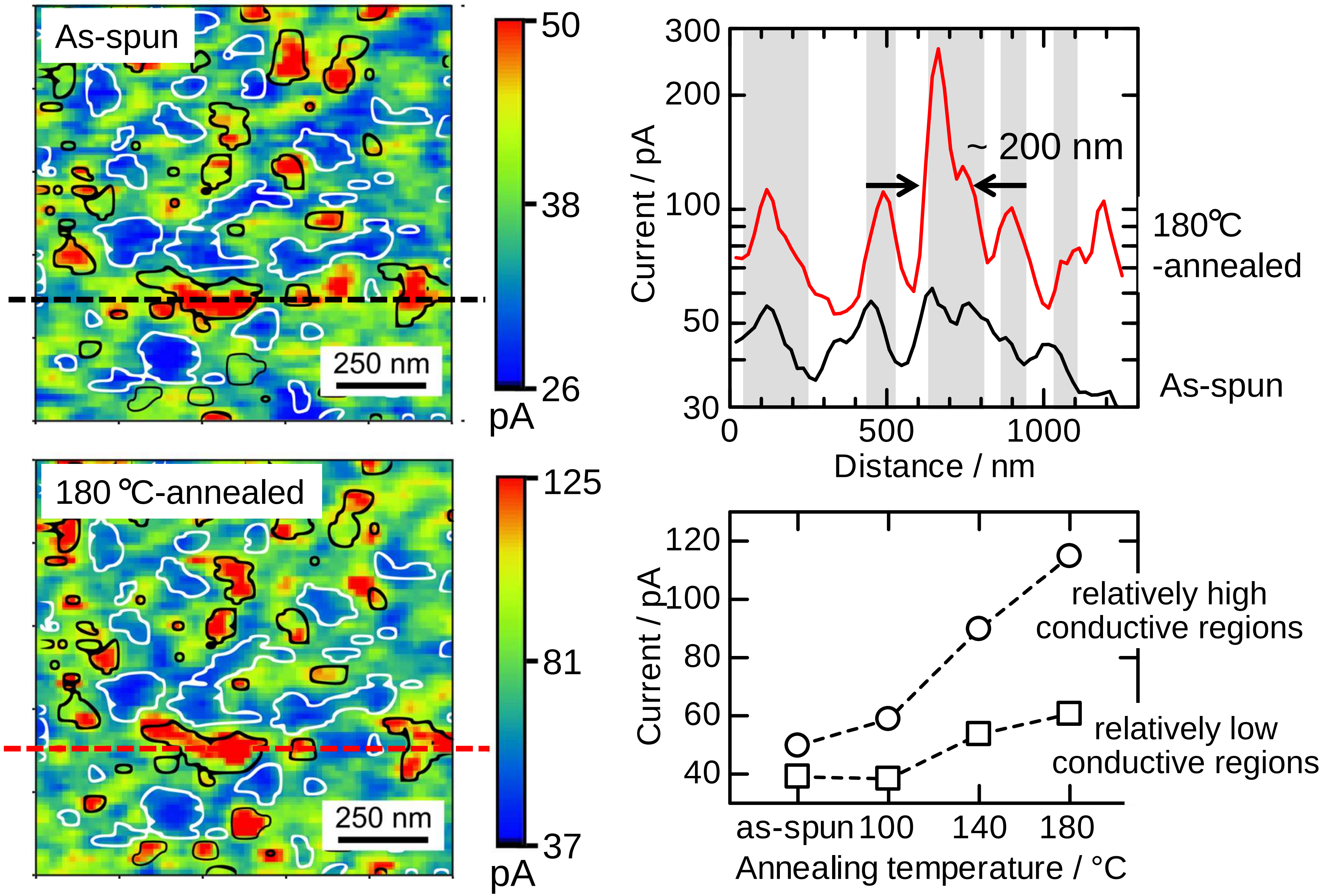




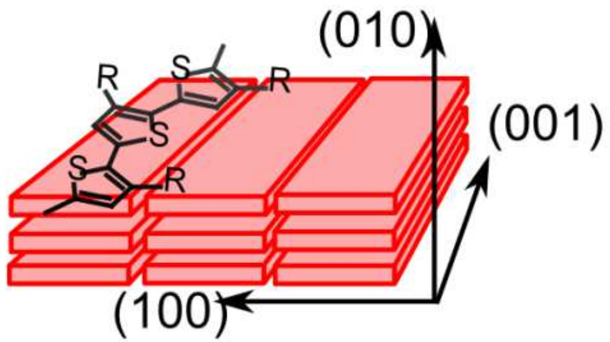
The relatively high current (high conductive) region in a film was outlined in black and relatively low current (low conductive) region was outlined in white, respectively.

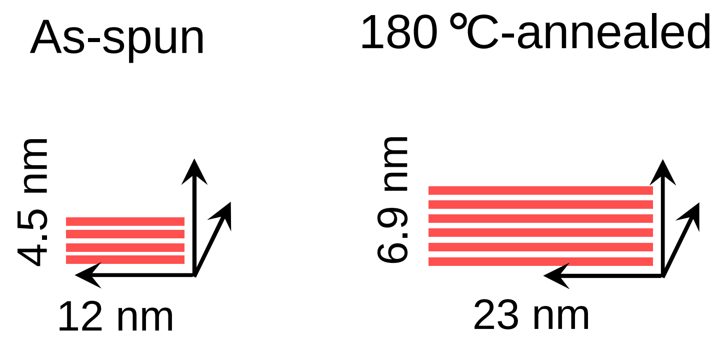
Spatial distributions of the relatively high and low conductive regions in the annealed film are well correlated with those in the as-spun film.

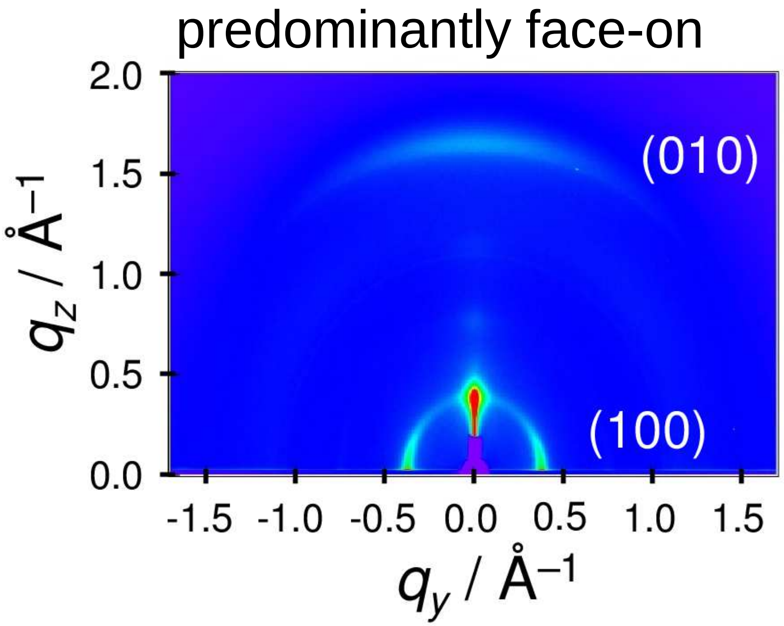
Distribution of Good Conductive Regions

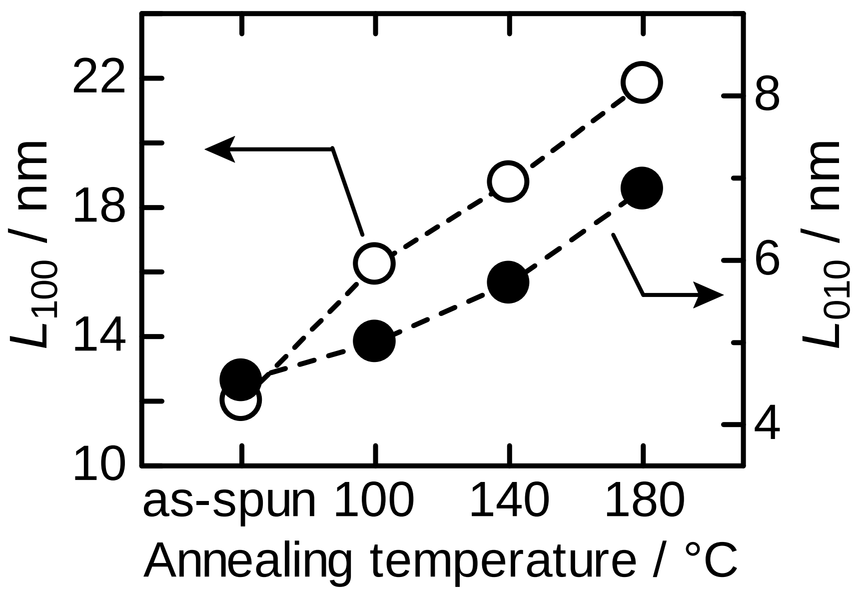


Growth of P3HT Nanocrystallites Measured by GIWAXS

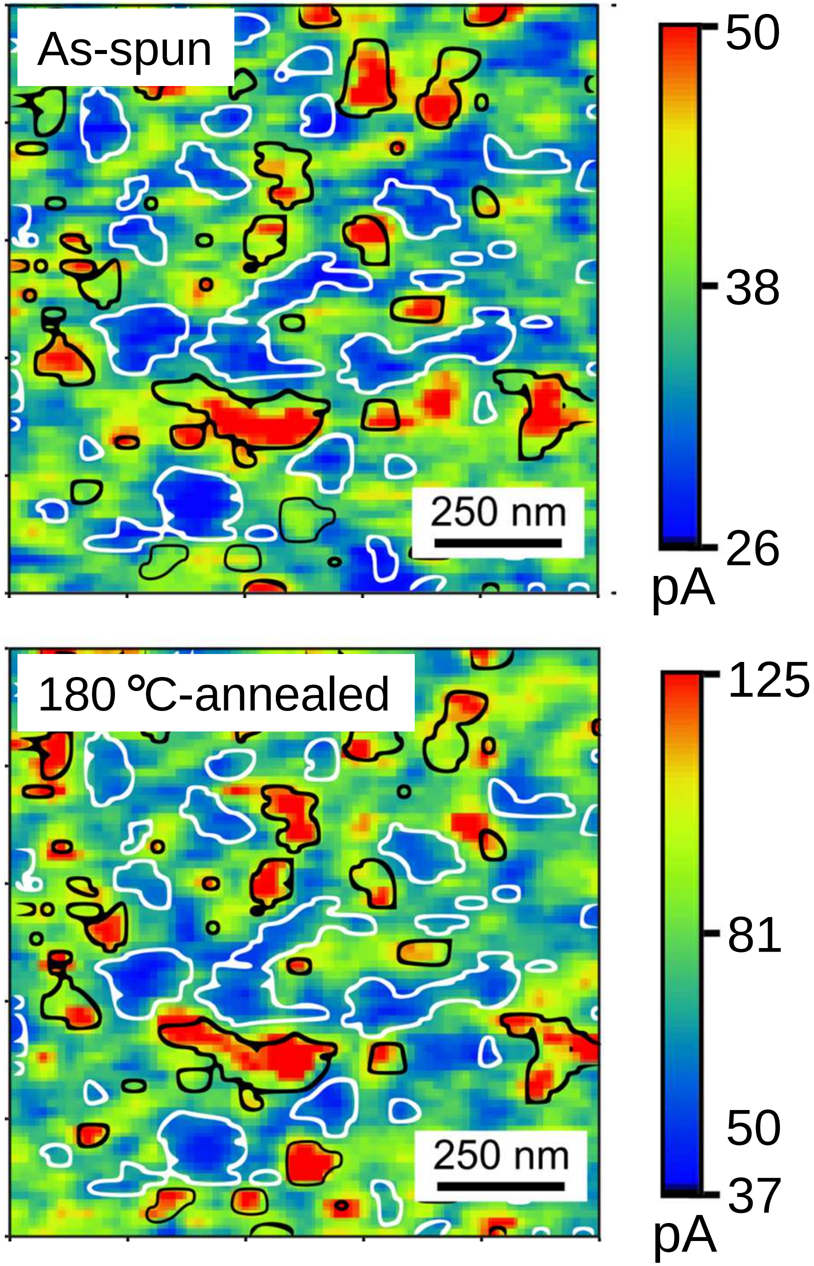








Nanostructure for Efficient Hole Transport of P3HT



From C-AFM current image

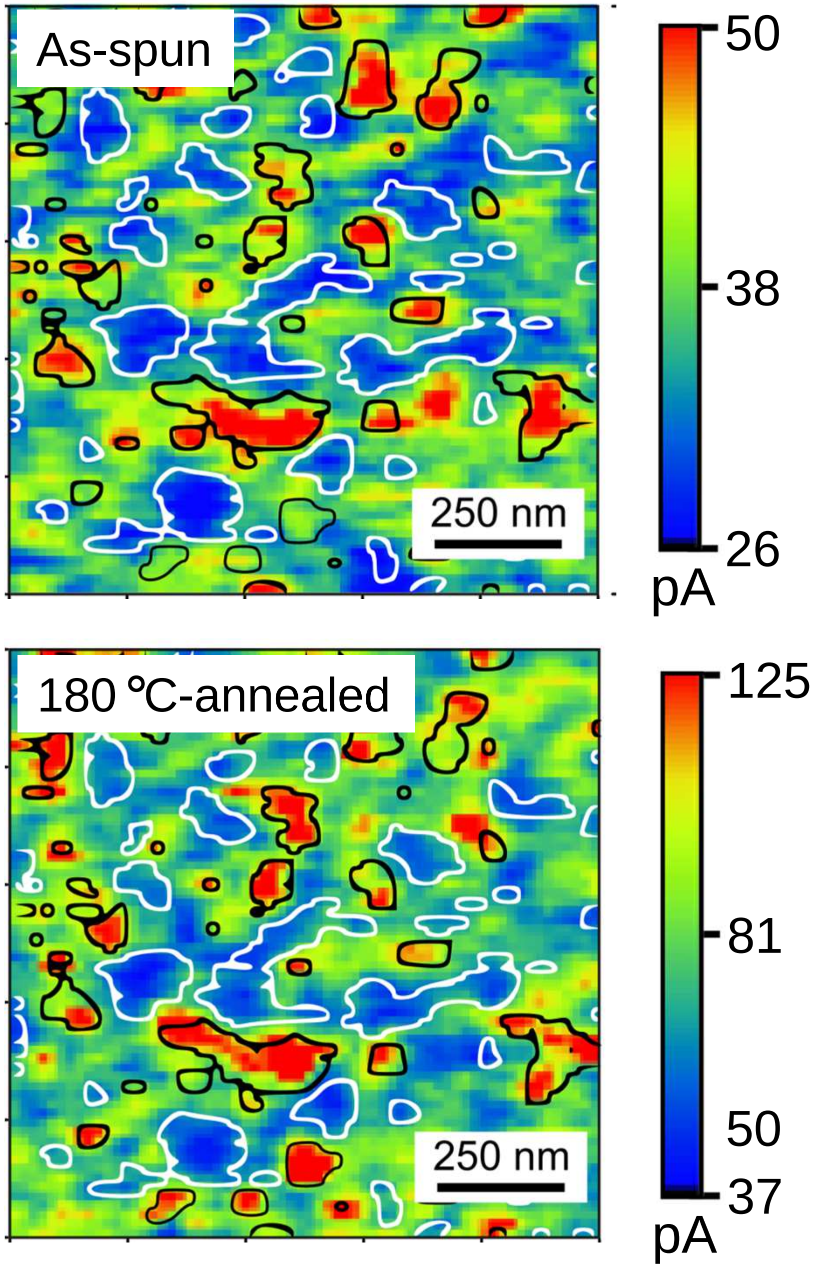
- ✓ Size of the high conductive region was ~200 nm.
- ✓ The locations of the relatively high conductive regions in the annealed film were well correlated with those in the as-spun film.

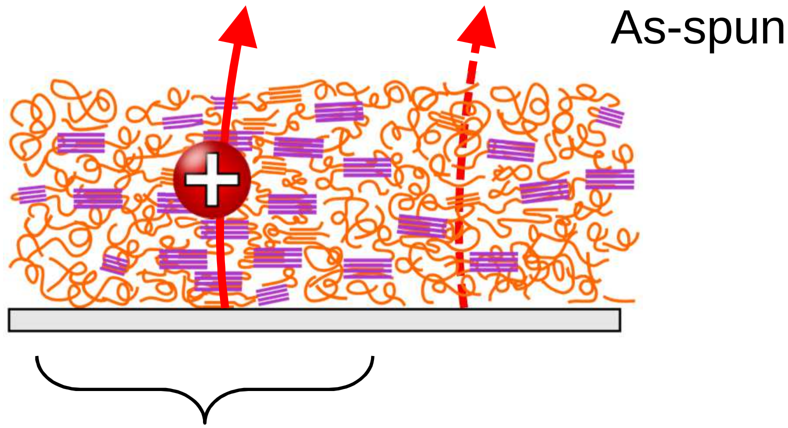
From GIWAXS analysis

- ✓ The size of P3HT crystallites was only 10 ~ 20 nm.
- ✓ They grew in size by several nm after thermal annealing.

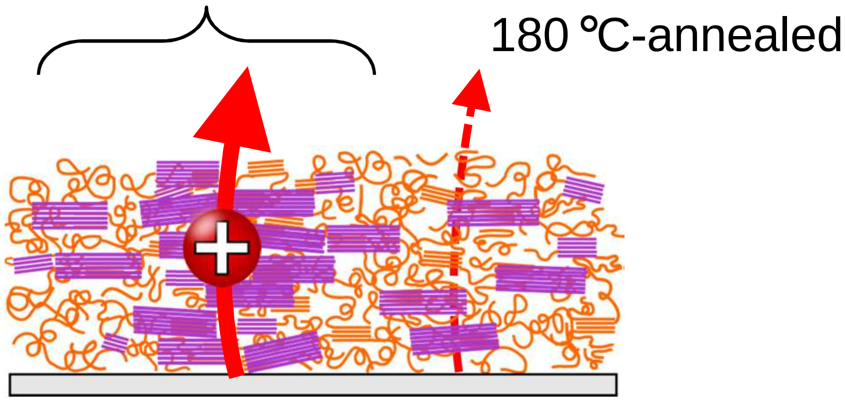
The relatively high conductive regions are assigned to the high density regions of P3HT nanocrystallites dispersed in the film.

Nanostructure for Efficient Hole Transport of P3HT





For the high density regions, the electrical connectivity among the crystallites was effectively improved by the growth of individual crystallite size, leading to the formation of preferred hole-transporting pathways in the direction of film thickness..



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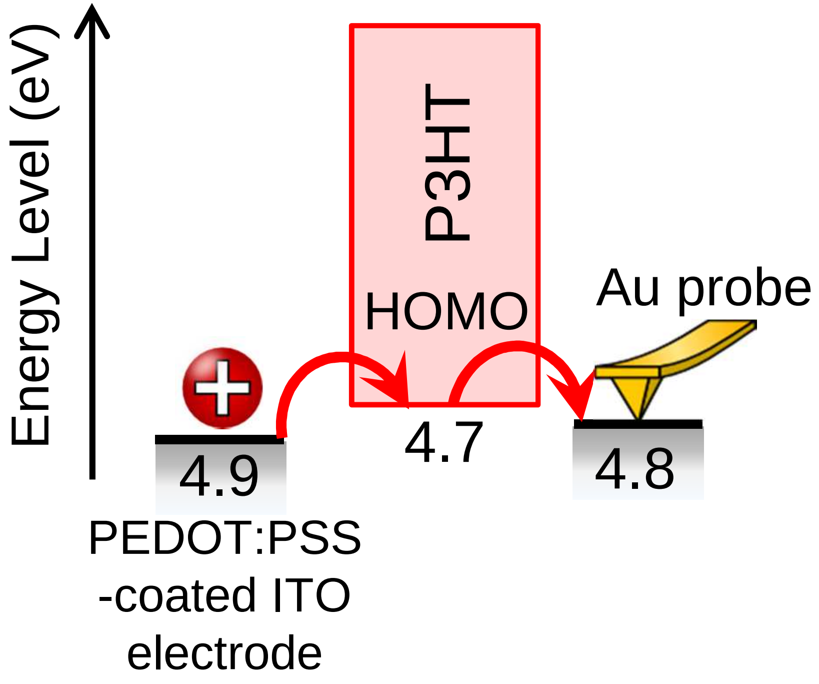
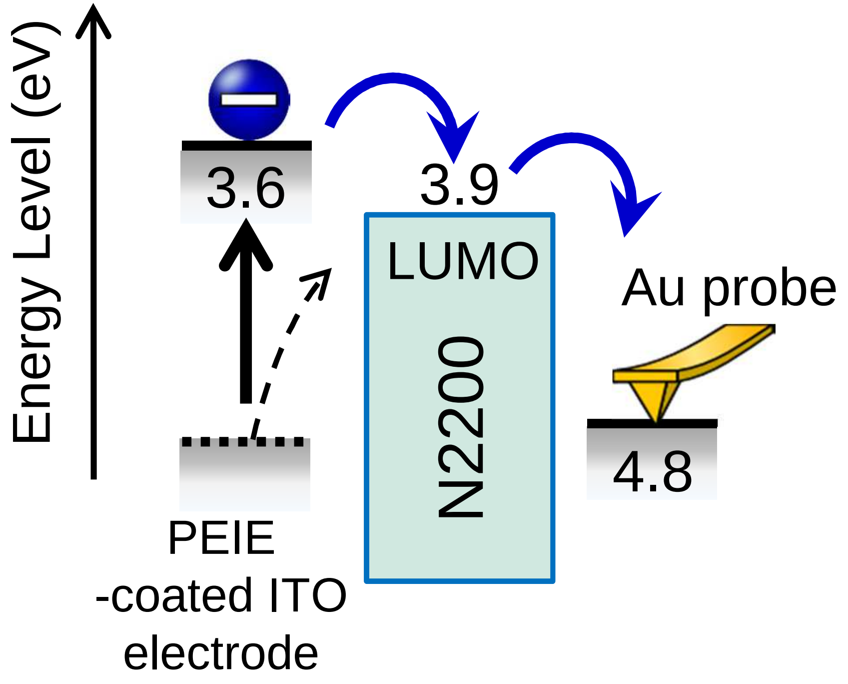
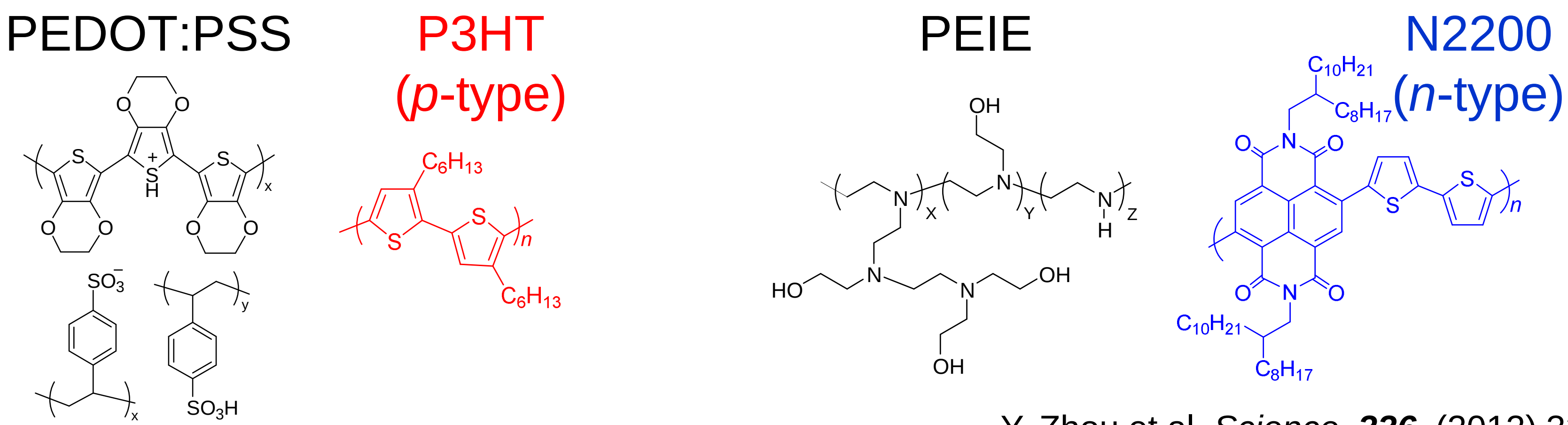
Design of Hole and Electron Injection Electrodes



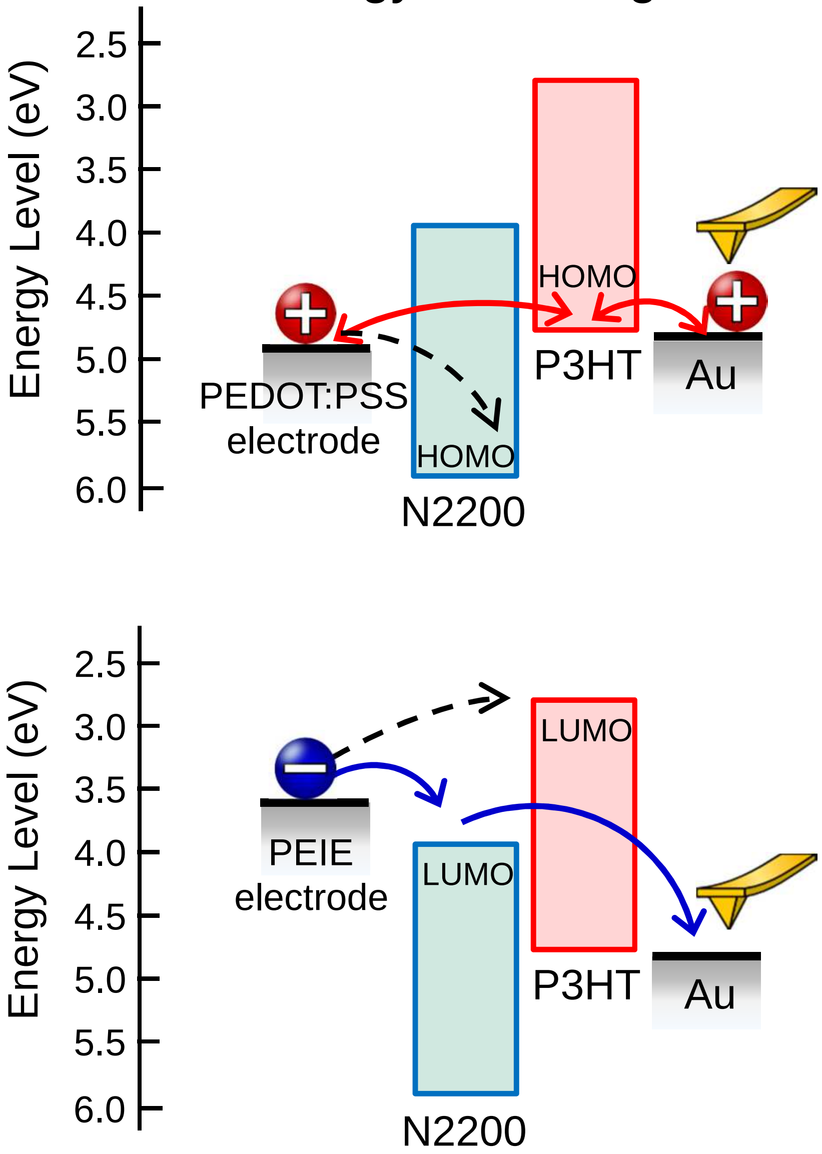




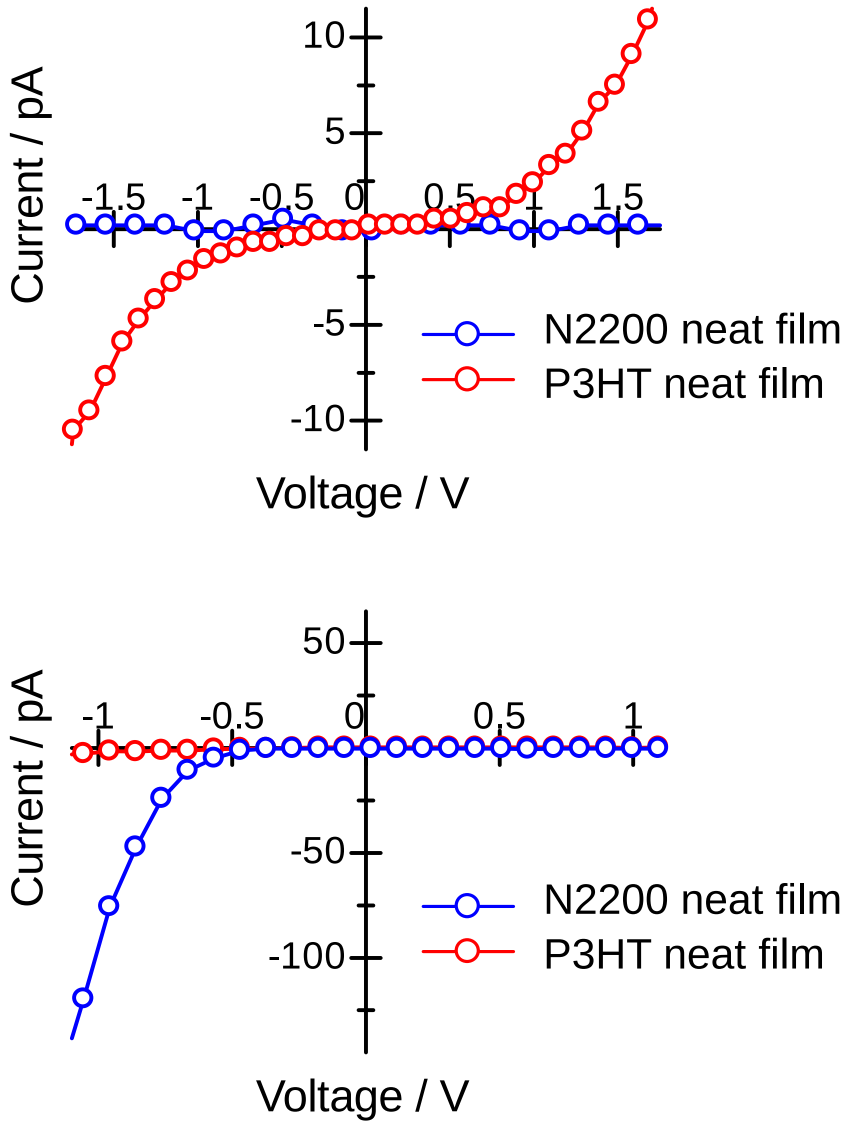
Y. Zhou et al. *Science*, ***336***, (2012) 327.

Selective Measurements of Hole and Electron Current

Energy level diagram

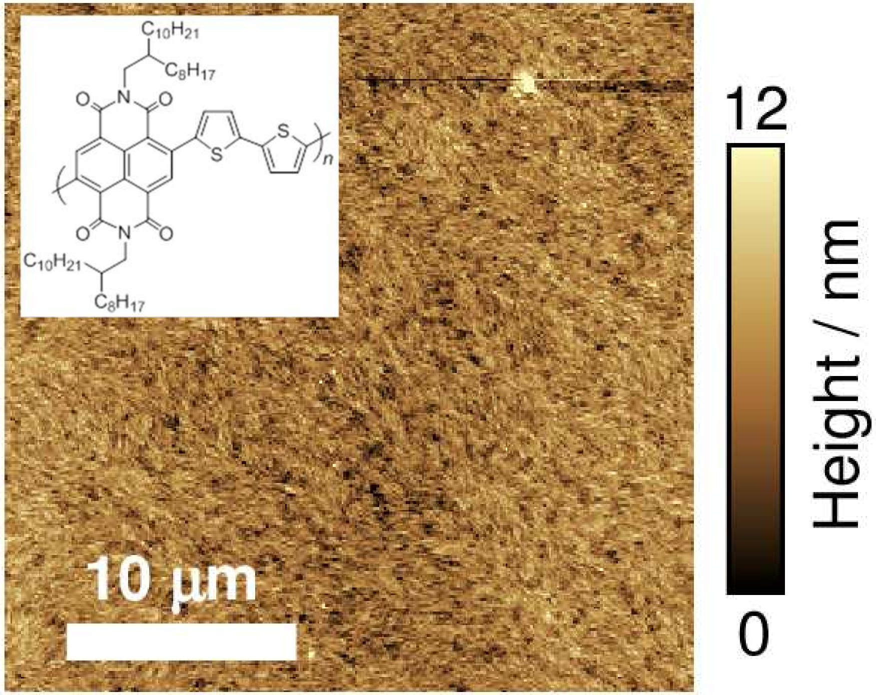


C-AFM local *I*–*V*

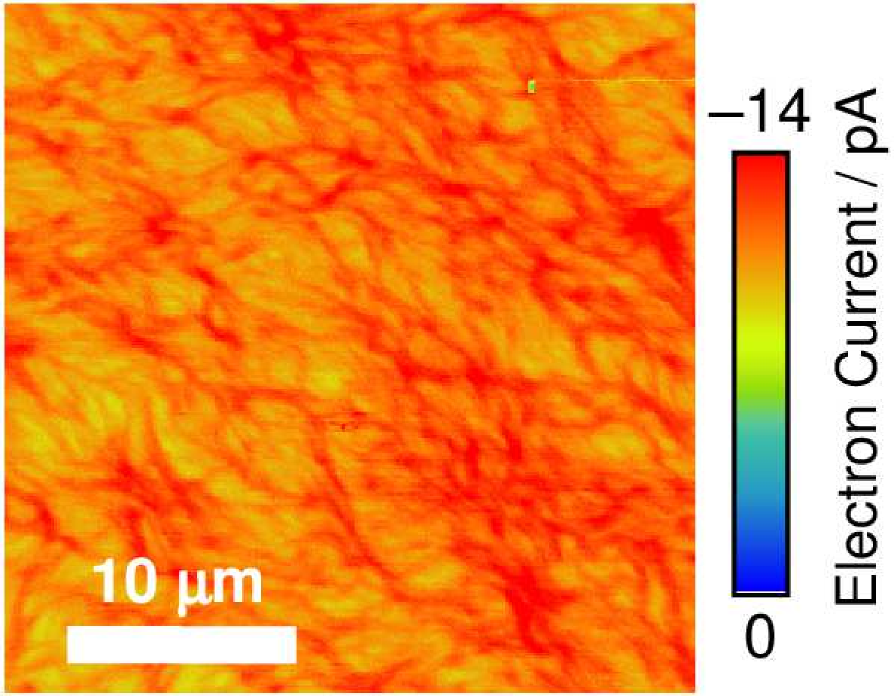


Nanostructures for Electron Transport of N2200

Topography

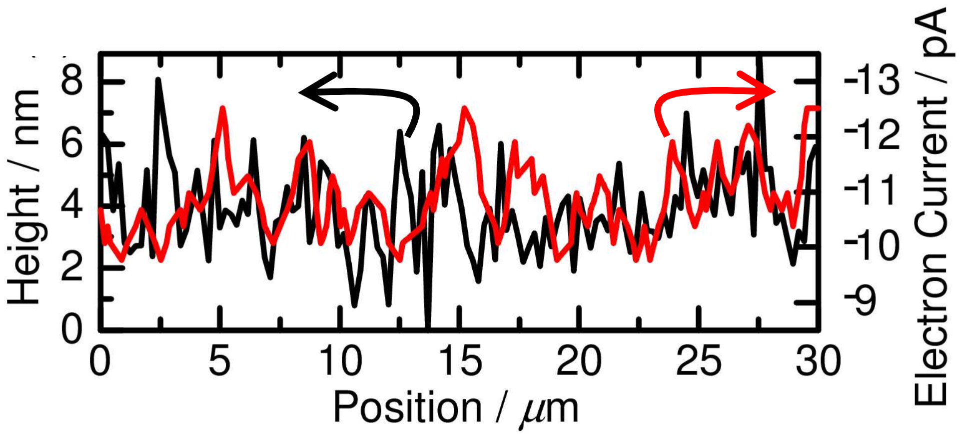


Electron current



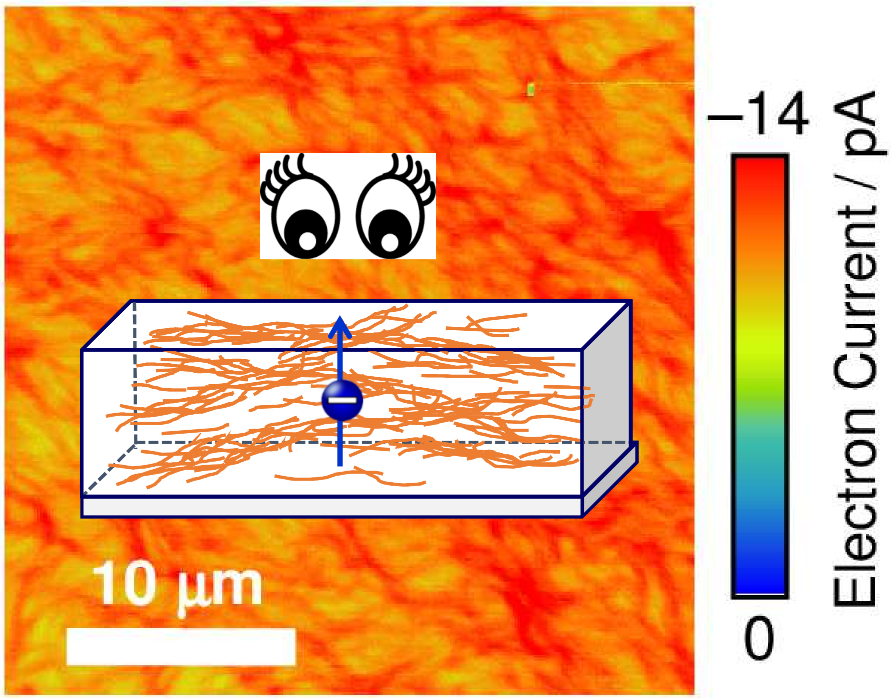
Long-range ordering structures on μm length scale, which could not distinguished in the topographical image.

Nanostructures for Electron Transport of N2200



There is not a strong correlation between the topographical structures and the current magnitudes.

Electron current



Electron-current image is considered to represent a difference in the density of locally ordered (fibril-like) polymer structures in the film.

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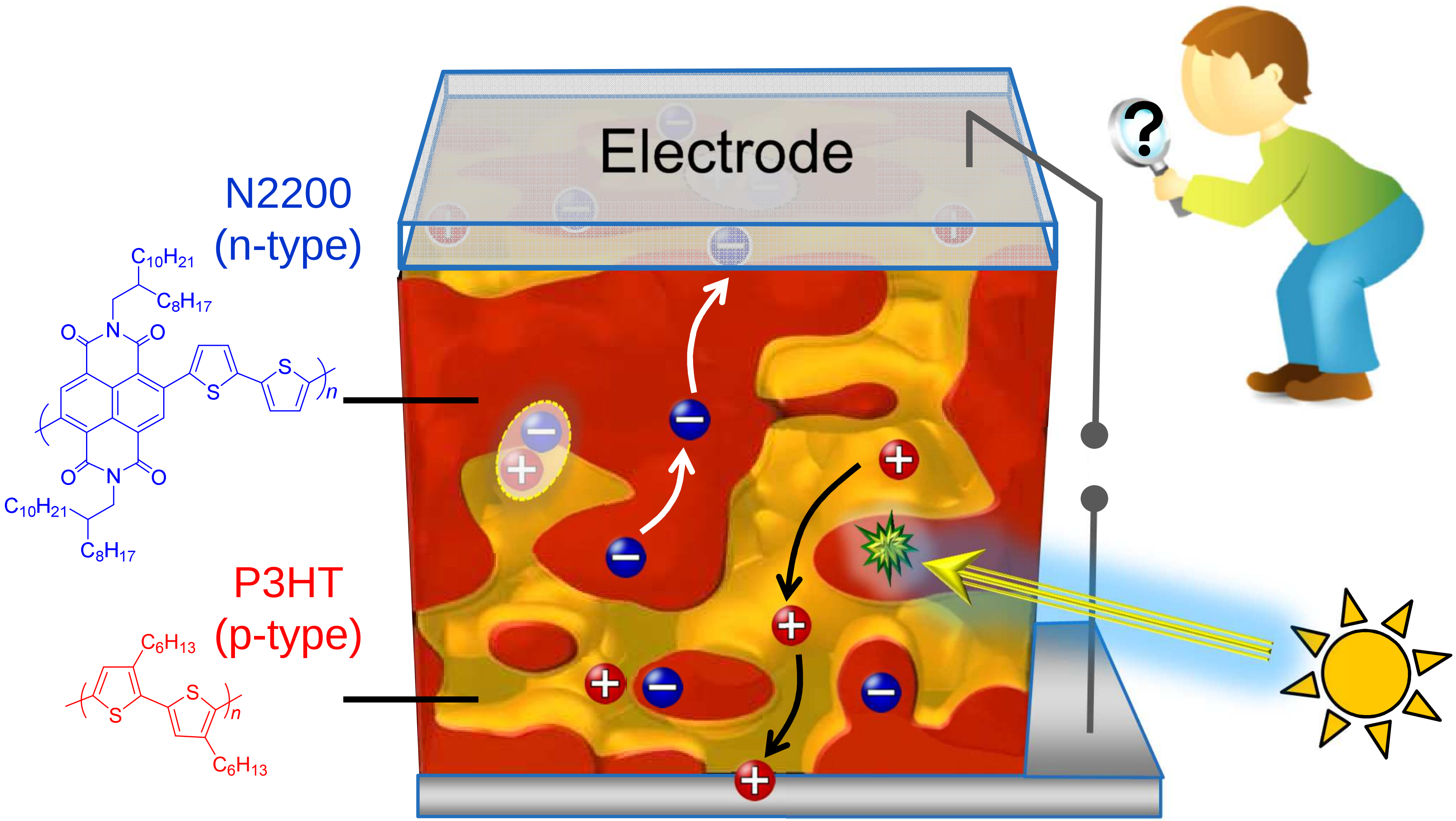
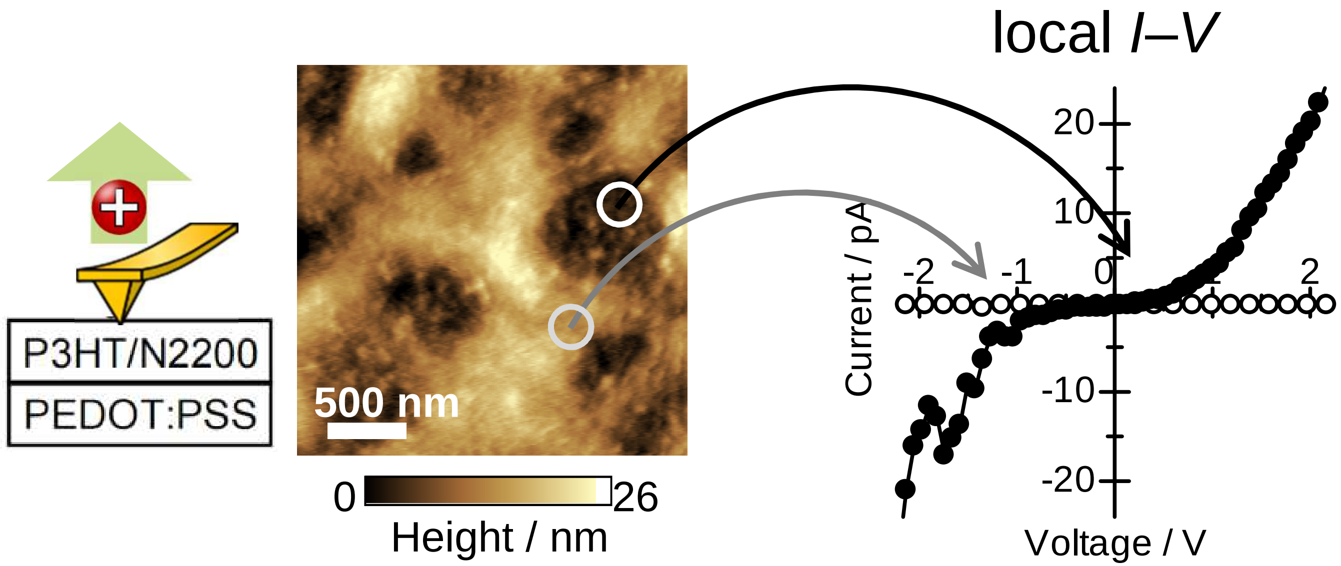
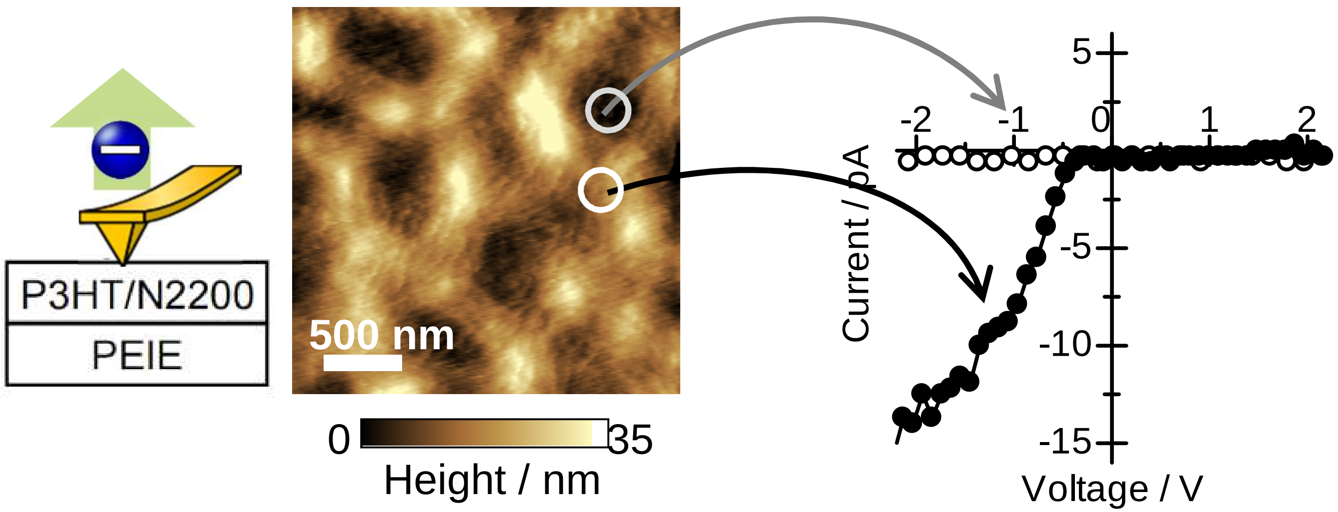
Charge Transport of *p/n* Polymer Blend



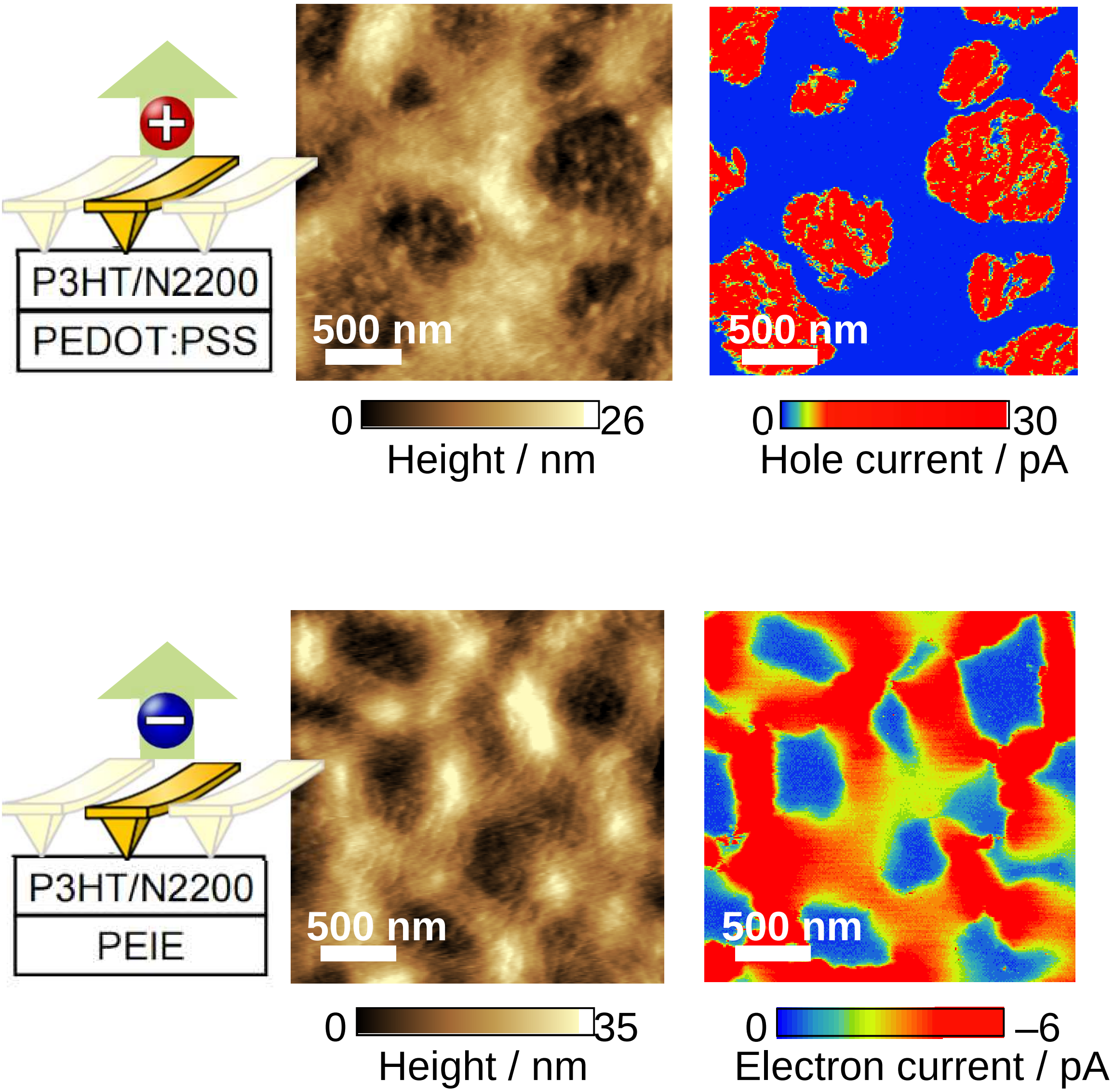
Direct observation of charge transport on a nanometer scale is critical for understanding a morphology-function relationship for the development of an efficient solar cell.

Local Charge Transport Properties of P3HT/N2200 Blend



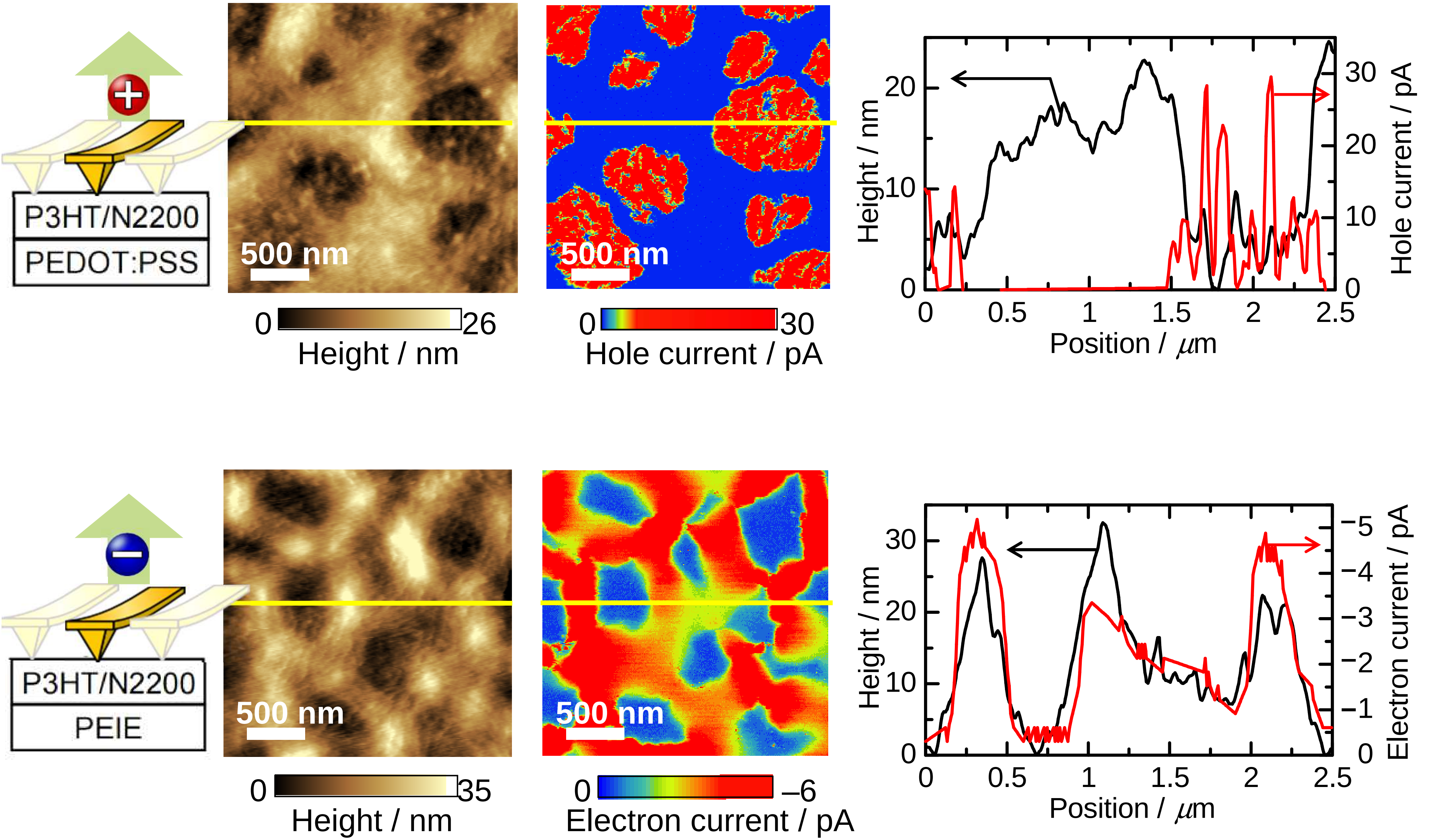


Hole and Electron Transport in P3HT/N2200 Blend

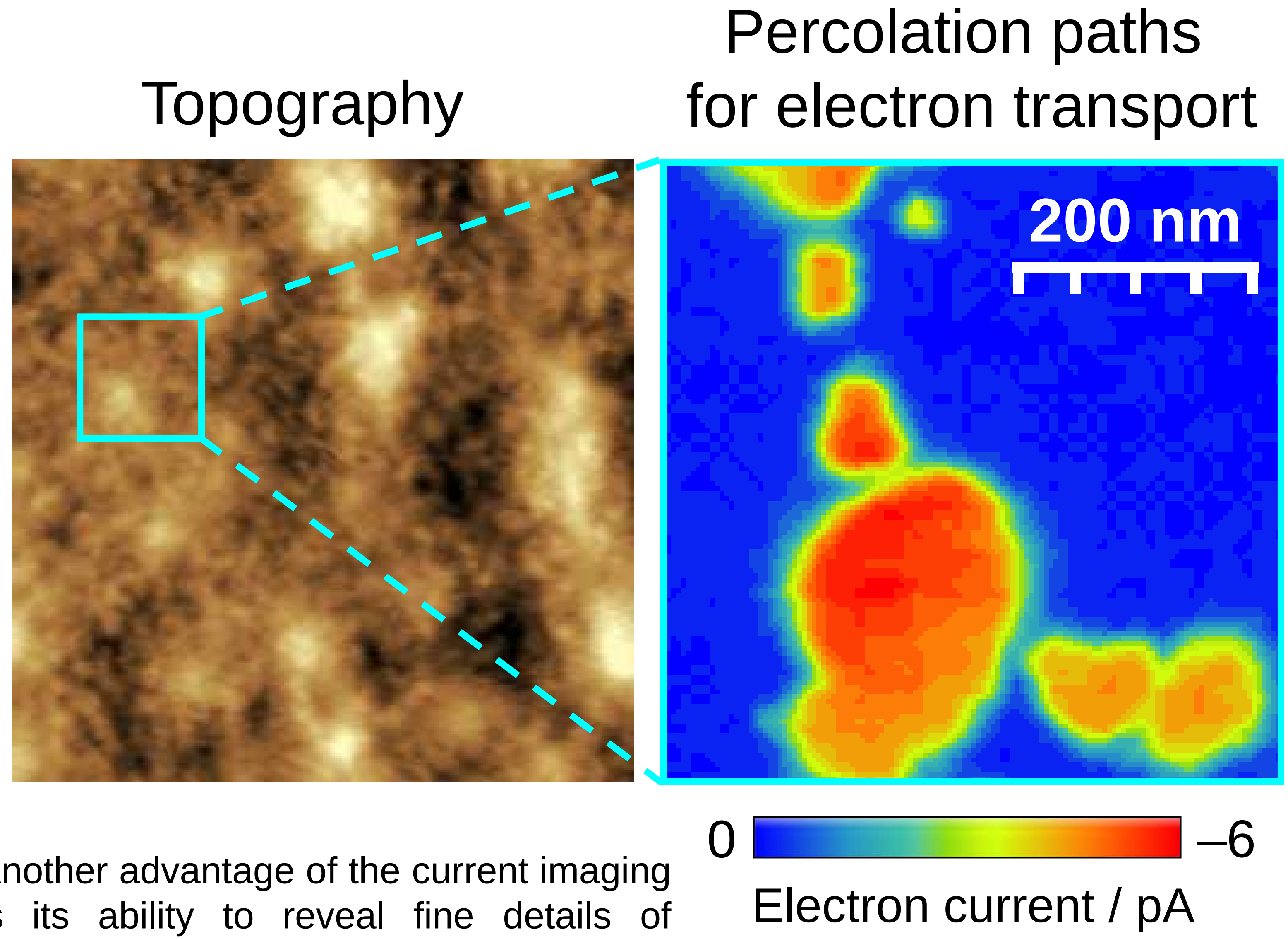


The distribution of the hole- and electron-transport ability in the blend film were visualized by scanning the probe over the film surface.

Hole and Electron Transport in P3HT/N2200 Blend

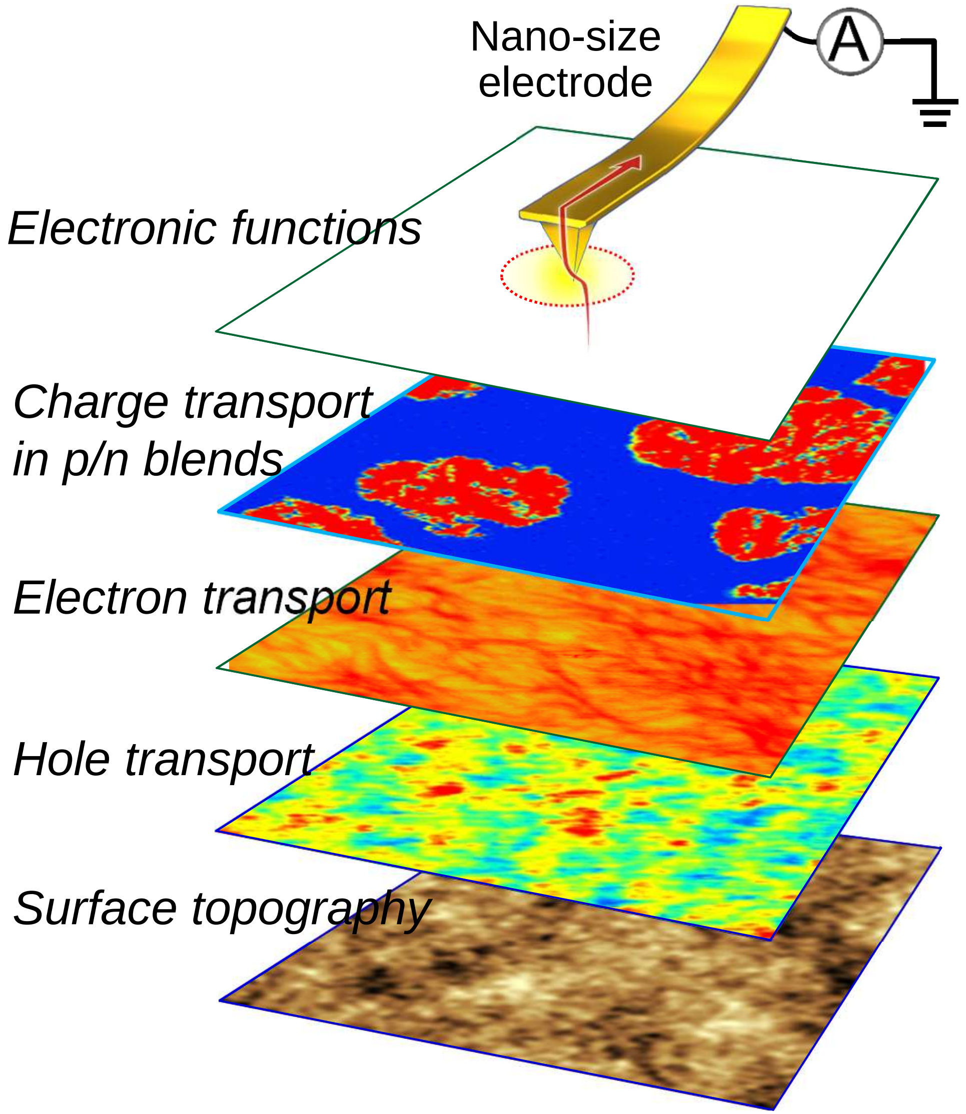


High-Magnification Electron-Current Images



Another advantage of the current imaging is its ability to reveal fine details of nanoscale structure of the blends, which is obscured in topographical imaging.

Summary



C-AFM current images reveal fine details of nanostructures for both hole- and electron-transport of polymer films, which are not easily distinguished in the topographical image.

The advantages of C-AFM to electrically resolve nanostructures of polymer films will contribute to further understanding of the mechanisms for the excellent charge transport and the creation of novel device functions.

Supported by CREST program from the Japan Science and Technology Agency (Prof. Koichi Yamashita, University of Tokyo)