

Indigenous Africans toward New solar cell technology

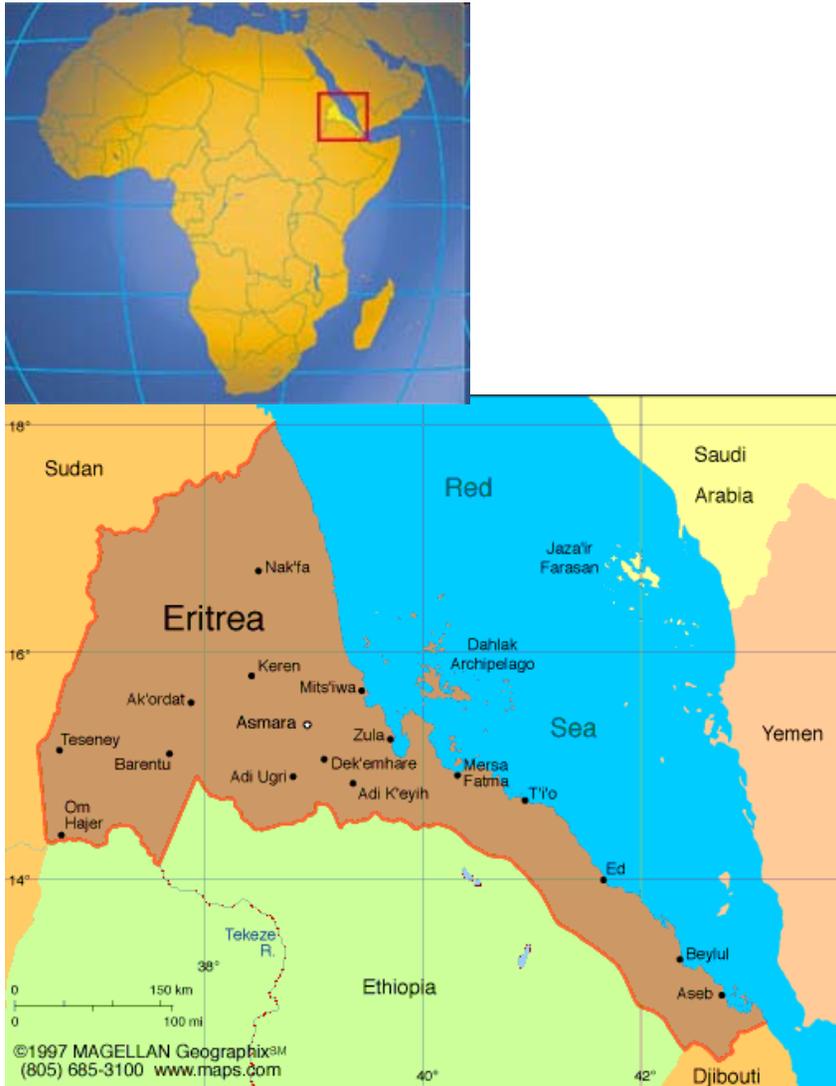
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University of Cincinnati/Oak Ridge National Lab

NanoPower Africa

11/08/2011

GEOGRAPHY



- Located in northeastern Africa, Eritrea has about 620 miles (1,000 kilometers) of coastline along the west coast of the Red Sea.

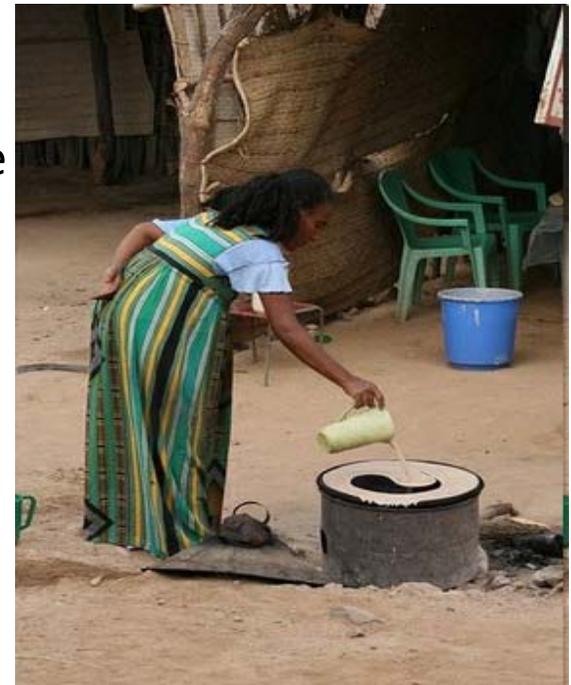
- The population in Eritrea is ~3 million (1994), divided between nine ethnic groups.
- The highland Tigrinya group constitutes about half of the population. More than 75 percent of the population lives in rural areas.

Food and Economy

Food in Daily Life.

Eritrean cuisine is a reflection of the country's history.

- *injerra* is commonly eaten in the rural areas. It is a pancake-like bread that is eaten together with a sauce called *tsebhi* or *wat* . The sauce may be of a hot and spicy meat variety, or vegetable based.
- In the urban centers one finds the strong influence of Italian cuisine, and pasta is served in all restaurants.



Basic Economy

- The Eritrean economy is totally dependent upon agricultural production. Over 75% of the population lives in the rural areas and conducts subsistence agricultural production.

Major Industries

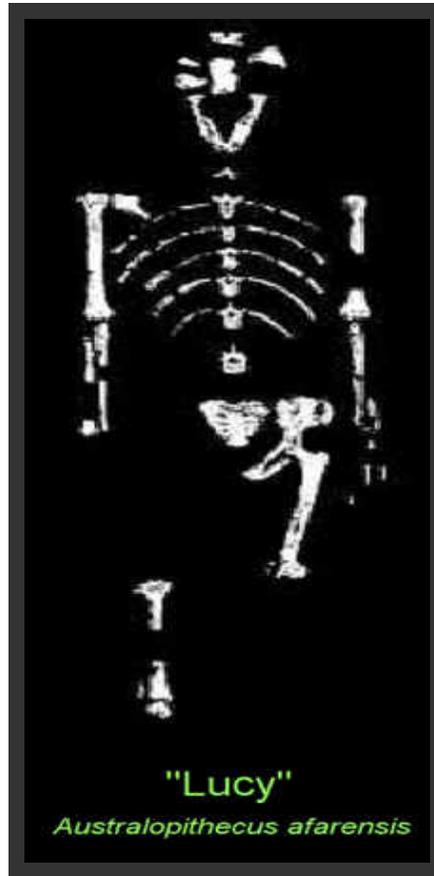
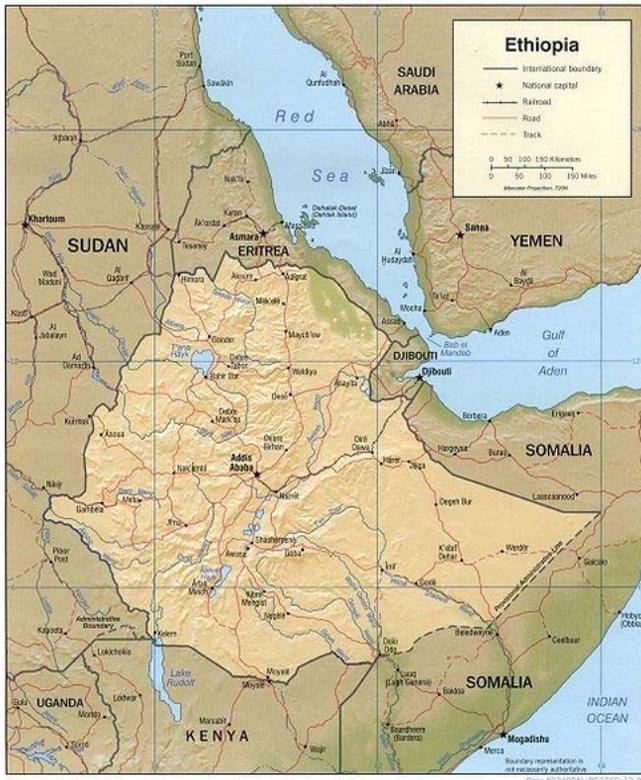
- The marginal industrial base in Eritrea provides the domestic market with textiles, shoes, food products, beverages, and building materials. If stable and peaceful development occurs, Eritrea might be able to create a considerable tourism industry based on the Dahlak islands in the Red Sea.
- produced many resources like gold, ivory, copper, platinum ,frankincense, potash, and natural gas.

The History and culture of Ethio-Eritrea

- History covering civilizations dating back to 4000 BC, the great empire of Axum, the dynasty of rulers that include: Queen of Sheba up to the Solomonic Dynasty founded by Menelik, lasting until 1974 when the 237th Solomonic monarch, His Emperor Haile Selassie, was overthrown.



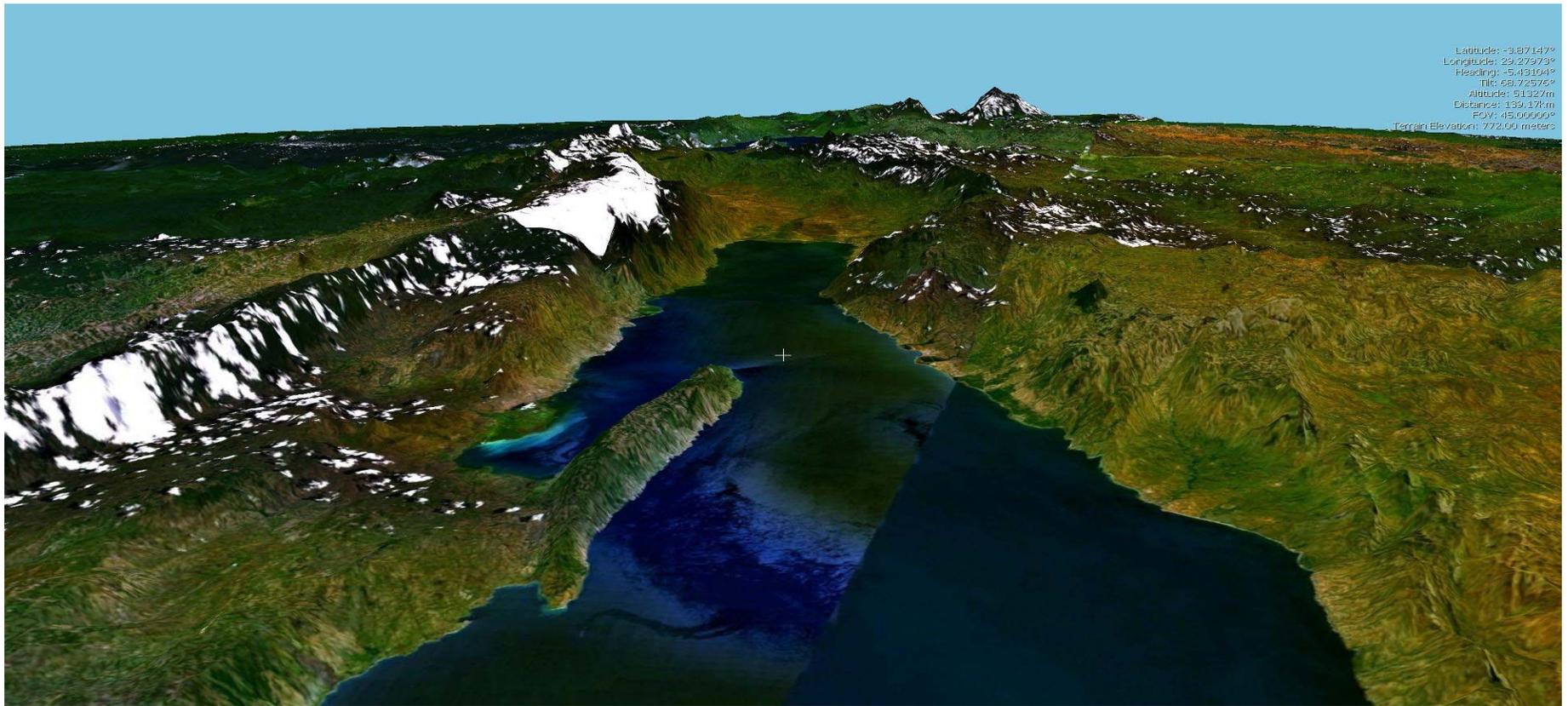
“*Australopithecus afarensis*” →



- Archaeologists have discovered remains of early hominids in Ethiopia’s Rift Valley, including *Australopithecus afarensis*, or “Lucy,” thought to be 3.5 million years old. By ca. 7000 B. C.

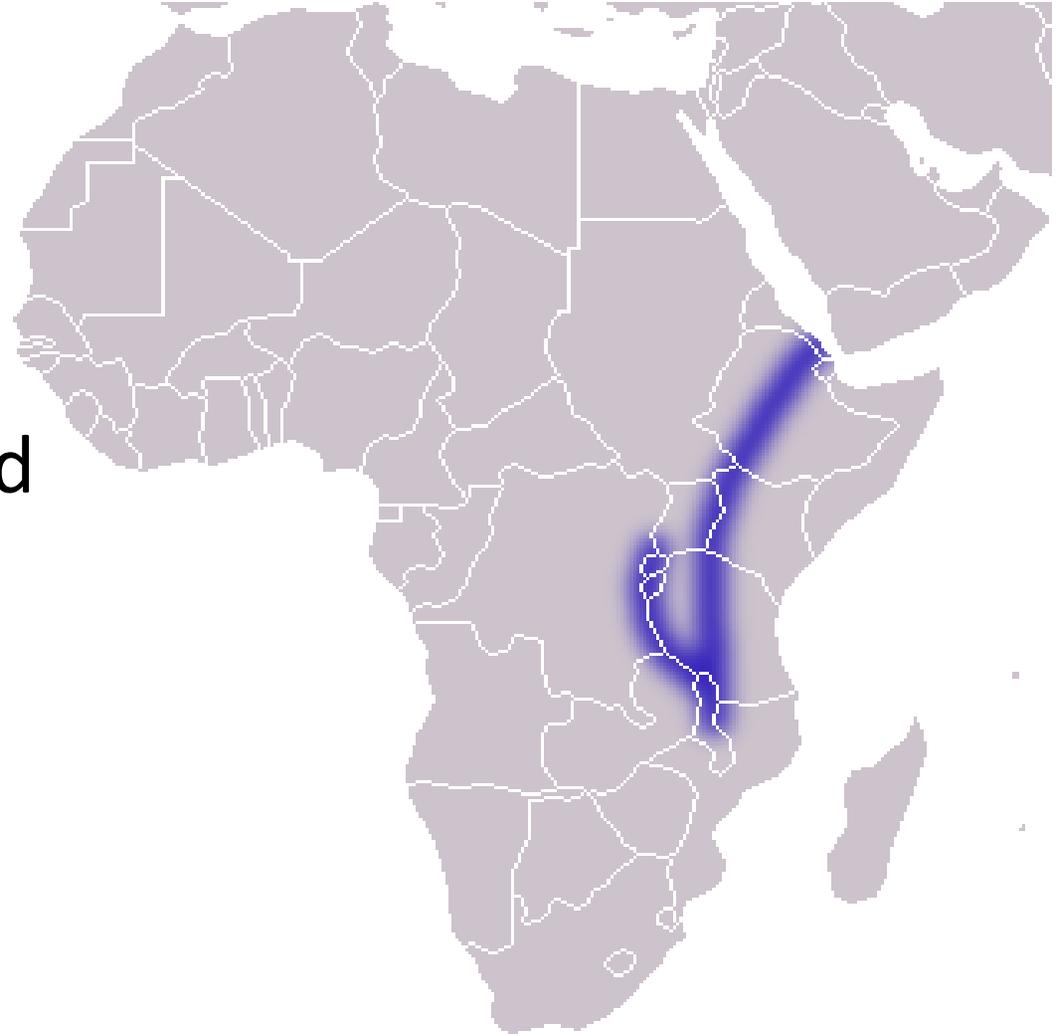
Great Rift Valley

- which is a crack in the surface of the earth and runs north and south for about 4000 miles .



Great Rift Valley

The Great Rift Valley is a 4,000 mile giant fault, or break in the earth's crust. It extends from the Red Sea to the Zambezi River.



- The Abay (Blue Nile), Ethiopia's largest river,
- the Tekezé, and the Baro flow west into the Nile River in Sudan,
- The Awash flows east through the northern Rift Valley and disappears into saline lakes in the Denakil Depression.
- In the south, the Genale and Shebele flow southeastward into Somalia; the Omo drains the southwest and empties into Lake Turkana on the border with Kenya.

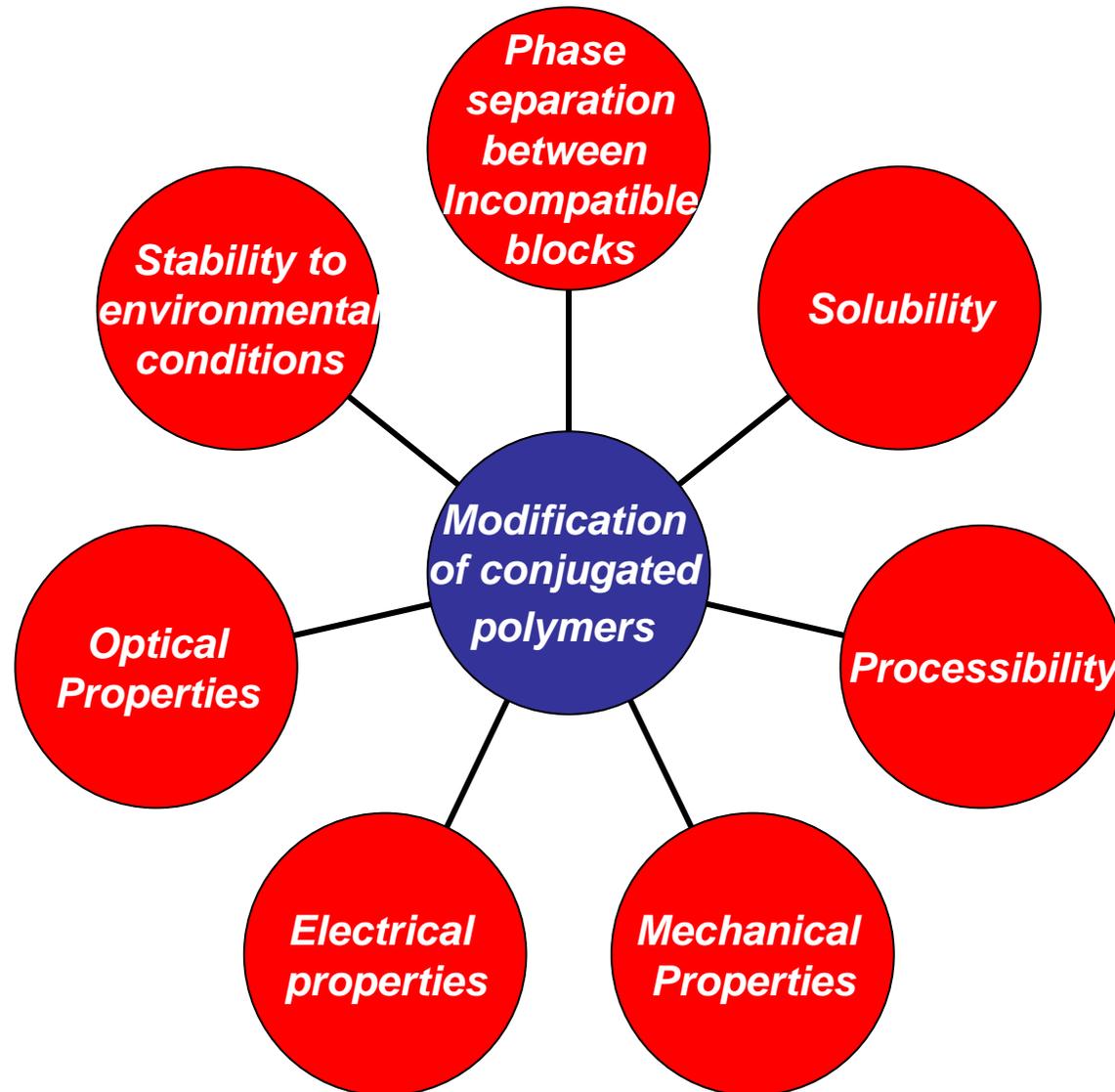


Energy

- Less than one-half of Ethio-Eritrea towns and cities are connected to the national grid.
- Petroleum requirements are met via imports of refined products, although some oil is being hauled overland from Sudan. Exploration for gas and oil is underway in the Red sea region In general, Ethiopians rely on forests for nearly all of their energy and construction needs; the result has been deforestation of much of the highlands during the last three decades.

Overview of ***organic photovoltaic thin films***

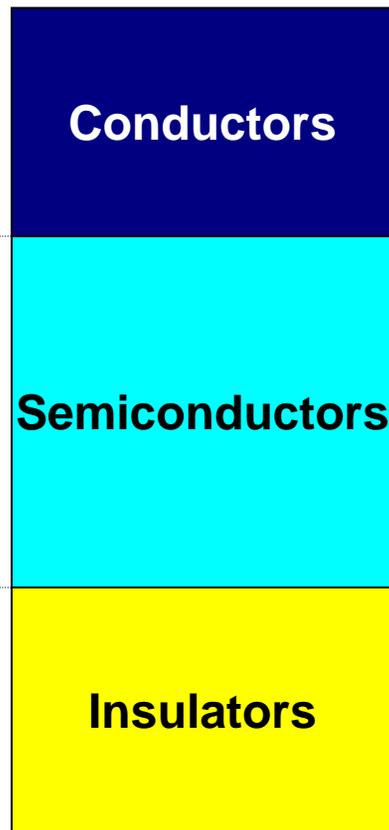
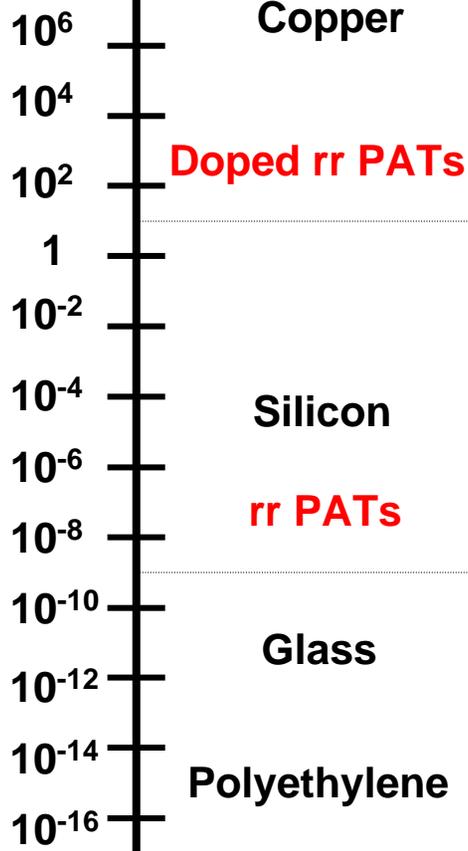
Semiconducting Polymers integrated in block-copolymer structures



Semiconducting Polymers

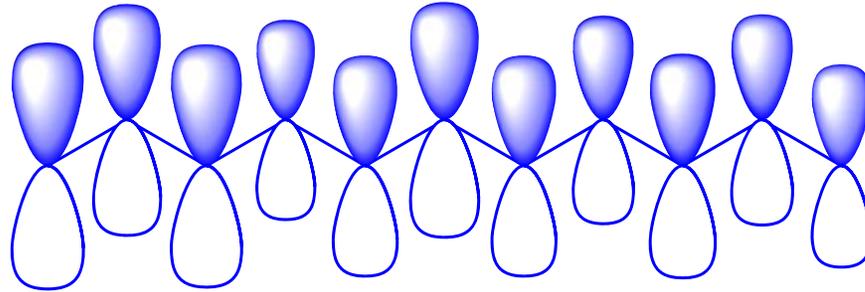
Conductivity

S/cm ↑



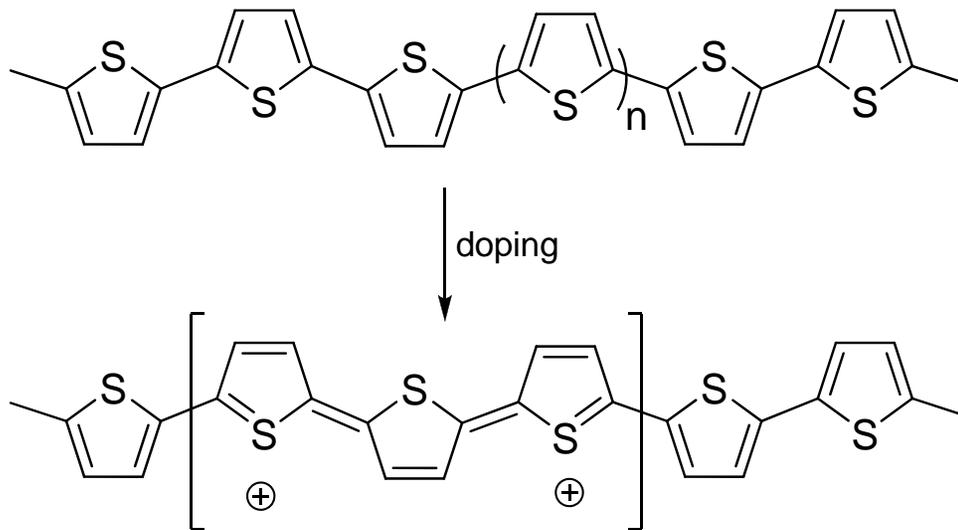
1977		Polyacetylene
1979		Poly(p-phenylene)
1979		Polypyrrole
1979		Poly(p-phenylene vinylene)
1982		Polythiophene
1989		Poly(3,4-ethylene dioxythiophene) PEDOT
1992		Regioregular Poly(3-alkyl thiophene)(rr-PATs)

Semiconducting Polymers



➤ sp^2 hybridized C have p_z orbitals that line up to form connected electron clouds where electrons/holes can travel through.

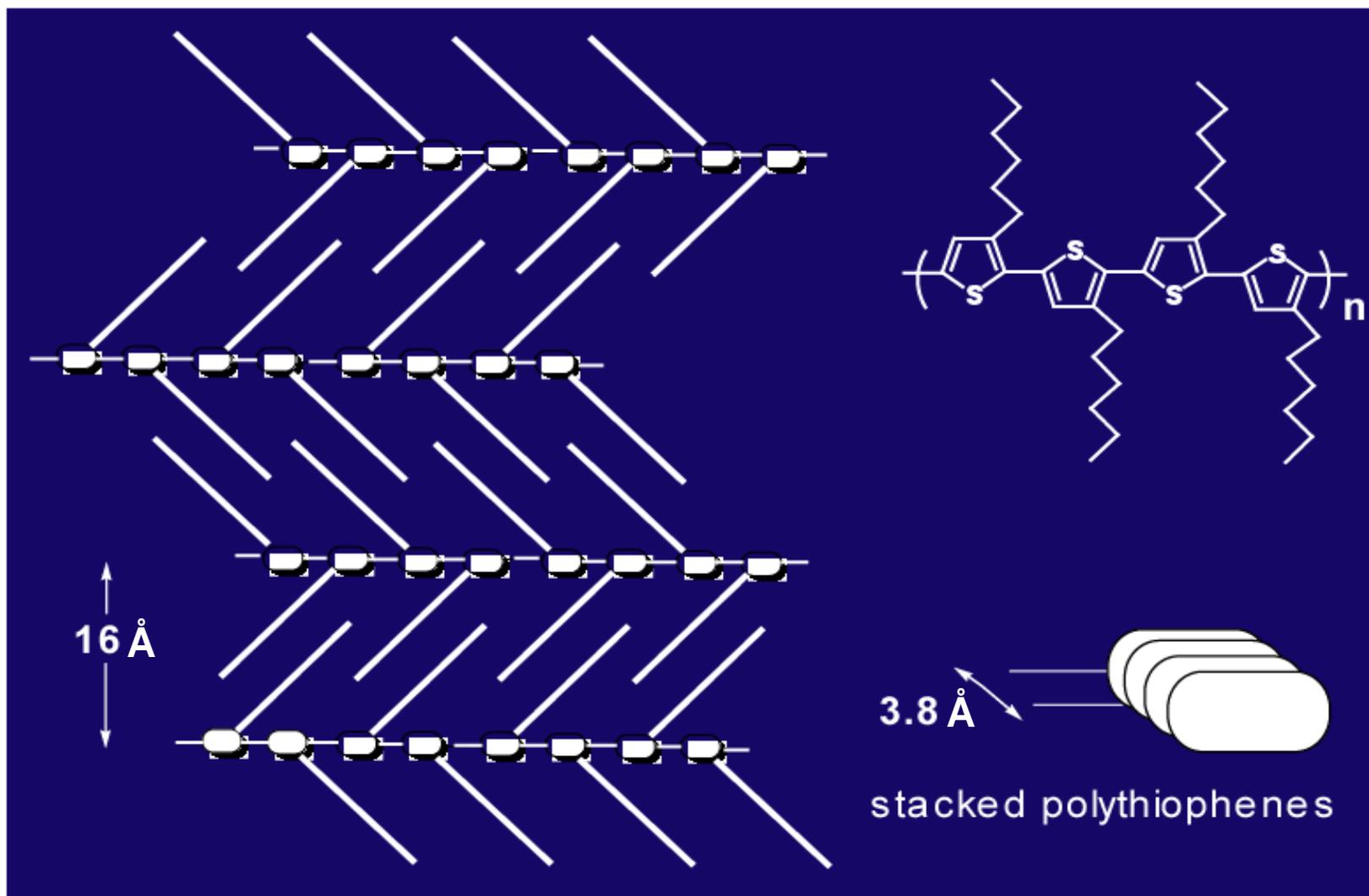
➤ And when doped with an oxidant → p-type semiconducting polymers → holes are the charges.



$\sigma = 10^{-6} - 10^{-8} \text{ S/cm}$
semiconductor

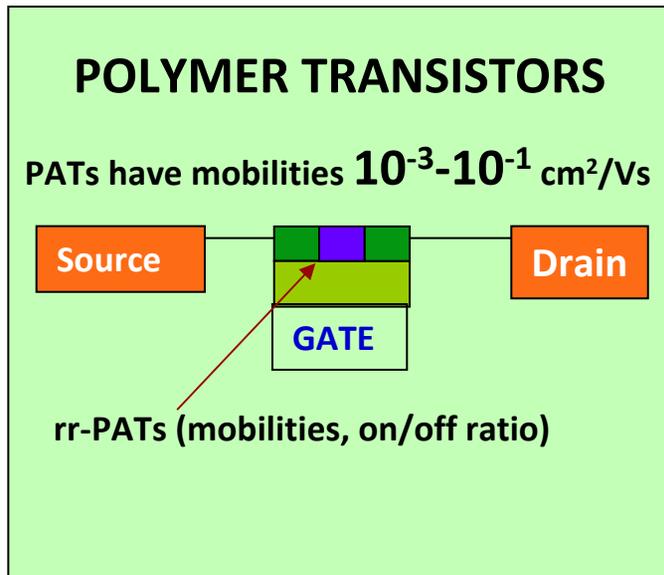
$\sigma = 10 - 10^3 \text{ S/cm}$
conductor

Regioregular Poly(3-Alkylthiophene) (PATs)

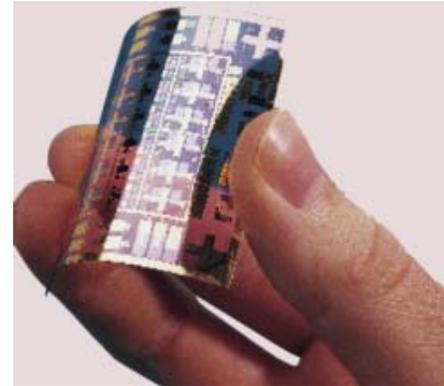


rr PATs self-assemble to form flat stacks resulting in high conductivities upon doping.

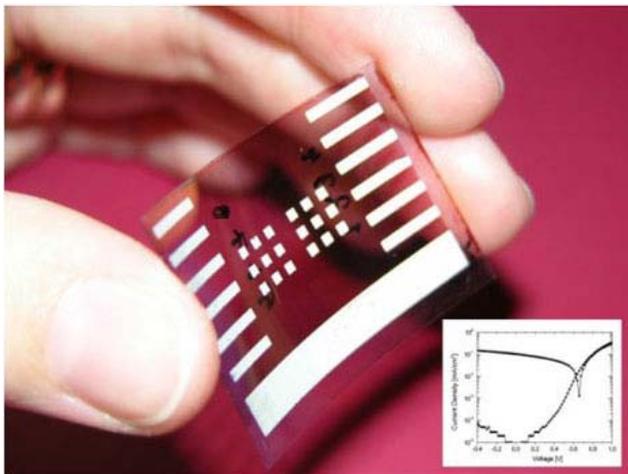
Applications of Semiconducting Polymers



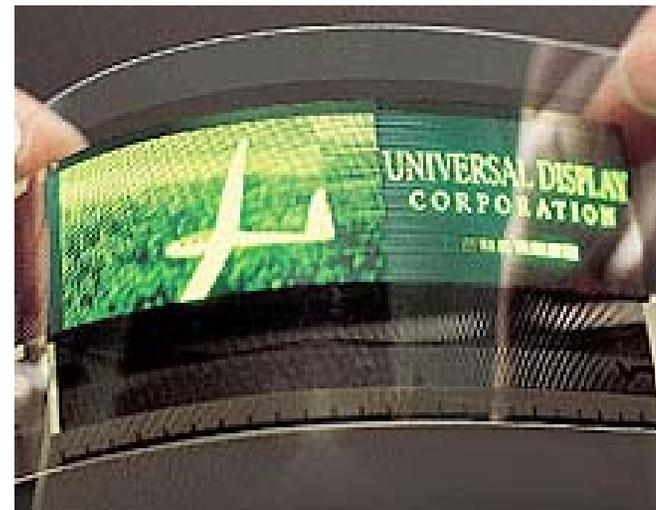
Plastic Field-Effect Transistors



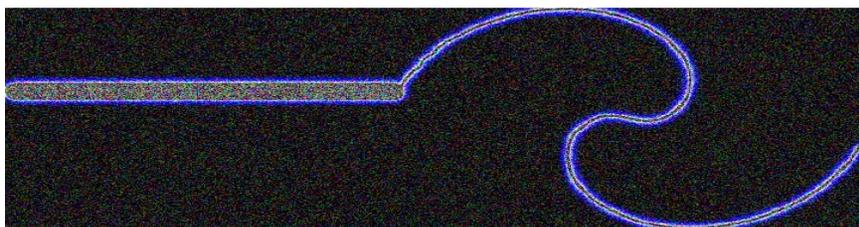
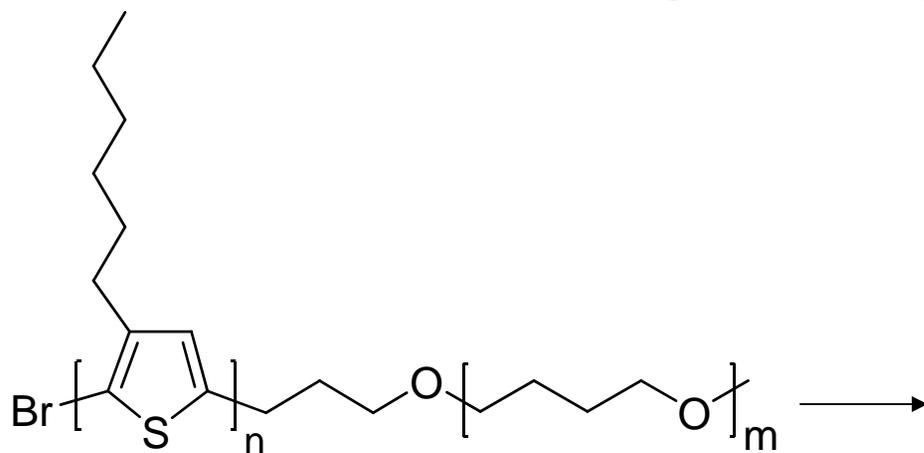
Polymer Solar Cell



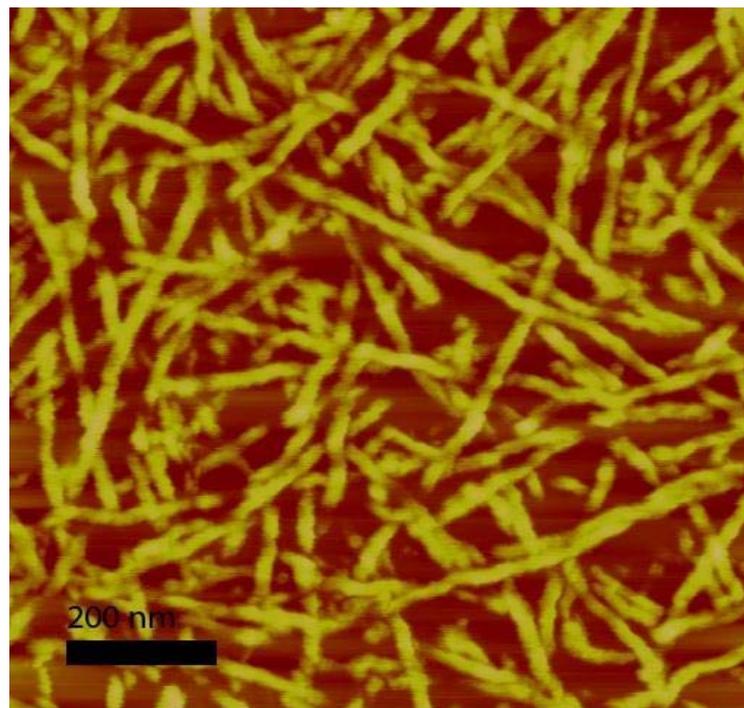
Organic Light-Emitting Diodes (LEDs)



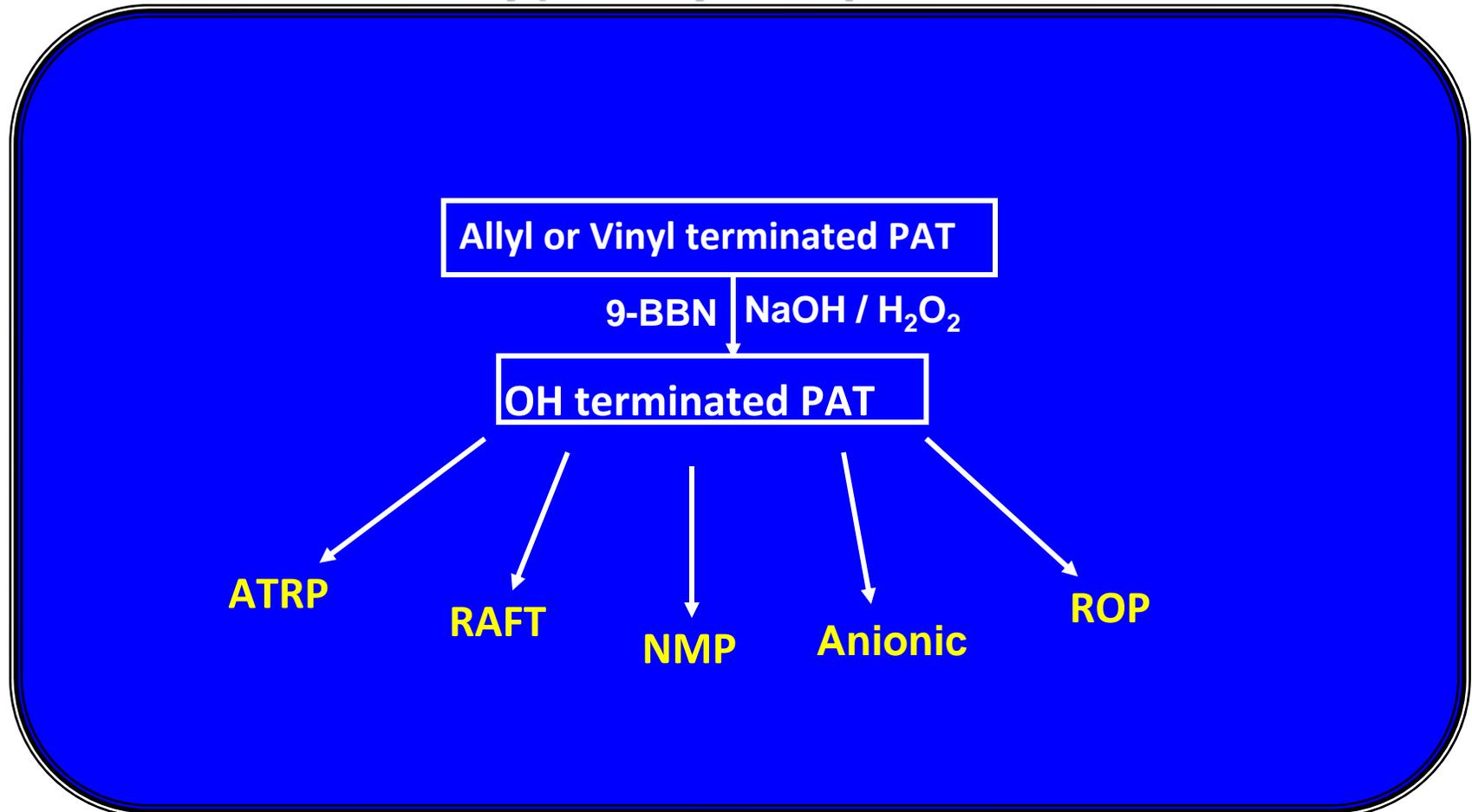
SYNTHESIS OF DI-BLOCK COPOLYMERS CONTAINING REGIOREGULAR POLY(3-HEXYLTHIOPHENE) AND POLY(TETRAHYDROFURAN) BY A COMBINATION OF GRIGNARD METHATHESIS AND CATIONIC POLYMERIZATIONS



Rod-coil diblock copolymer



Conducting Block Copolymers Containing Poly(3-Alkylthiophene)



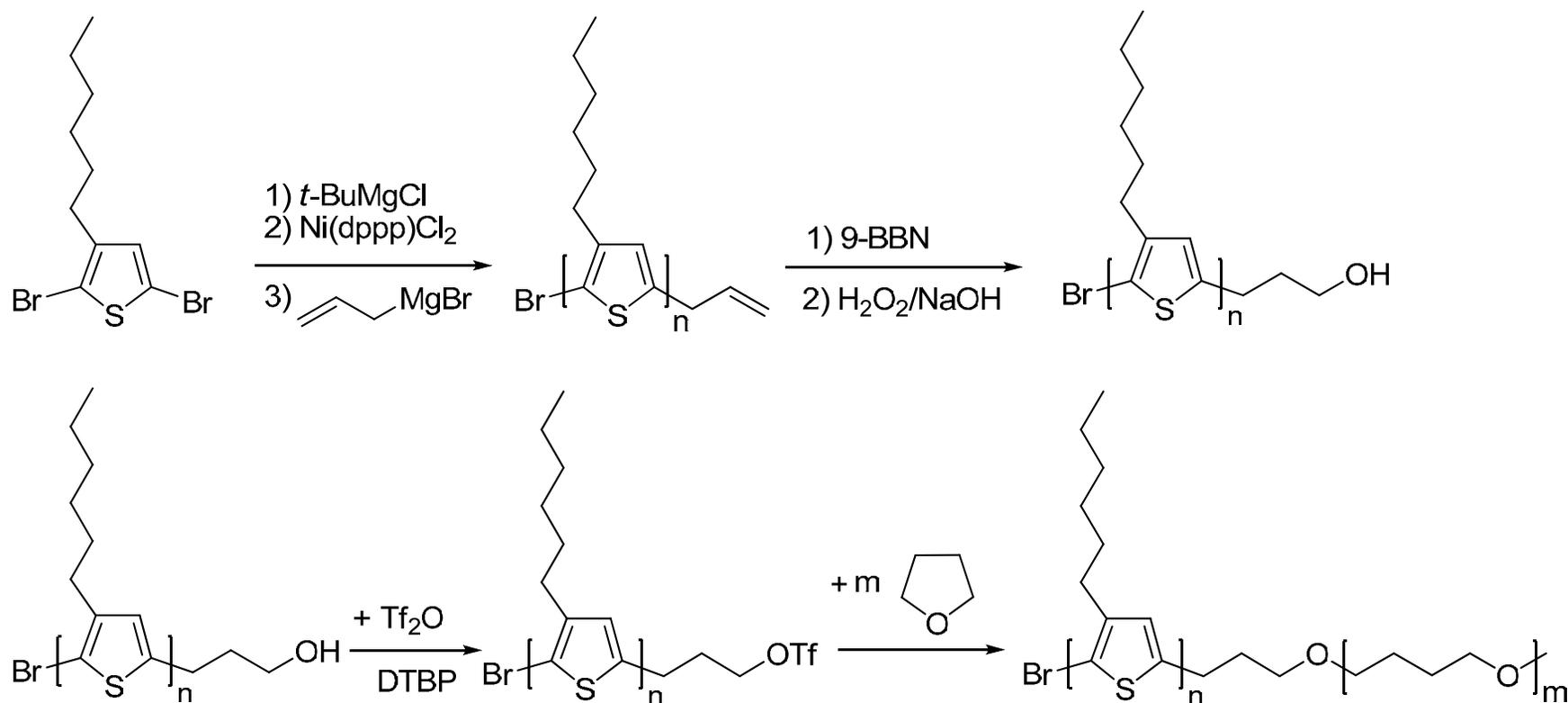
PAT = Poly(3-alkylthiophene)

➤ *Cationic polymerization has never been employed for the synthesis of polythiophene di-block copolymers*

Challenges of Cationic Polymerization

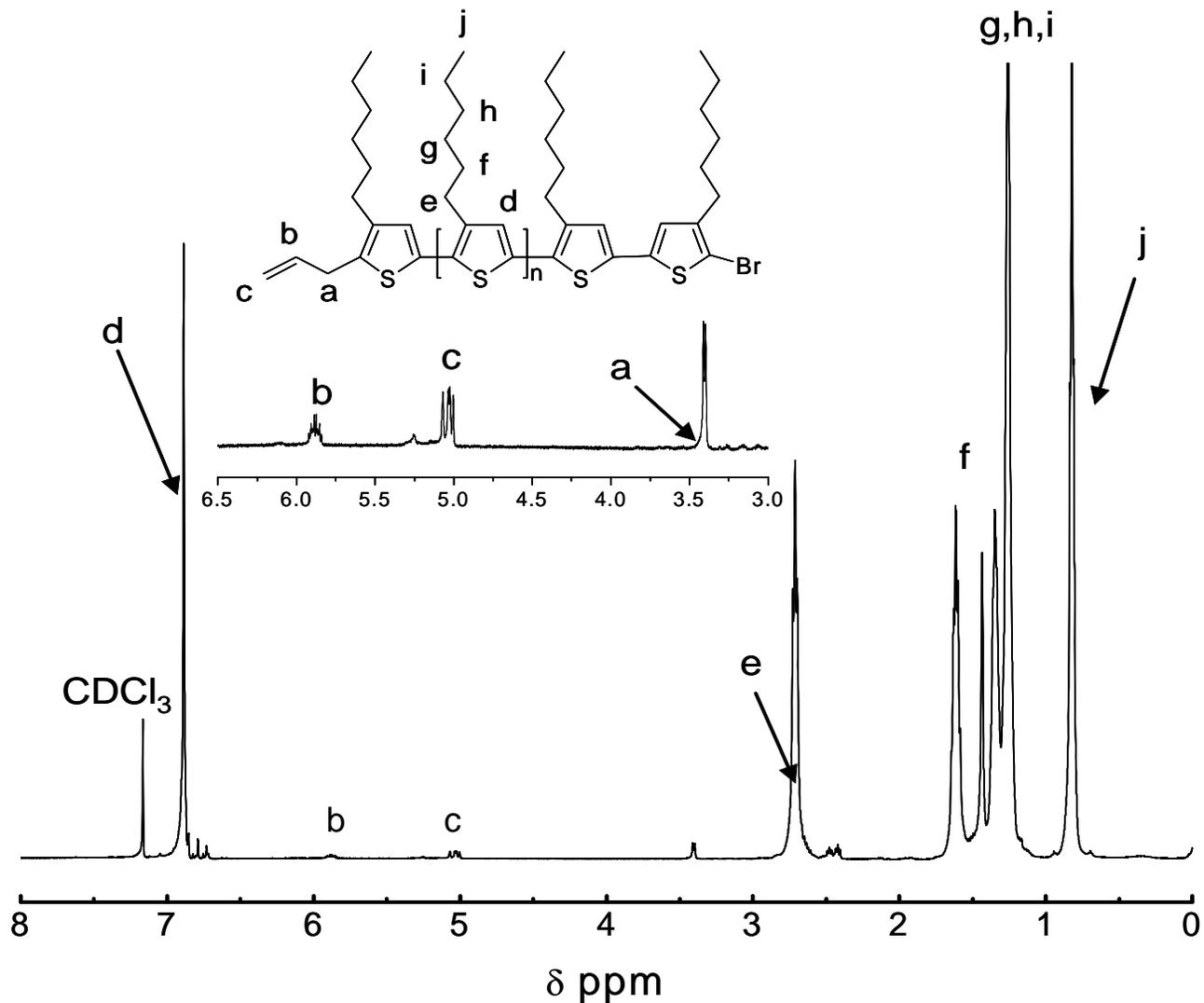
- Sensitive to traces of nucleophilic impurities and oxygen
- Reproducibility issue
- However, a *controlled* polymerization is possible under stringent reaction conditions:
 - low temperatures
 - highly purified monomer and solvents
- Ring-opening polymerization of tetrahydrofuran can be achieved only by cationic polymerization

Synthesis of Poly(3-hexylthiophene)-*b*-Poly(tetrahydrofuran) Block Copolymer by Cationic Polymerization



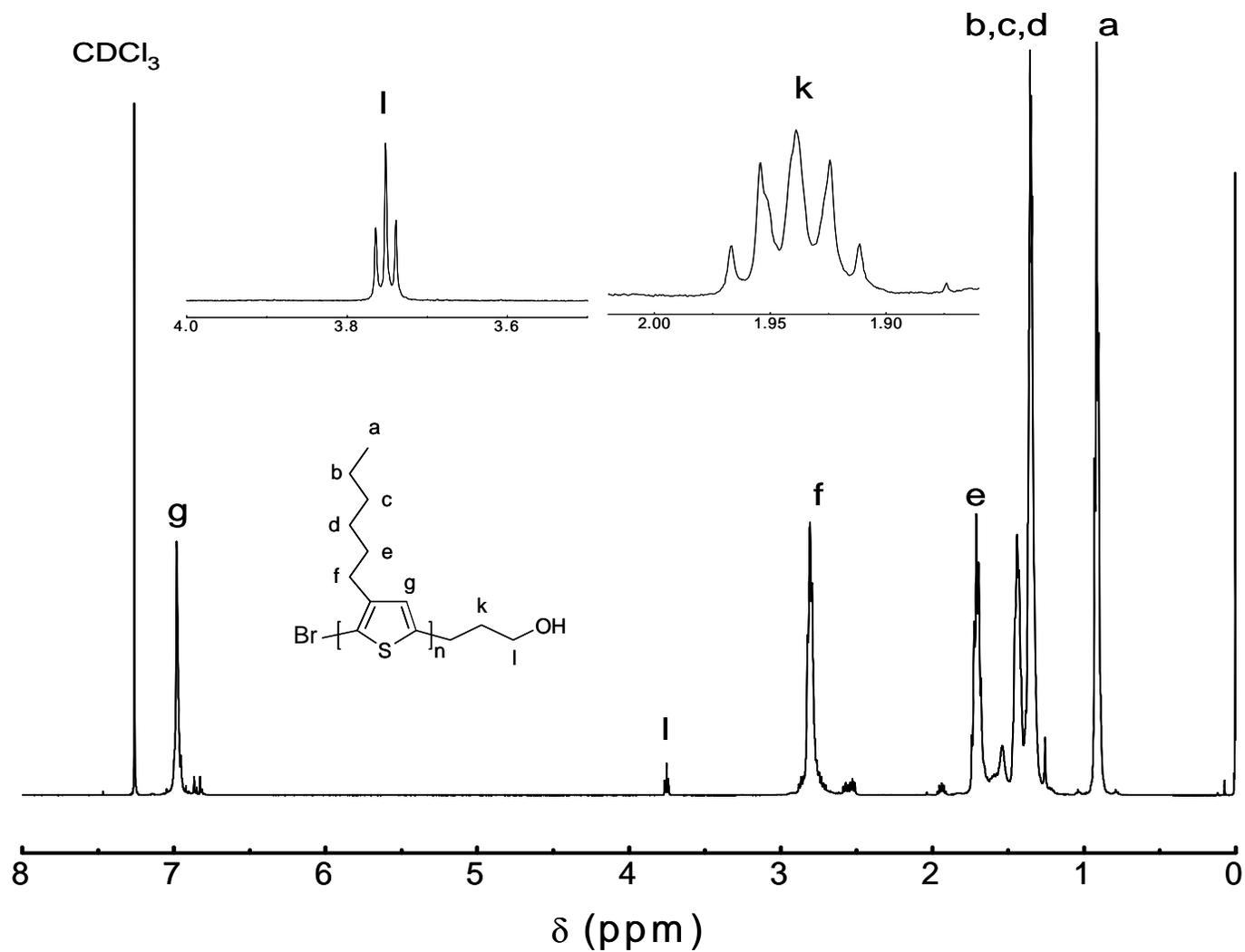
Alemseghed, M. G.; Gowrisanker, S.; Servello, J.; Stefan, M. C.
***Macromol. Chem. Phys.* 2009, 210, 2007-2014**

^1H NMR of Allyl-terminated poly(3-hexylthiophene)

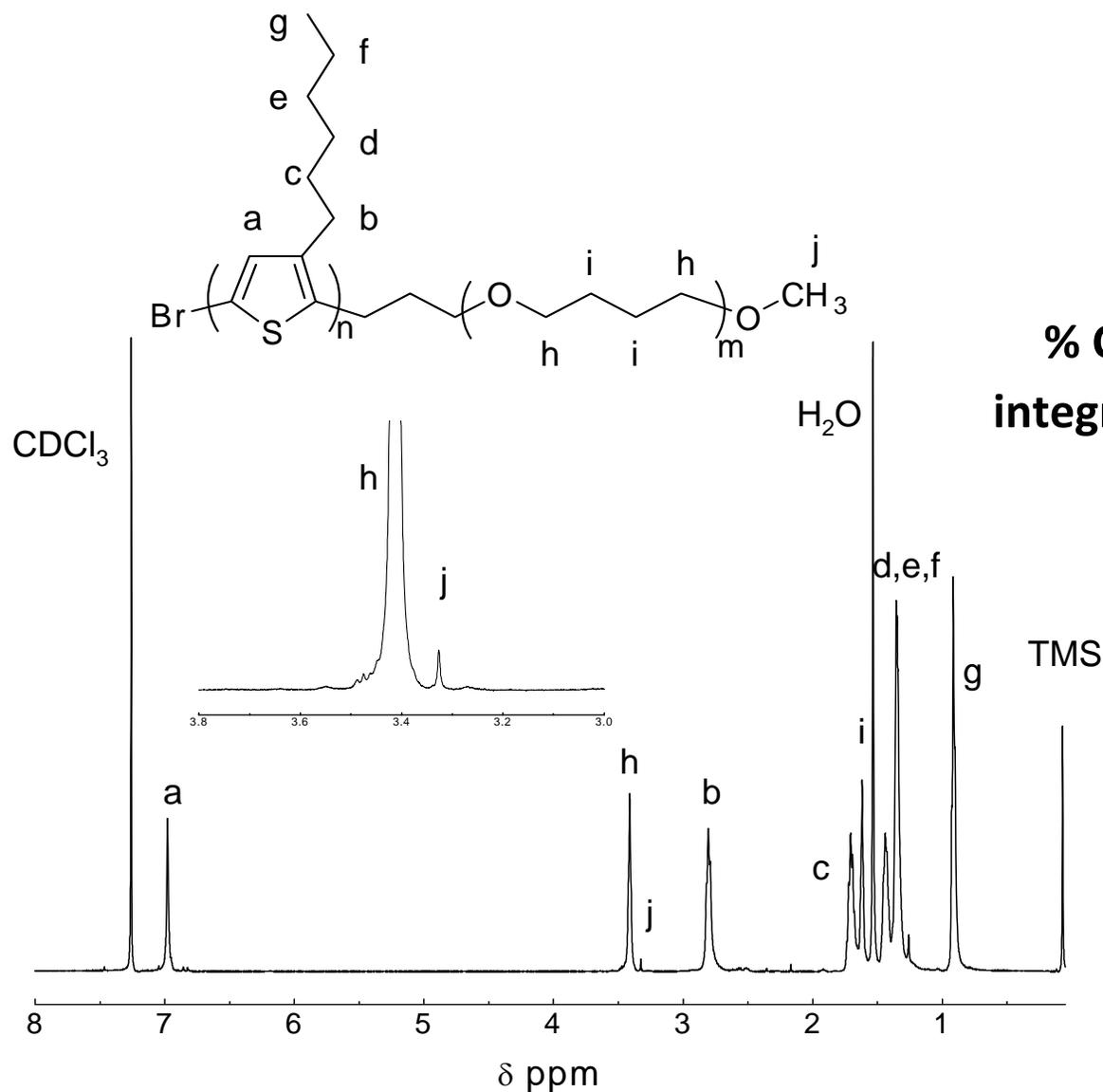


$$\text{DP}_n = e / a = 45, \text{M}_n(\text{SEC}) = 8560 \text{ g/mol}; \text{PDI} = 1.16$$

^1H NMR of hydroxypropyl-terminated poly(3-hexylthiophene)



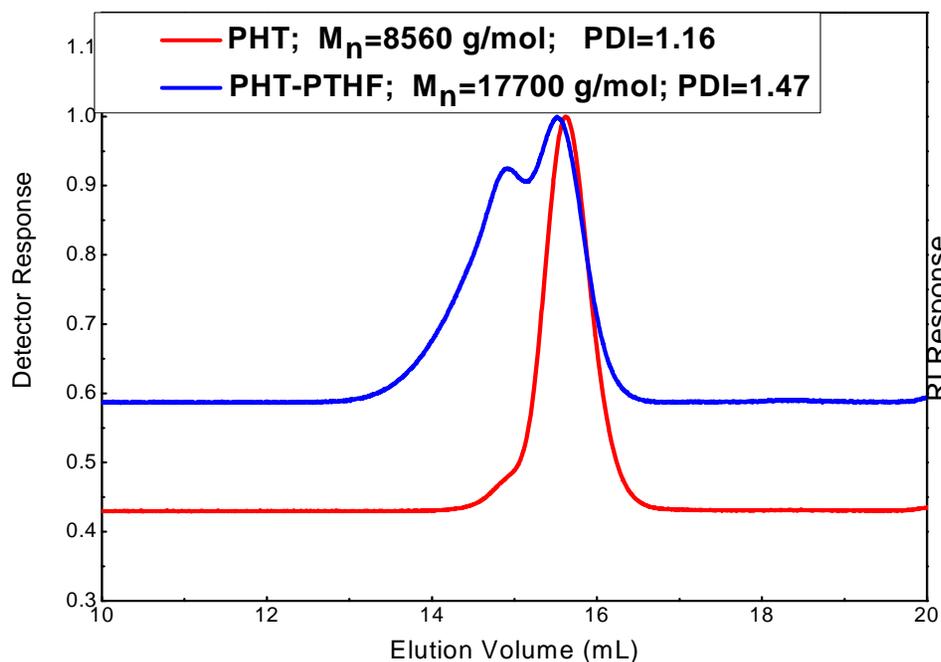
^1H NMR spectrum of poly(3-hexylthiophene)-*b*-poly(tetrahydrofuran) di-block copolymer



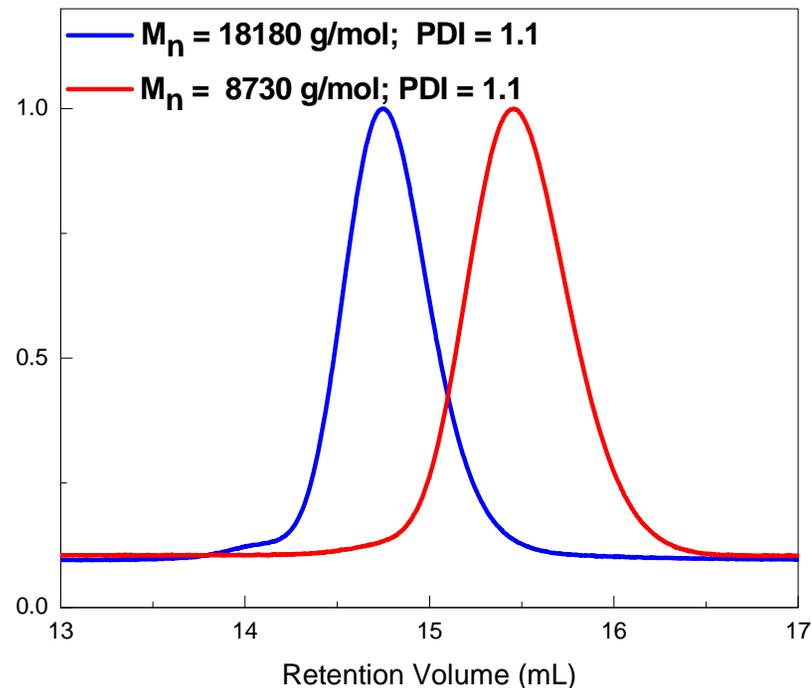
- 74% P3HT
- 26% PTHF

% Composition =
integrating b/h peaks

GPC traces of allyl-terminated P3HT and poly(3-hexylthiophene)-*b*-poly(tetrahydrofuran)



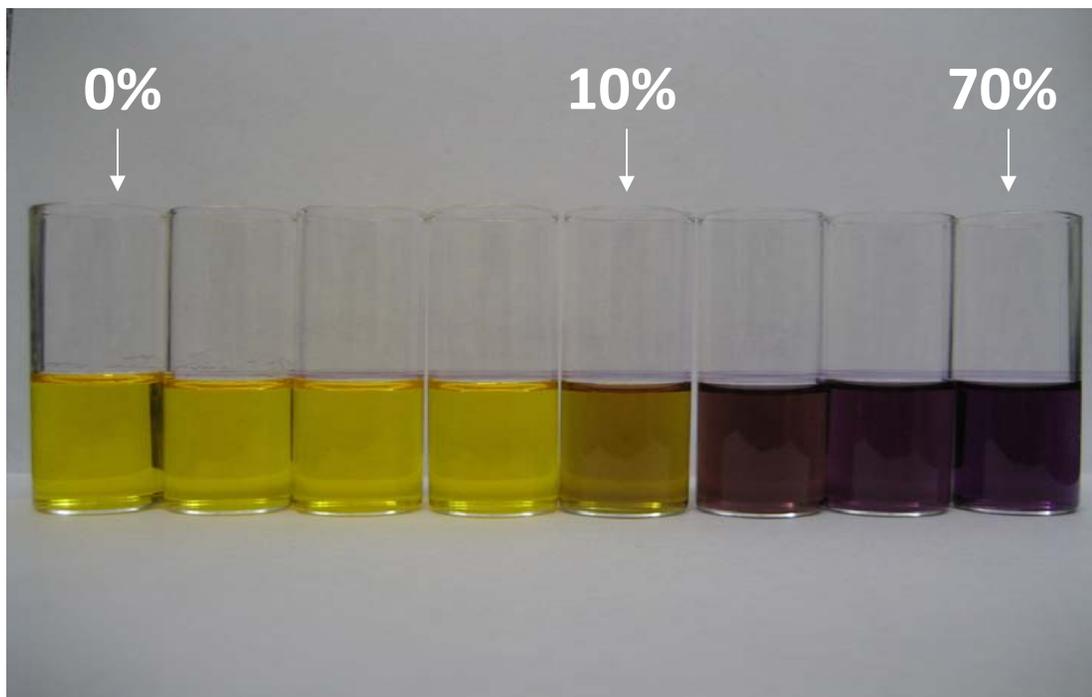
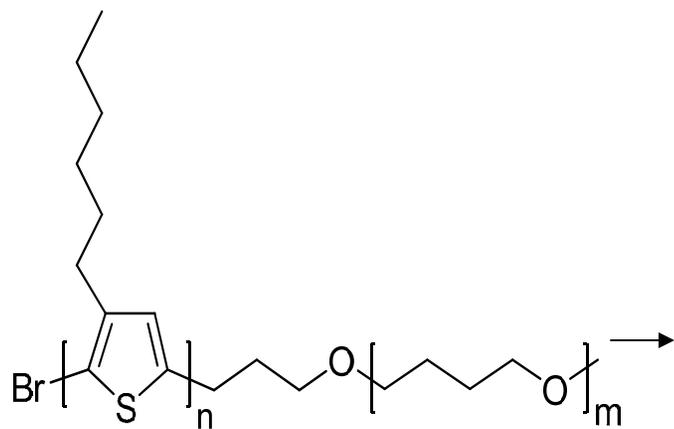
THF : CHCl₃ = 1:1



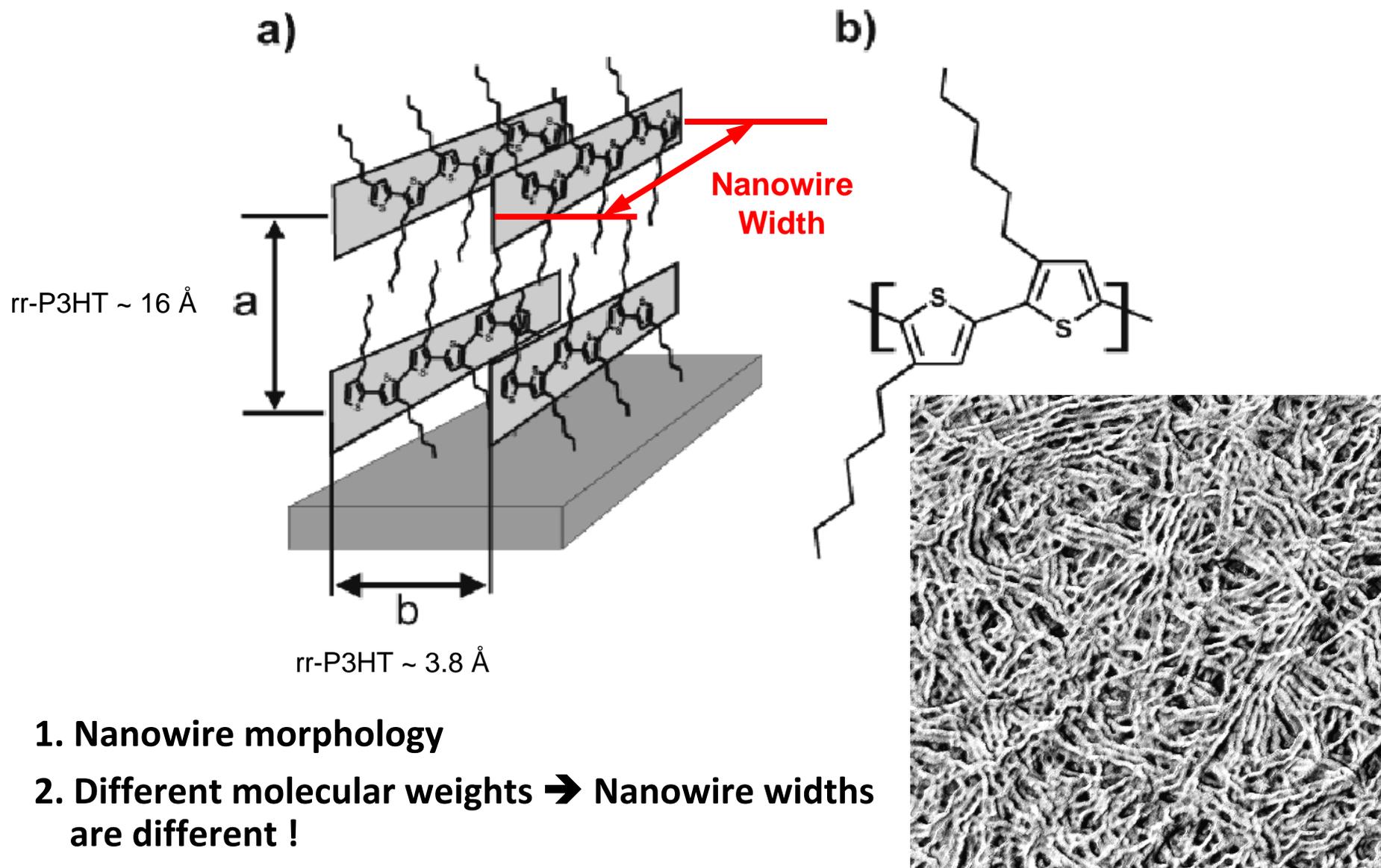
THF : CHCl₃ = 1:3

[PHT-OH] : [TfO₂] : [DTBP] = 1 : 45 : 70; [THF] : [PHT-OH] = 9230 : 1

UV-Vis Solvatochromic Behavior of poly(3-hexylthiophene)-*b*- poly(tetrahydrofuran)



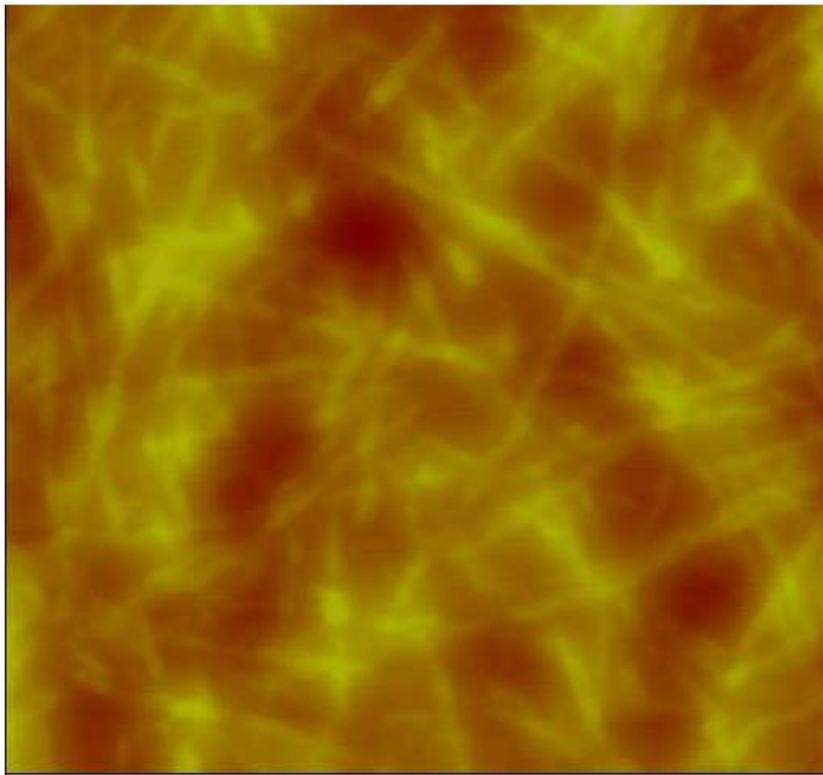
Nanofibrillar Morphology of Poly(3-hexylthiophene)



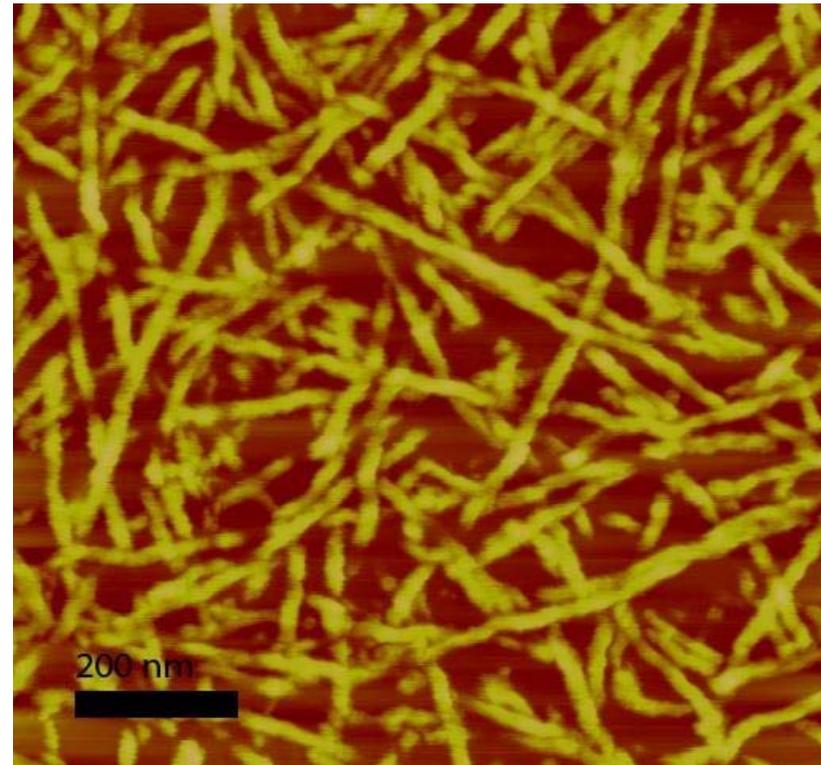
1. Nanowire morphology

2. Different molecular weights → Nanowire widths are different !

Tapping Mode AFM (TM-AFM) Image of poly(3-hexylthiophene)-*b*-poly(tetrahydrofuran) Diblock copolymer



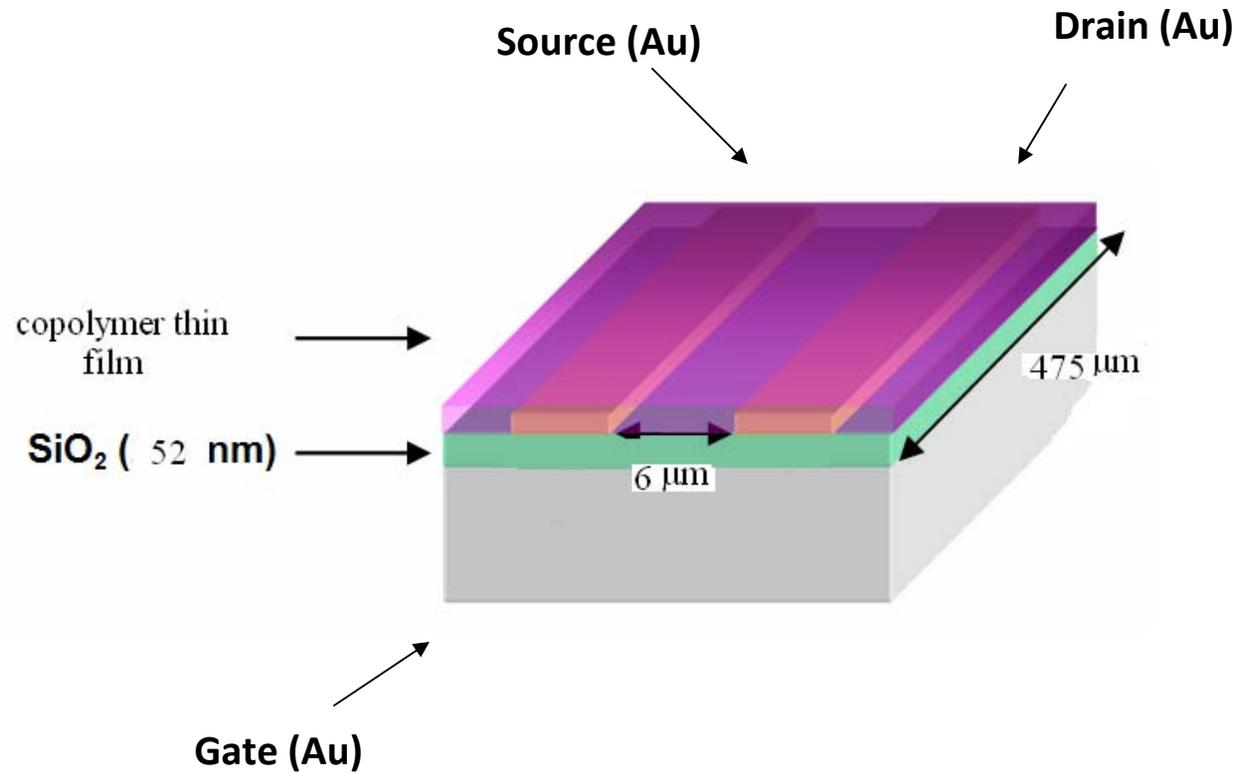
Height image



Phase image

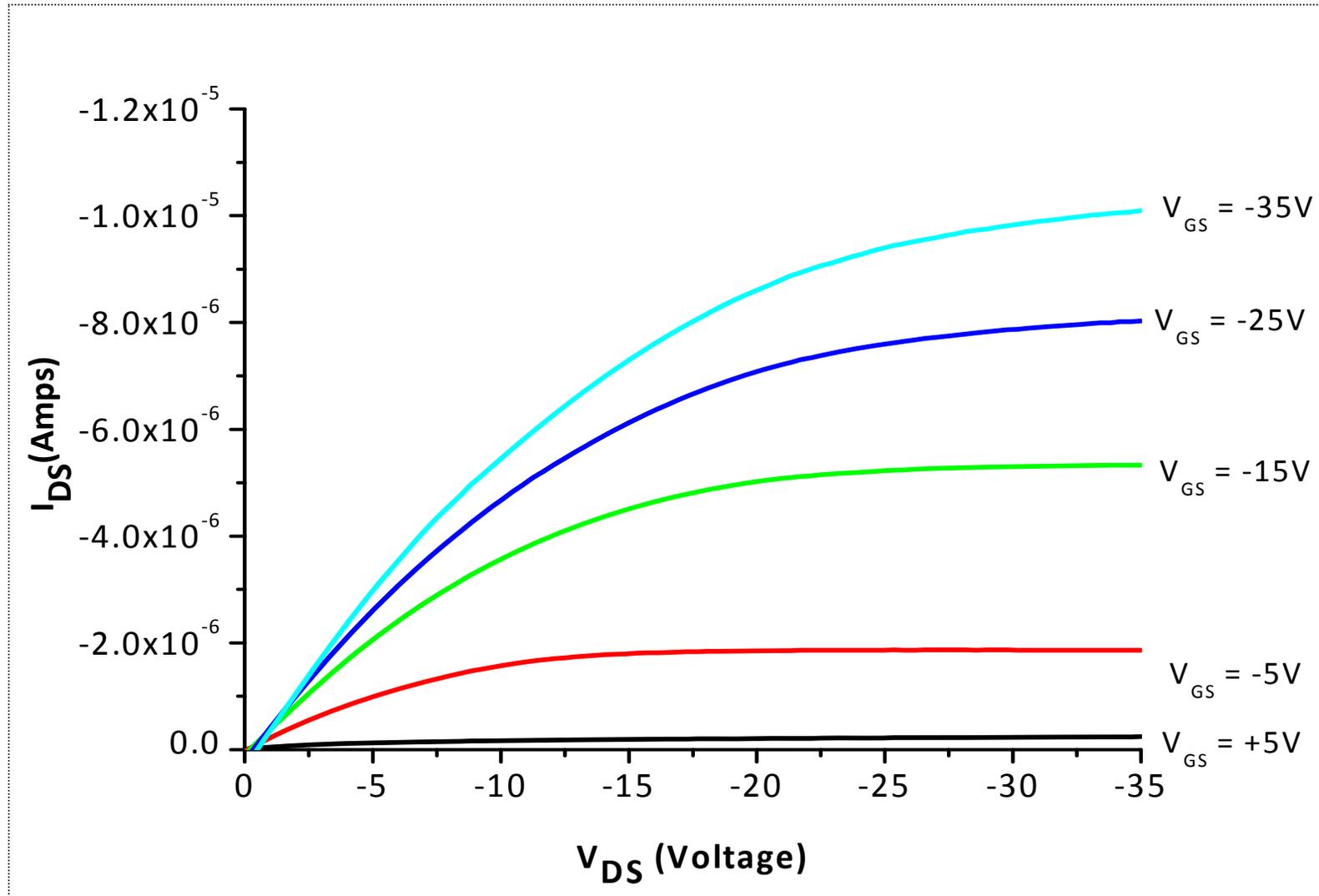
Alemseghed, M. G.; Gowrisanker, S.; Servello, J.; Stefan, M. C.
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Mobility Measurement for the Di-block Copolymer

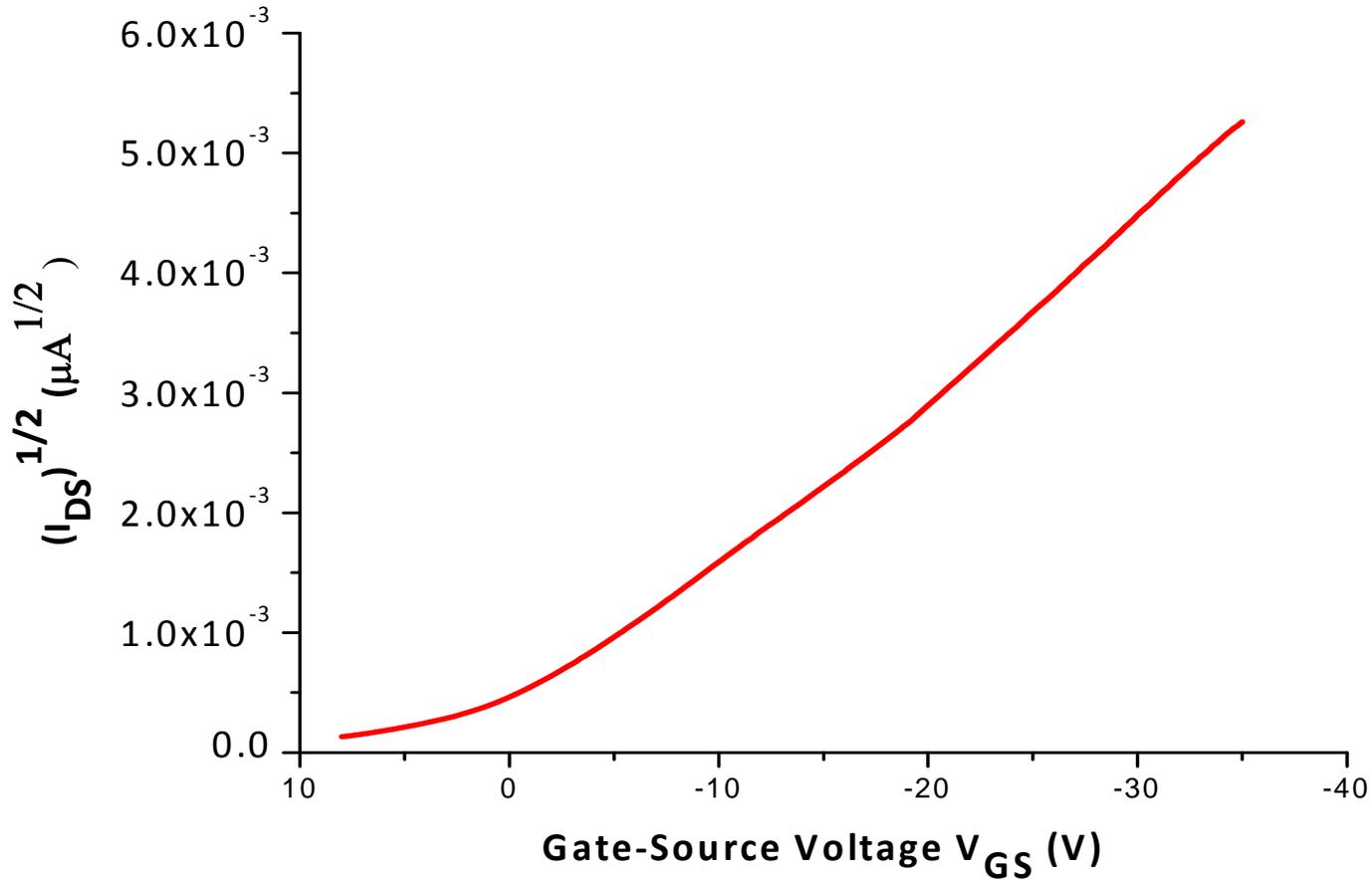


Mobility: charge carrier drift velocity per unit electric field

I-V Curve of the Di-block Copolymer



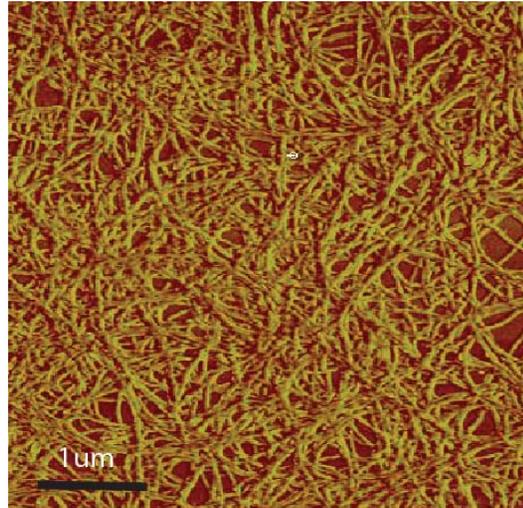
Transfer plot of the Di-block copolymer



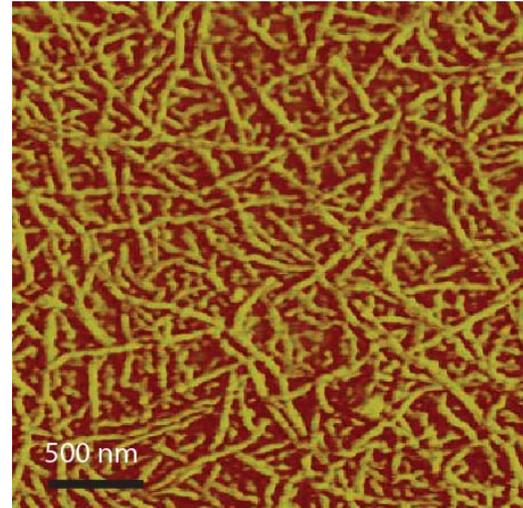
Mobility = $8.9 \times 10^{-3} \text{ cm}^2/\text{Vs}$, $V_T = -1.72 \text{ V}$, on/off = 10^4

Surface morphology of poly(3-hexylthiophene)-*b*-poly(2-ethyl-2-oxazoline) di-block copolymers (AFM)

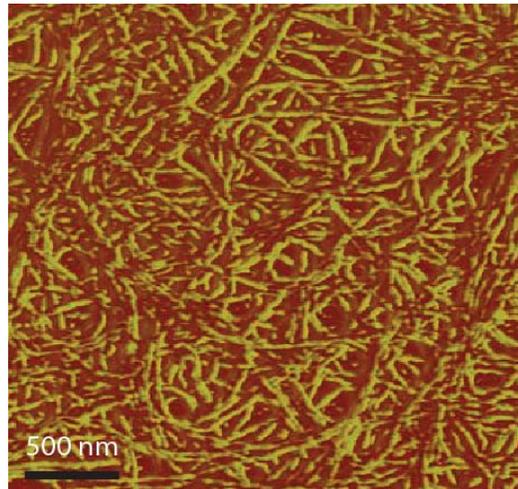
Allyl-terminated
P3HT; Mn= 7550
g/mol



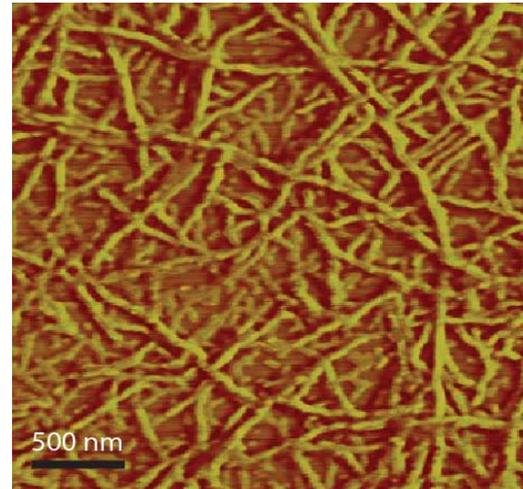
5 mol% PEOXA
Mn=8,240 g/mol



15mol% PEOXA
Mn=10,024
g/mol



30 mol% PEOXA
Mn=11,720 g/mol



➤ Shorter and dispersed nanofibrillar morphology observed in the di-block copolymers when compared with *rr*-P3HT as the % mol PEOXA increases.

Introducing a photochemical component- Quantum Dots

Challenges:

- **Sunlight wasted** - Known photocatalysts are mostly UV/near-UV-active
- **Large overpotentials** - Large reorganization energies of charge transfer reactions in polar media
- **Self-quenching** of charge carriers - Freely diffusing catalysts
- Lack of meaningful photocatalytic activity measurements:
 - Photochemical **quantum yields** – **system dependent**, insufficient
 - **Turnover numbers** – critical/complementary ($\text{/time}^{-1} \times \text{power}^{-1}$)
- **Applicability** depends on: Stability, tune-ability, process-ability, scale-up

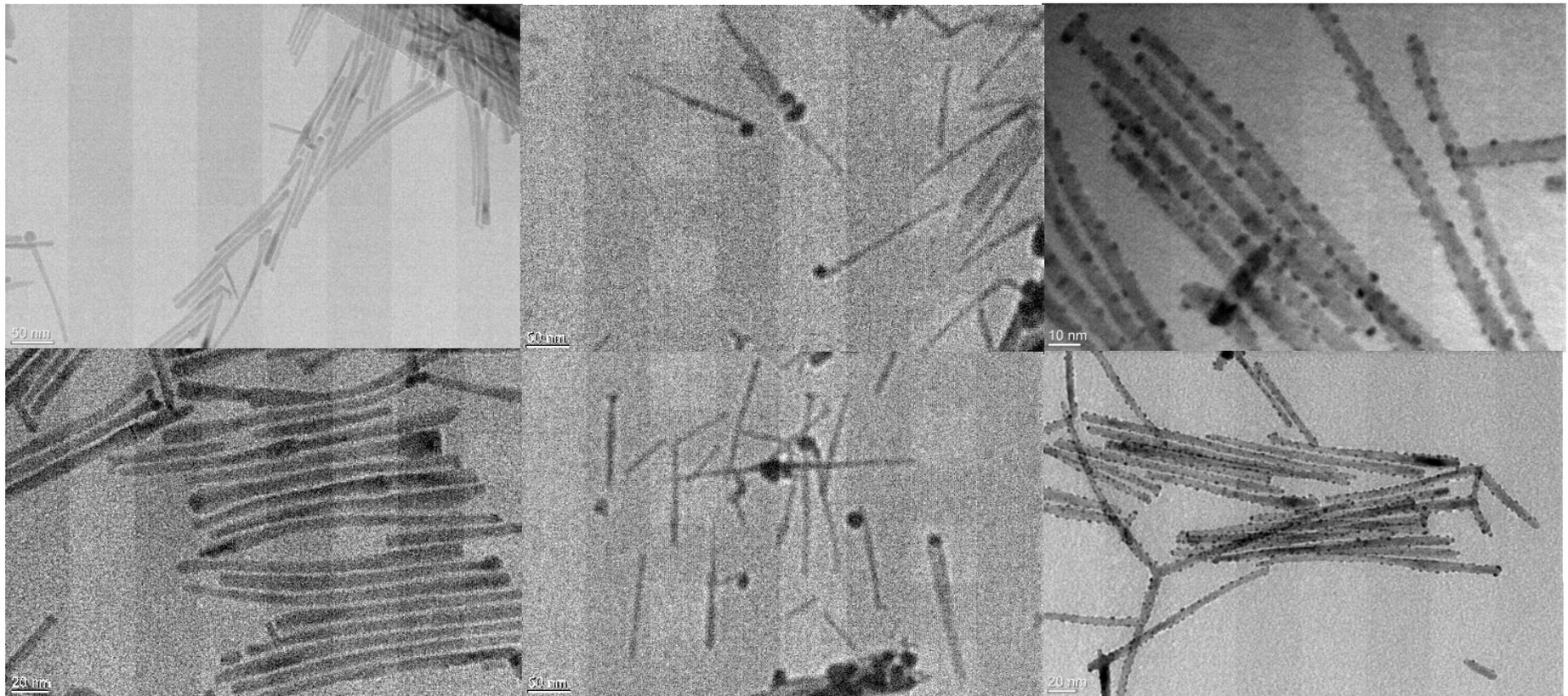
Fabrication of antenna heterostructures

CdS rods



(light ↓ CdS-Au heterostructures

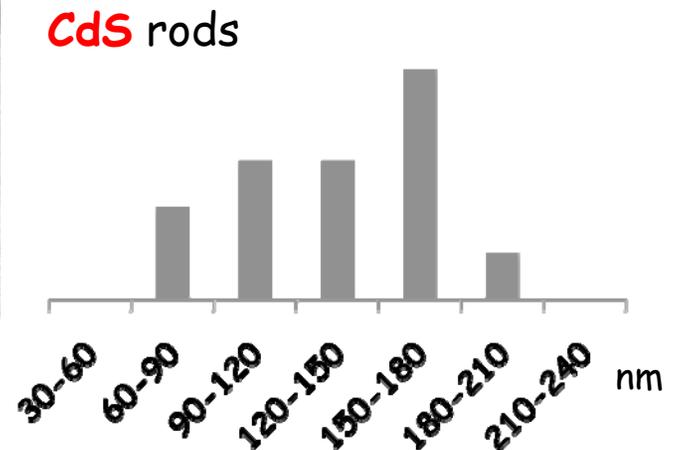
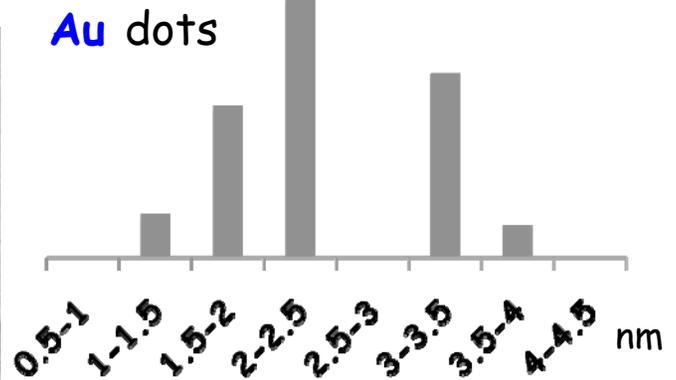
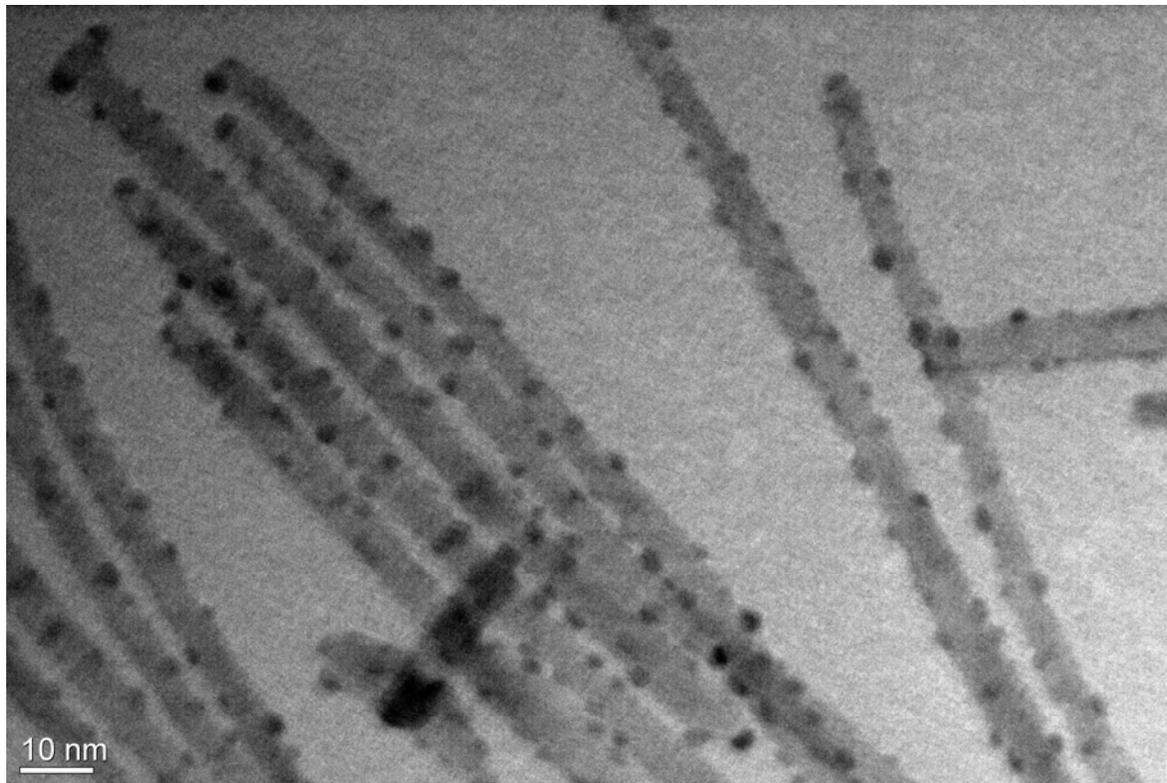
↓dark)



Mussie G. Alemseghed, T. Purnima A. Ruberu, and Javier Vela, " Controlled Fabrication of Colloidal Semiconductor-Metal Hybrid Heterostructures: Site Selective Metal Photo Deposition ". *Chem. Mater.* **2011, 23, 3571–3579**

Fabrication of antenna heterostructures

CdS-Au heterostructures

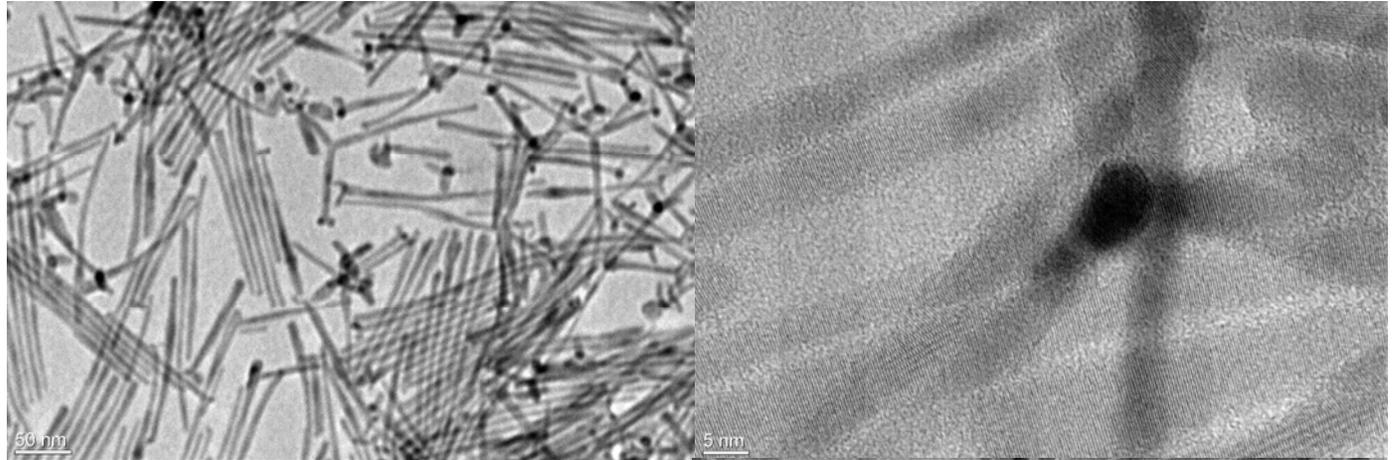


Mussie G. Alemseghed, T. Purnima A. Ruberu, and Javier Vela, " Controlled Fabrication of Colloidal Semiconductor-Metal Hybrid Heterostructures: Site Selective Metal Photo Deposition ". *Chem. Mater.* **2011**, 23, 3571–3579

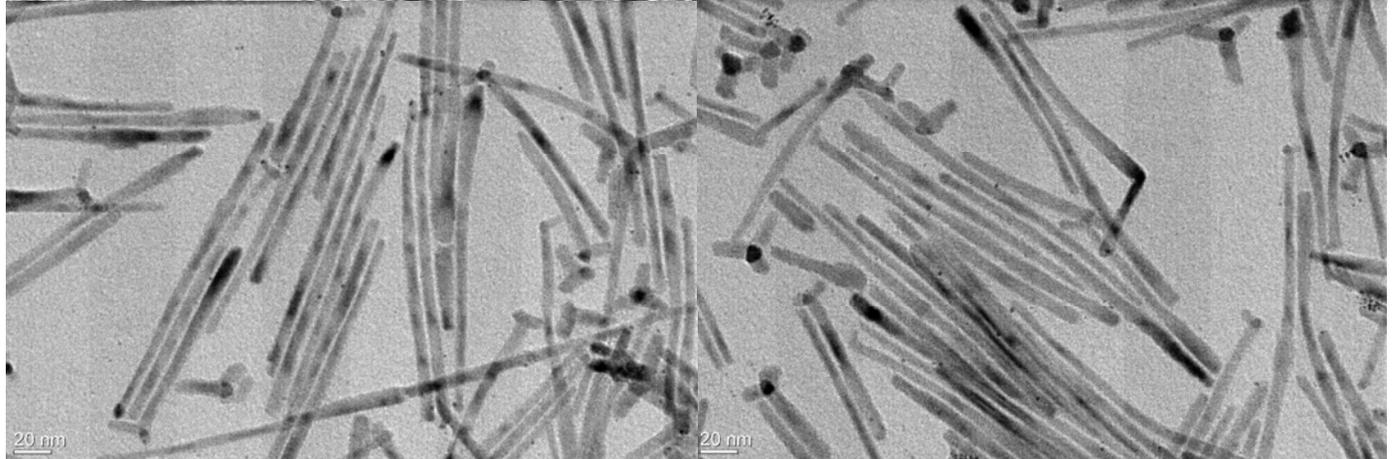
Fabrication of antenna heterostructures

CdS-Pt
heterostructures

High **CdS-Pt**
 $h\nu$, 1h →

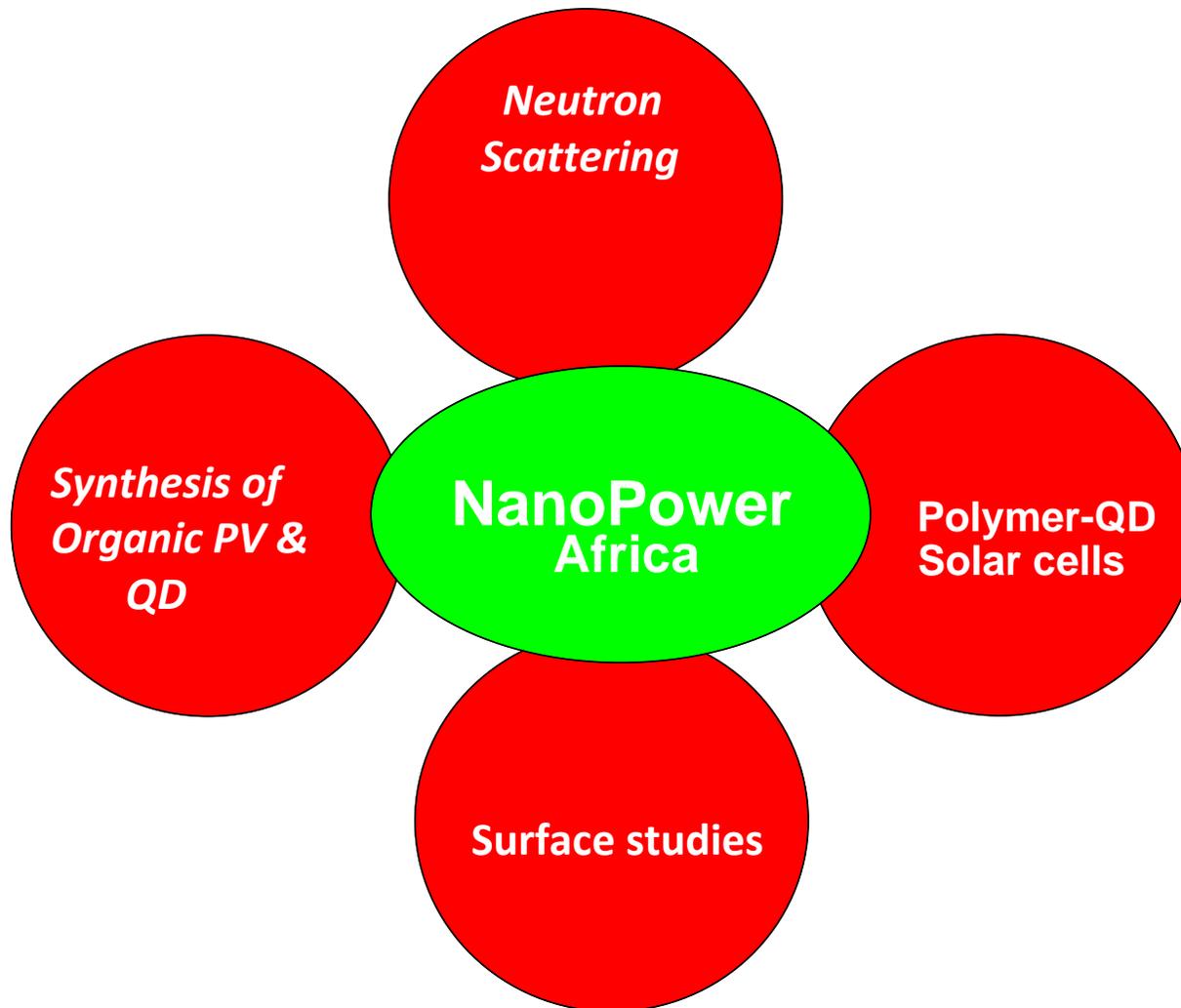


Low **CdS-Pt**
 $h\nu$, 3h →



Mussie Alemseghed

NanoPower Africa at ORNL/ANL



THANK YOU VERY MUCH !!!