Briefs of optoelectronic devices, and central research (debate) of optoelectronic devices: properties and processes.

Advantages of NSOM imaging when applied to film materials, which dominate the current organic optoelectronic devices.

Different operation modes of NSOM imaging and several examples:
1. Organic solar cells: local nanostructure and photoconversion relationship
2. Polymer dispersed liquid crystals;
3. Conjugate polymer films;
4. Bi-block polymer films;
5. Dentrimer films;
Scheme of a solar cell

- **PHOTONS**
- Front contact grid
- n-type
- p-type
- Back contact

[Diagram of a solar cell with an explanation of its components]
Some review papers on organic optoelectronic materials

**Nature Materials, VOL 2, 2003, p641**

**NEWS & VIEWS**

**ORGANIC SEMICONDUCTORS**

**An equal-opportunity conductor**

Until now, organic semiconductors, such as pentacene, have only allowed the flow of one type of charge. A new study confirms that—like their inorganic counterparts—both positive and negative charges can flow in the same material.

**HENNING SIRJANNAHS**

**Introduction to Organic Thin Film Transistors and Design of n-Channel Organic Semiconductors**

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**Chem. Mater. 2004, 16, 4436–4451**

**Organic Thin Film Transistors for Large Area Electronics**

By Christos D. Dimitrakopoulos and Patrick R. L. Malenfant

Optoelectronic devices (materials)

• Optoelectronic materials are both optical and electrical active.

1. **Optical** --- strong absorption and/or emission, polarization, or non-linear optical properties;

2. **Electrical** --- high efficiency for light-to-electricity conversion (photovoltaic), or electricity-to-light conversion (electroluminescence).

• Optoelectronic materials can be organic or inorganic semiconductors, or even metals (nanocrystal state, e.g. silver nanoparticle (prism, rod) as non-linear optical materials, see George Schatz work at NW).

• Organic semiconductor has now attracted more interests in development of optoelectronic devices, due to the vast options of organic molecular structures --- covering the whole visible spectrum and can be tuned to be both n- and p-type semiconductors.

• The recently developed microscopic and spectroscopic techniques has enabled the measurement at higher resolution, thus helping understanding the basic properties and processes of optoelectronic materials.
Central debates of optoelectronic materials

- Mechanism: electrical excitation $\rightarrow$ electron-hole recombination $\rightarrow$ light emission, or the reverse.
- Performance of organic optoelectronic devices depends on exciton (electron-hole pair) diffusion, exciton dissociation at p-n junctions, charge carrier mobility, which in turn are all determined by the intermolecular interaction --- self-assembled nanostructures.
- Huge amount of debates and conflict concerned the similar device or even the same materials.
- For example, for the same material PTCDI (see slide), the charge carrier mobility has been measured in a wide range, from $\sim 10^{-5}$ to $\sim 1.0$ cm$^2$ V$^{-1}$ s$^{-1}$, and the exciton diffusion has been reported to be from nm to µm.
- While various organic materials and device structures have been developed and explored, the primary challenge is still to understand the fundamental photoinduced processes and physical requirements for improving the photoconversion, especially at microscopic or nanoscopic levels.
PTCDI molecules: a n-type semiconductor

R = alkyl, aryl, polyoxyalkyl;
R' = functional moieties: amine, carboxylic, thiol, etc.
NSOM imaging of optoelectronic devices (materials)

- Major imaging modes for NSOM: emission (for LED) and bias modulation (for photovoltaic devices).
  *See scheme of local detection of emission, to be drawn on board.
- A combination of emission and bias modulation affords in situ investigation of photovoltaic devices -- calibrating of solar cell materials.
- High spatial resolution --- revealing structure dependence of device performance; single-particle measurement pave the way for nanoelectronic devices (nanowires, nanorods …).
- The ultra fine laser spot from NSOM tip provides highly local and precise excitation of small nanomotifs, like a nanowire. *See the slide.*
- Tunable with femtosecond *pulsed* laser system for ultrafast charge or energy transfer processes.
- Tunable with polarization systems for molecular packing structure, which determines both the charge mobility and exciton diffusion.
- Recently developed nanoscale spectrometry: NSOM Raman --- useful for addressing local optical properties and molecular interaction at interface (particularly at transition metal surface, which is often used as electrode in optoelectronic devices).
NSOM imaging of exciton diffusion in a nanowire
Direct Photocurrent Mapping of Organic Solar Cells Using a Near-Field Scanning Optical Microscope

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Research outline

- Direct photocurrent mapping of organic solar cells (OSCps) using a novel NSOM setup;
- By raster scanning the light output from the NSOM across the OSC surface, it is possible to collect *height and photocurrent images simultaneously* with a high lateral resolution.
- The photocurrent images demonstrate that film inhomogeneities and segregation effects strongly influence OSC device performance.
Far-field current-voltage characteristics of the ITO/PEDOT-PSS/MEH-PPV-PCBM/Ca/Ag devices fabricated under 4 mW 532 nm illumination.

Inset: Corresponding incident photon collected electron (IPCE) efficiency spectra.
Topographic and current images of an ITO/PEDOT-PSS/MEH-PPV-PBCM/Ca/Ag device.

Two main features are observed:
large dark regions (marked A);
small bright regions (marked B).

The feature marked C corresponds to a small bright feature in the center of the large dark region (A).

The inset shows the height (black, solid) and current (red, dotted) traces taken along the white line. The scale bar is 5 \( \mu \text{m} \) in length.
Composite 3D image of the **height** and **current** map images.

Red $\rightarrow$ higher current;
Blue $\rightarrow$ low current.
Extended NSOM system for multimode imaging and spectroscopy measurements.
Advantages of NSOM imaging of film structures and properties

- Revealing the heterogeneous structure (distribution) of mixed films (e.g. polymer blends) --- transmissivity, emission intensity (different location), emission wavelength (different component), Raman scattering (surface vs. bulk). All these cannot be revealed using only AFM height measurement or optical microscopes.
- Direct correlation between local structure and spectroscopy properties --- e.g., quantum size effect for nanoparticles, local environment effect of proteins/enzymes.
- High spatial resolution --- mesoscopic investigation of films or devices. Nanoscopic organization is critical for charge migration and energy transport.
- Tunable for time resolved studies and polarization measurement --- crucial for photonic materials.
- Feasible for bias modulation --- applying a voltage between the tip and substrate.
Linear polarized emission from a nanowire under NSOM

(A) NSOM topography image of a nanobelt assembled from propoxyethyl-PTCDI; belt thickness is about 50 nm. (B, C) NSOM emission images collected (by PMT) after a polarizer at horizontal and vertical positions; (D) Emission intensity of a single nanobelt depending on the angle between the polarizer and the long-axis of nanobelt. The inset (cartoon) shows the tilted packing of molecules along the long-axis of the nanobelt. The polarizer is indicated as an arrow.
Different operation modes of NSOM imaging for different optical materials

- Transmission;
- Emission: collected by objective (backward vs. front face)
- Emission: collected by tip (normally excited at front face at an appropriate angle)
- Raman scattering: surface enhanced Raman scattering (SERS) on transition metals like Silver --- excitation via tip, collection via objective.
Optical Microscopy Studies of Dynamics within Individual Polymer-Dispersed Liquid Crystal Droplets

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Polymer-dispersed liquid crystal (PDLC)

- PDLC thin films find a variety of applications in a range of optical devices.
- These include their use in electrically switchable (smart) windows, optical shutters, flexible displays, diffractive optics, and photorefractive systems.
- PDLCs consist of (sub)micrometer-sized birefringent LC droplets encapsulated within what is usually an optically transparent polymer.
- The molecular organization within the encapsulated LC droplets depends on the elastic constants of the LC and the interfacial anchoring conditions.
- In their native state, the fast (or slow) optical axes of these droplets are usually randomly aligned, causing the materials to strongly scatter light.
- When polymers and LCs with proper refractive indices are employed, application of an electric field causes the films to become optically transparent to normally incident light.
- This field-induced change results from reorientation of the LC directors within the droplets.
An office cube with smart windows
An building with smart windows
NSOM based on shear force mode

What is polarization?

Nonpolarized light vibrates in all directions. The vertical component passes through the first polarizer. However, the second polarizer does not allow the vertical component to pass through.
For isotropic materials, like glass, the polarization of the incident light remains the same.
Cross-polarized optical microscopy

thin section of tremolite under cross-polarized light
Images and models of several LC droplets. Panel A shows a topographic image of an ellipsoidal droplet. Panels B and C show NSOM birefringence images of two bipolar ellipsoidal droplets having optical axes oriented perpendicular and parallel to the film plane, respectively. Panel D shows a topographic image of a collapsed ("toroidal") droplet. Panel E shows the NSOM birefringence image of the droplet shown in panel D. Panel F shows a topographic image of a dye-doped PDLC sample showing several collapsed droplets. Panels G and H show MPEFM images of bipolar and toroidal droplets, respectively. Panel I shows a MPEFM image of a PDLC droplet of radial configuration. Panels J-L show models for the LC organization in bipolar, toroidal, and radial droplets, respectively. Appended arrows show the incident and detected polarizations. MPEFM: multiphoton excited fluorescence microscopy.
Measuring Local Optical Properties: Near-Field Polarimetry of Photonic Block Copolymer Morphology

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FIG. 1. NSOM images of PS-\(b\)-PI BC. Transmission (top), topography (middle). The plot (bottom) shows topography (solid) and transmission (dashed) along the white line (2.1 \(\mu\)m) in the topography image, smoothed over a three-pixel bin. Labels \(a\) and \(b\) show edge dislocations and lamellar separations, respectively.
Spatial Imaging of Singlet Energy Migration in Perylene Bis(phenethylimide) Thin Films

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Figure 1. Schematic of typical organic semiconductor-based solar cell.
Figure 2. Experimental setup for far field/near field fluorescence imaging of PPEI microcrystals.
Figure 3. (a) Topography and (b) the simultaneously recorded near-field fluorescence image of PPEI microcrys- tals. (c) Far-field fluorescence imaging of PPEI microcrys- tals. Sample in (a–c) was solvent annealed extensively. (d) Spatial images of 633 nm HeNe laser from 
early field optical probe (left spot) and 680 nm emission (right spot) from a single PPEI microcrystal. (e) Spatial images of 633 nm HeNe 
laser (left spot) and 680 nm emission from a 150 nm thick PPEI film. 
(f) Spatial images of 680 nm emission from a 200 nm diameter 
fluorescent latex sphere (left spot) and a 50 nm thick PPEI film. (g) 
Topography of bare ITO and a PMT-coated ITO (I and II, respectively). 
(h) Topography of a 670 nm thick PPEI film on ITO and a 670 nm thick 
PPEI film on PMT-coated ITO (I and II, respectively). The 
samples were on the same underlying glass substrate and annealed under 
identical conditions. (i) Topography and fluorescence NSOM of a 24 
nm thick PPEI film on bare ITO (I and II, respectively). (j) Topography 
and fluorescence NSOM of a 24 nm thick PPEI film on PMT-coated 
ITO (I and II, respectively). The samples in (i,j) were on the same 
underlying glass substrate and annealed under identical conditions. The 
seal is the same in (g–j). Images (a–d) were obtained with objective 
1 and images (e–j) with objective 2.
Electric Field Modulated Near-Field Photo-Luminescence of Organic Thin Films

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Figure 1. (a) Molecular structure of ZnODEP and proposed model of molecular stacking with some defects along the stacks. (b) Charge trapping photocapacitive device composed of ITO/ZnODEP/SiO_{2}/Si layer structure and proposed model of charging under illumination. (c) Device equivalent structure composed of ITO/ZnODEP/impurity-layer/Al-Coated Near-Field Probe.
A Molecular Yarn: Near-Field Optical Studies of Self-Assembled, Flexible, Fluorescent Fibers

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fluorescence NSOM images of a thin PVS film incorporating fluorescent fibers (PIC).
Polarization-dependent fluorescence near-field images of a ringlike fiber.
Intermolecular Coupling in Nanometric Domains of Light-Harvesting Dendrimer Films Studied by Photoluminescence Near-Field Scanning Optical Microscopy (PL NSOM)

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NSOM setup: tip collection
a

Coumarin 2
$\lambda_{\text{max}} = 365$ nm
$\lambda_{\text{em}} = 435$ nm

Coumarin 343
$\lambda_{\text{max}} = 446$ nm
$\lambda_{\text{em}} = 490$ nm

b

G1

G2

G3

G4