ΕΠΙΣΤΗΜΗ ΚΟΙΝΩΝΙΑ
ειδικές μορφωτικές εκδηλώσεις

ΕΘΝΙΚΟ ΙΔΡΥΜΑ ΕΡΕΥΝΩΝ
National Hellenic Research Foundation

Σχεδιάζοντας το αύριο: τα υλικά του μέλλοντος

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10 Φεβρουαρίου 2015

Future materials trends

- It is impossible to predict future discoveries and inventions; what we can predict, however, are societal needs.

- The last 50 years a vast amount of resources went toward defense needs (Cold War era, post-Cold War era).

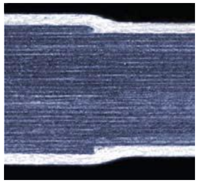
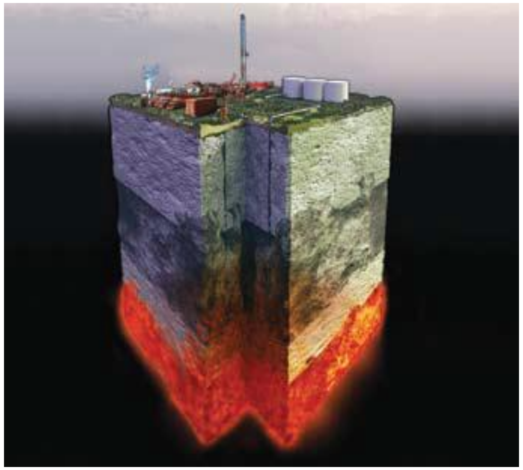
- The next 50 years we need to address significant problems that our society needs. These pertain to basic human needs such as energy, health, transportation, housing, packaging and distribution of food, recycling, etc.—all matters that affect quality of life on this planet.

- It is one thing to be the recipient of funds and to do work as directed by an agency; it is another to influence policy and to ensure that resources become available for critical global needs.

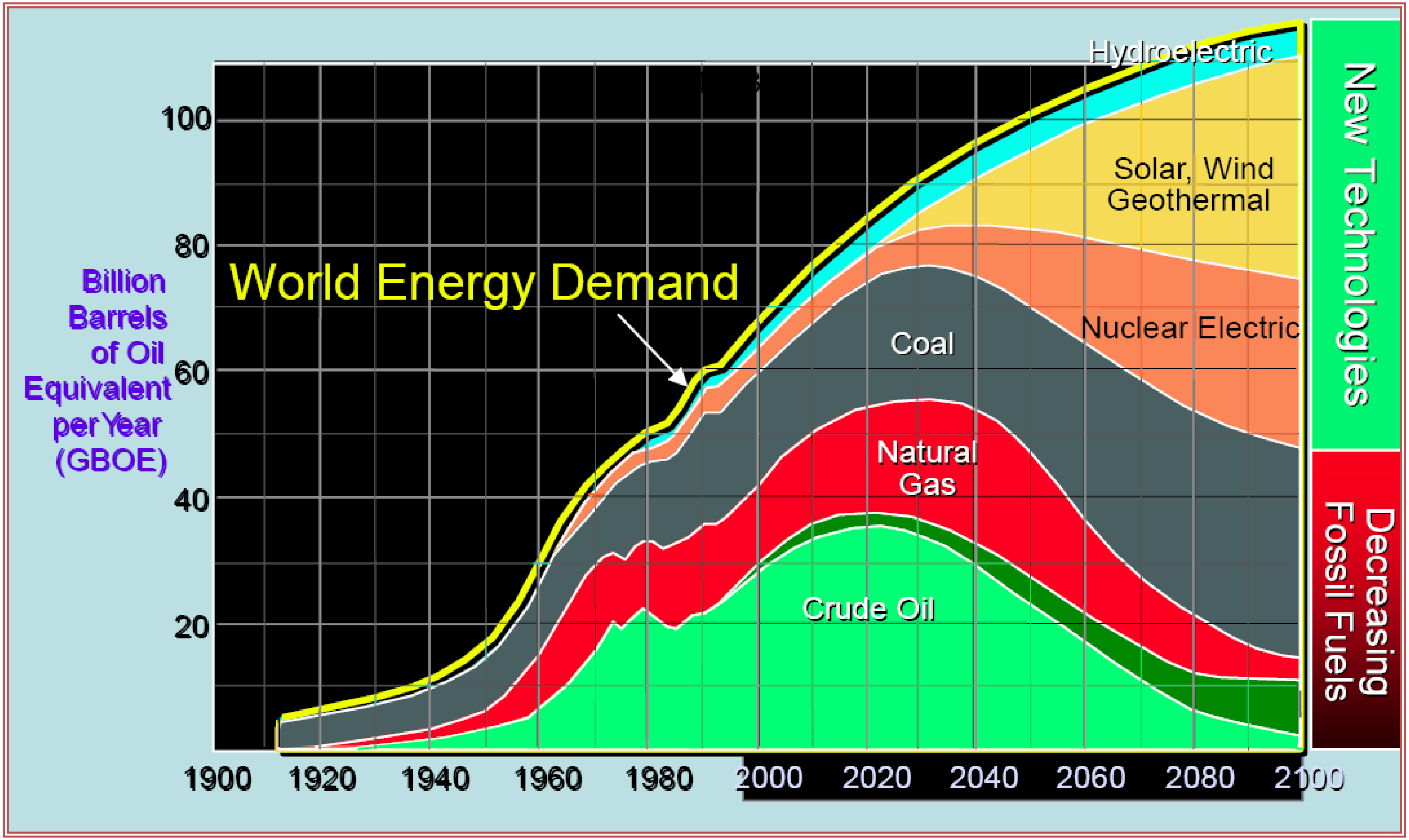
Future Energy Issues

- Energy materials
  - Solar Power
  - Wind Power
  - Geothermal
  - Fossil Energy
  - Biofuels
  - Hydrogen
  - Energy storage and transmission



World Energy Landscape

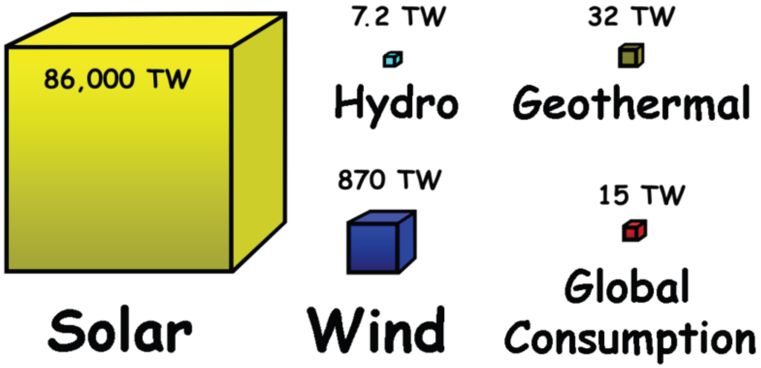


European Union Energy Targets

2020=20+20-20

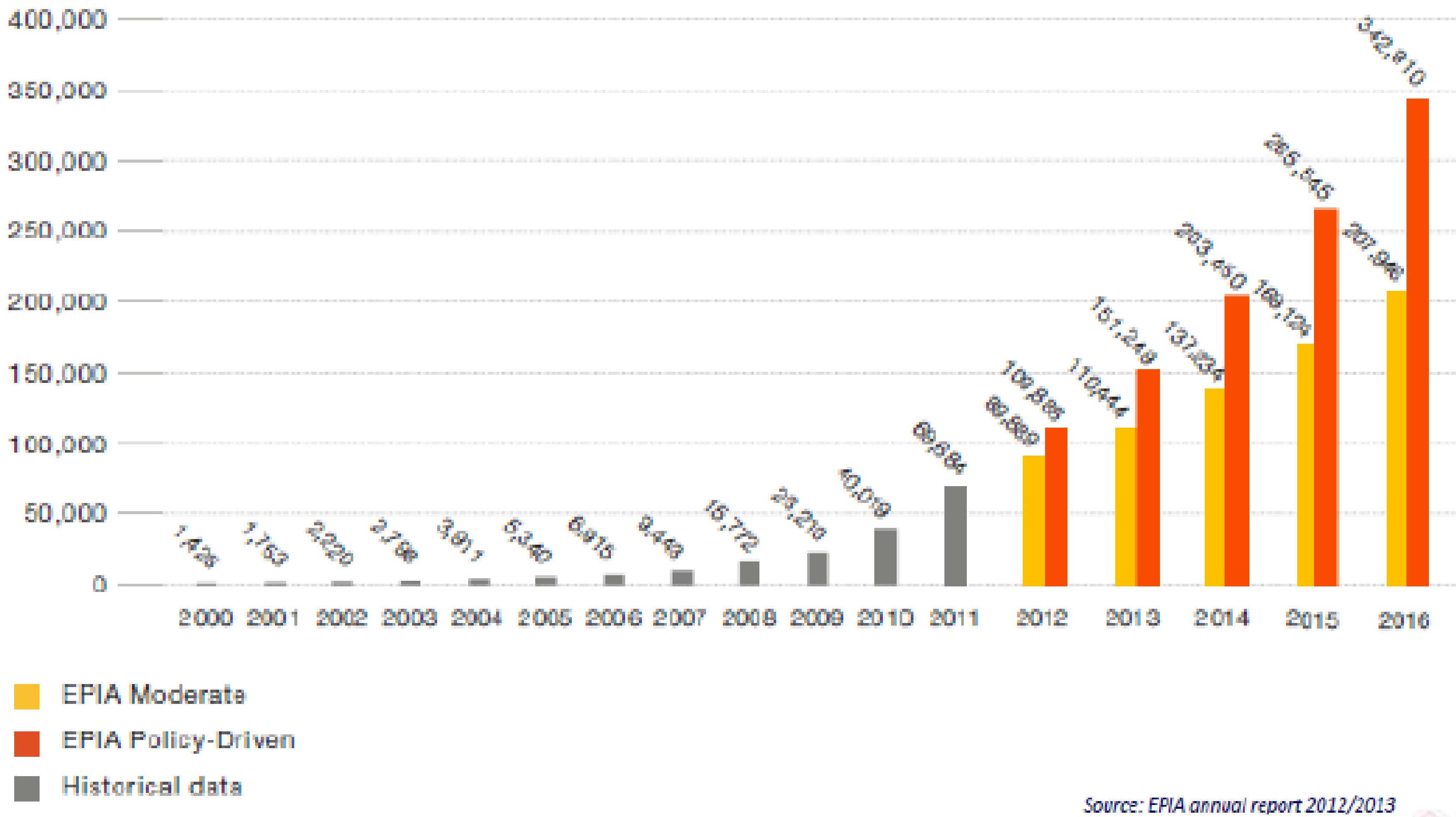
By the 2020:

- the 20% of the energy we use must come from renewable sources
- we must improve the energy efficiency of the 20%
- we must reduce the production of CO2 of the 20



Evolution of Photovoltaics

The motivation is not about where we are, but where

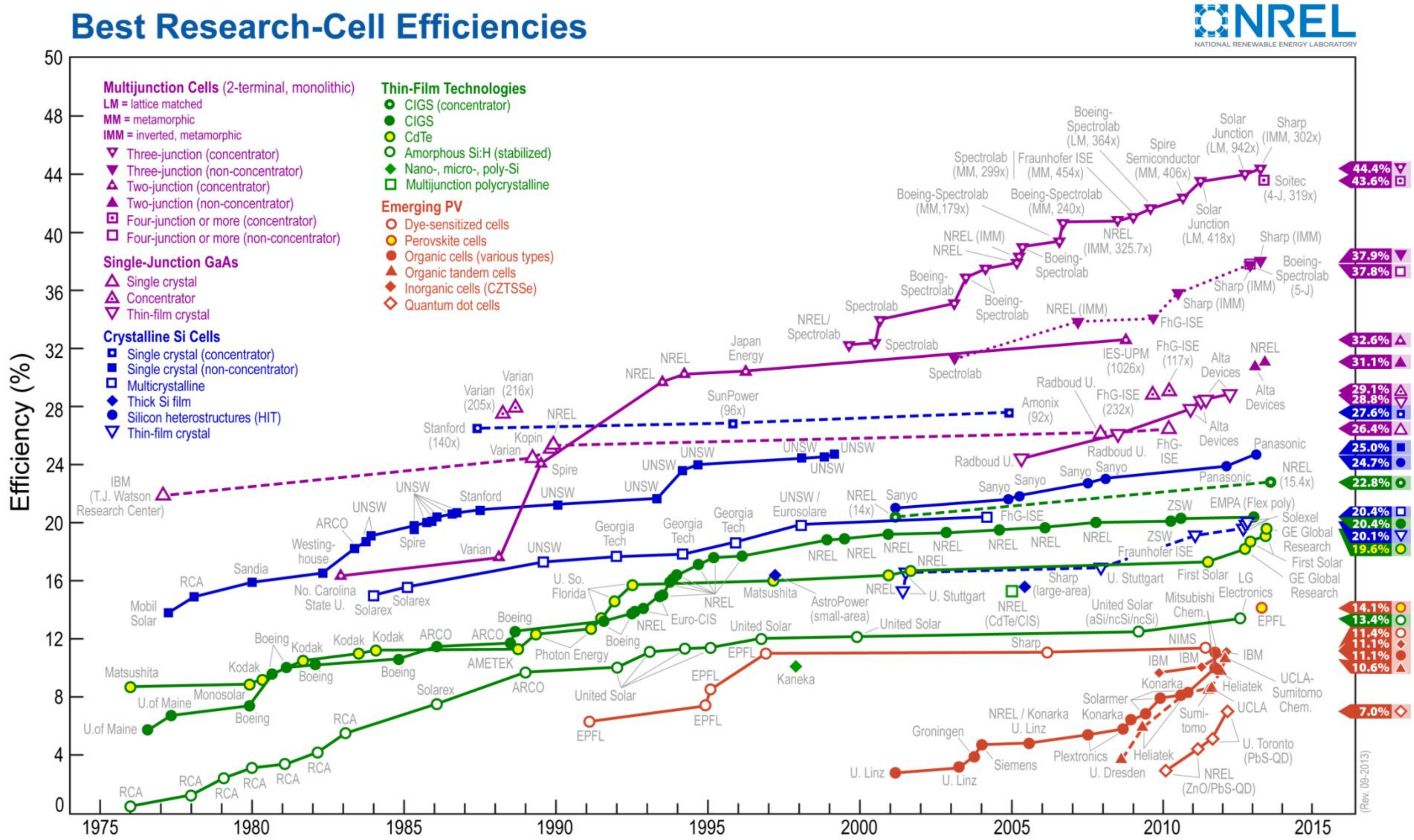


Source: EPIA annual report 2012/2013

PVs a GW Technology

Solar Energy

- renewable energy source
- avg. light incident on earth's surface ~ 200 Wm^{-2}
- solar cells are photovoltaic devices
  - they convert light into electricity *without* applied bias



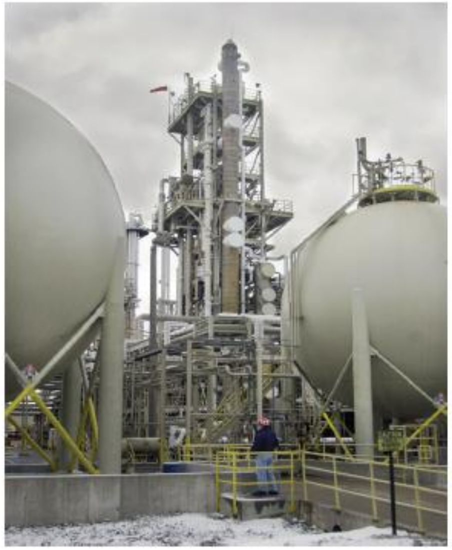
PV Technology Generations

1st Generation:
high-efficiency / high-cost
(single crystal, polycrystalline silicon, GaAs, III-V)

☺ Single junction for extracting energy from photons, approaching their theoretical efficiency maximum of 33%

☹ High cost manufacturing processes

These cells may take years to pay for their purchasing costs. It is not thought that first generation cells will be able to provide energy more cost effective than fossil fuel sources.

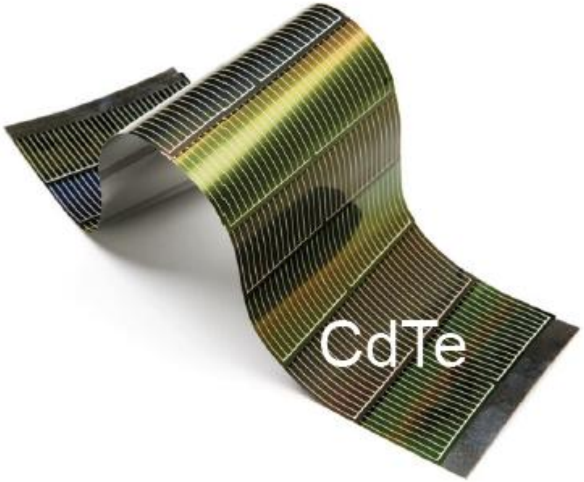


PV Technology Generations

2nd Generation:
low-cost / low-efficiency
(thin film solar cells, copper indium gallium selenide (CIGS), cadmium telluride (CdTe), amorphous silicon)

- ☹ 10-15% conversion efficiency
- ☺ Device design that allow the use of minimal materials and cheap manufacturing processes
- ☹ Toxic materials, not environmental friendly

These cells have the potential to be more cost effective than fossil fuel, though this may not occur until 2015 or later.



PV Technology Generations

3rd Generation:

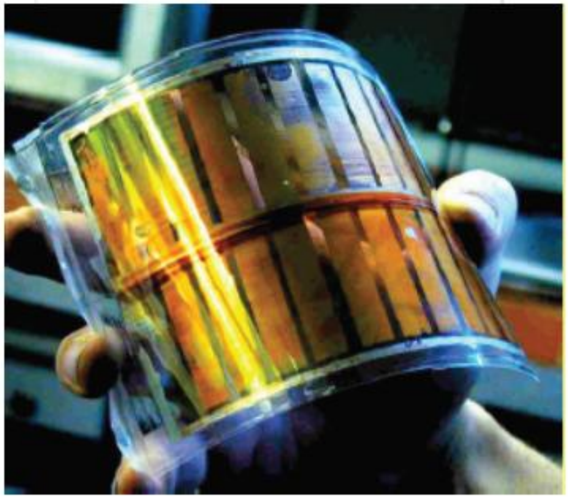
low-cost / high-efficiency

- conjugated polymers/molecules
- dye sensitized solar cell
- multi-junction photovoltaic cells, tandem cells, nanostructured cells.

Excitonic solar cells

HOT RESEARCH TOPIC!

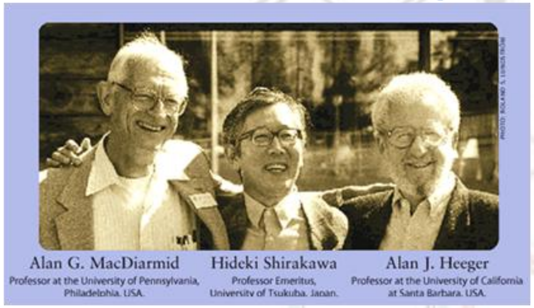
The goal of third generation solar cell research are low-cost, high efficiency cells; finding novel approaches to obtain efficiencies in the range of 30-60%. Some analysts predict that third generation cells could start to be commercialized sometime around 2020.



Conjugated Polymers: The Core Materials for Various Optoelectronic Applications

Light Emitting Diodes (LEDs)

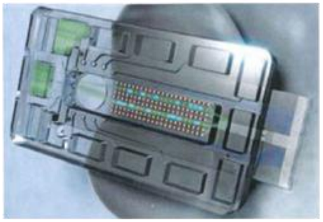
Nobel Prize in Chemistry 2000



for the discovery and development of

Conjugated Polymers

Optical Sensors & Biosensors



Field Effects Transistors (FETs)

Organic (Plastic) Solar Cells (OPVs)

Comparing 1st and 3rd Generation Technology

The Technology…

'Traditional' p-n junctions PV

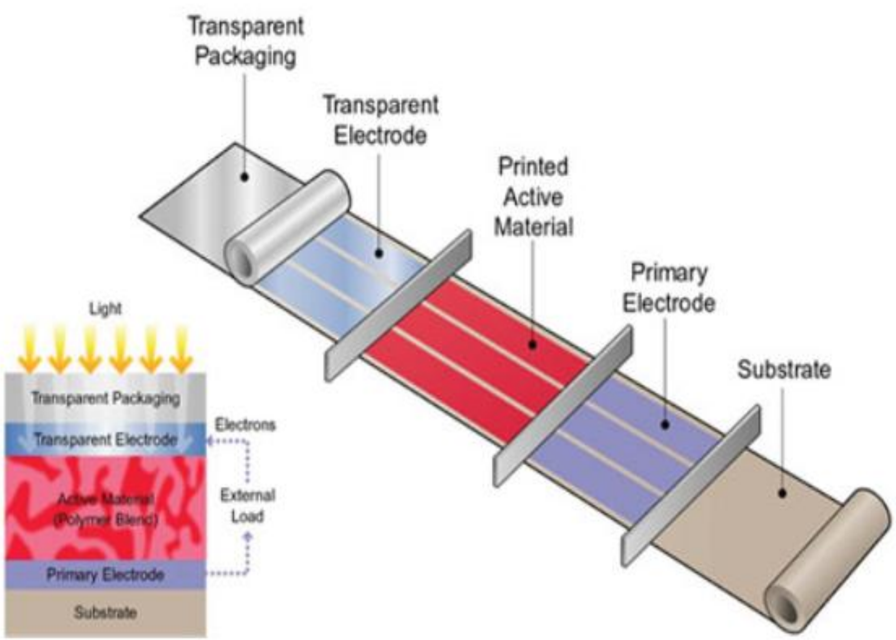
- Complex and expensive processes (high temperatures, high vacuum technologies)
- Strong environmental footprint
- Very expensive plants installation.
- Limited basic materials
- Limited aesthetic options - black or blue only
- Extremely Fragile

Comparing 1st and 3rd Generation Technology

The Technology…

Excitonic Solar Cells

- Low cost materials and processes
- Flexible and lightweight
- Amenable to continuous, "roll-to-roll" manufacture
- Semi-transparent
- Color tunable



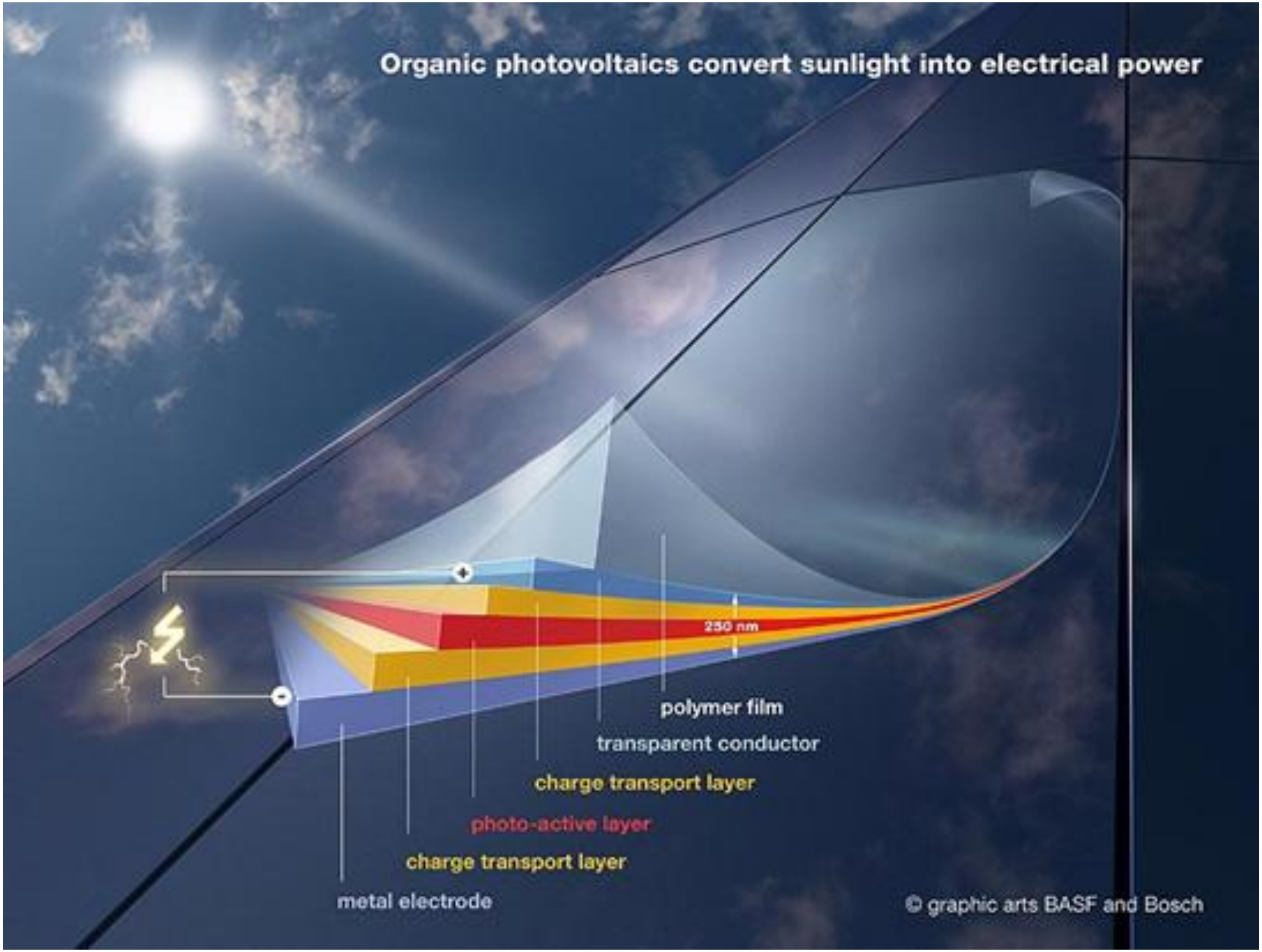
Organic Photovoltaic Roadmap

Which performance for which application?

Application	Mobile Electronics	Outside pillars for urban areas	Outdoor recreational remote	BIPV	Grid Connected
					
Efficiency %	< 5%	5-8 %	5-8 %	5-12%	> 10%
Lifetime	>1 year	3-5 years	3-5 years	> 10 years	> 10 years
Cost	Competitive compared to flexible inorganic PV	Competitive compared to flexible inorganic PV	Competitive compared to flexible inorganic PV	100 €/m²	Grid parity 0.15€/kW

Source: Solarmer

Organic Photovoltaics



Current applications of OPVs

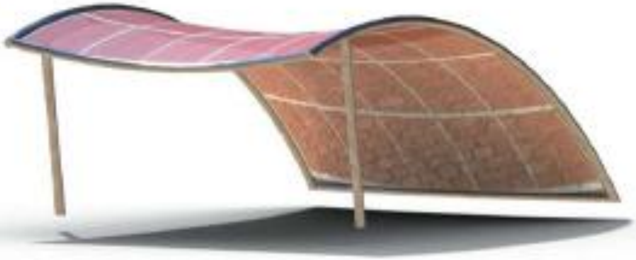
Niche markets

Bags & Chargers

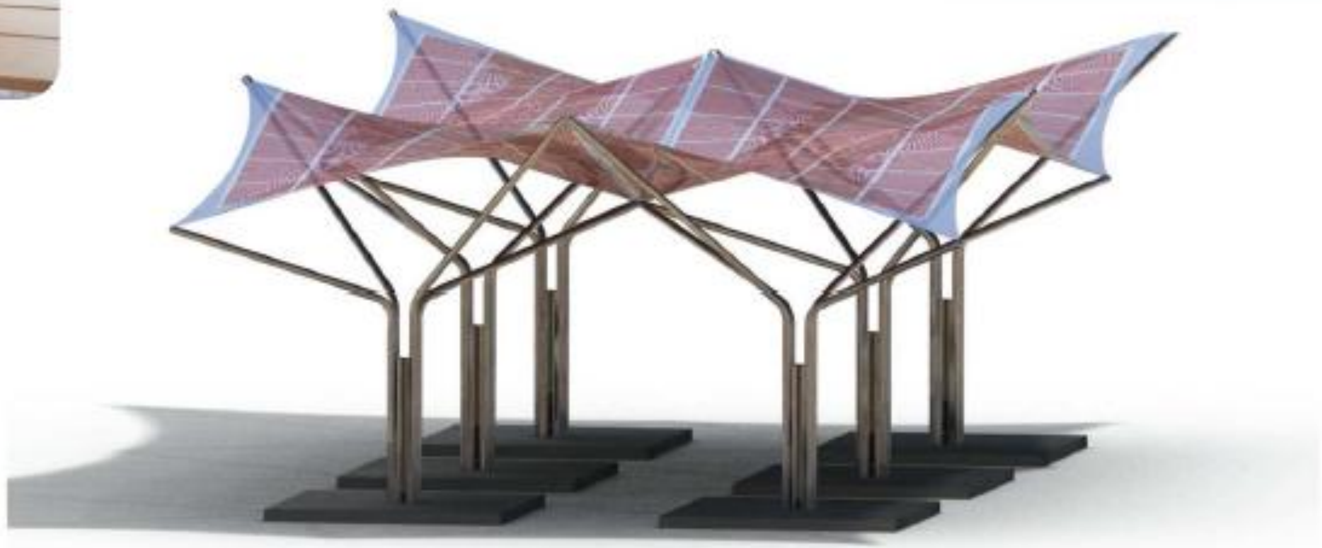
Big Bubble Bag (Italy)

Current applications of OPVs

Shading Elements



- Under development



Current applications of OPVs

Carports

Florida,

Integration: BAPV vs BIPV

Current technology BAPV

Production of building parts → Construction of building → PV modules **retrofitted over the existing** building envelope

Production of PV modules → PV modules **retrofitted over the existing** building envelope

Future technology BIPV

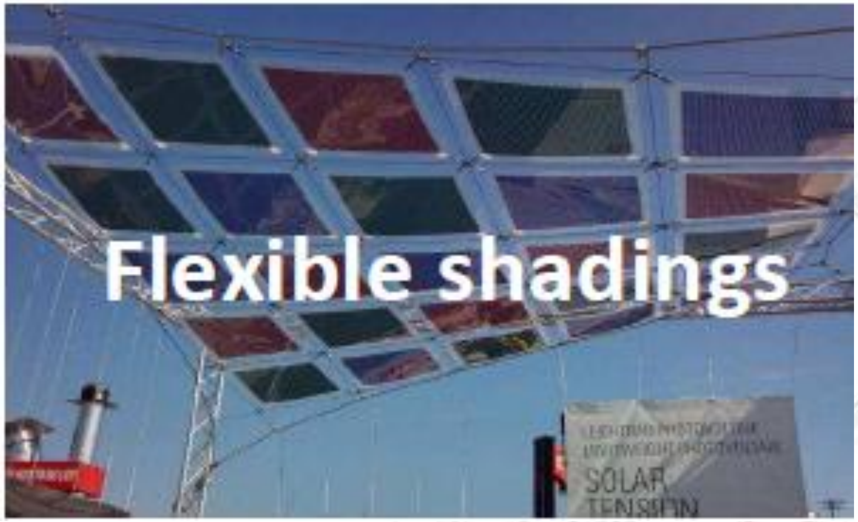
Production of PV modules → Production of facade elements **In-line integration of** PV modules → Construction of building with integrated PV

Integration BIPV

Beneficial features of OPV for production of BIPV:

- Requires no special care regarding breakage (unlike c-Si)
- No rigid supporting construction is needed
- Curved BIPV elements are possible
- Compatible with R2R production (*e.g.* onto continuous steel rolls)
- Module size can be matched exactly to BIPV element (not vice versa)

Flexible OPV in BIPV elements:



Economy of Scale

Lab

5 cm
1kWatt

Pilot

25 cm
4 MWatt

Production

150 cm
1GWatt

Vision of OPV manufacturing

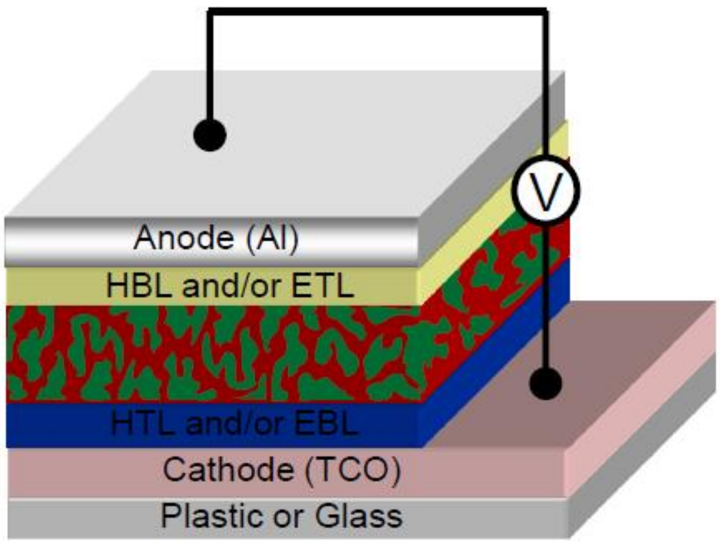
- Low Cost
  - Reduce energy consumption
  - Use abundant materials
- Continuous
  - Increased production efficiency
  - High throughput
- Scaleable
  - Upscale to large area
- Transferable
  - Produce locally

Target: large area, high volume, low cost production

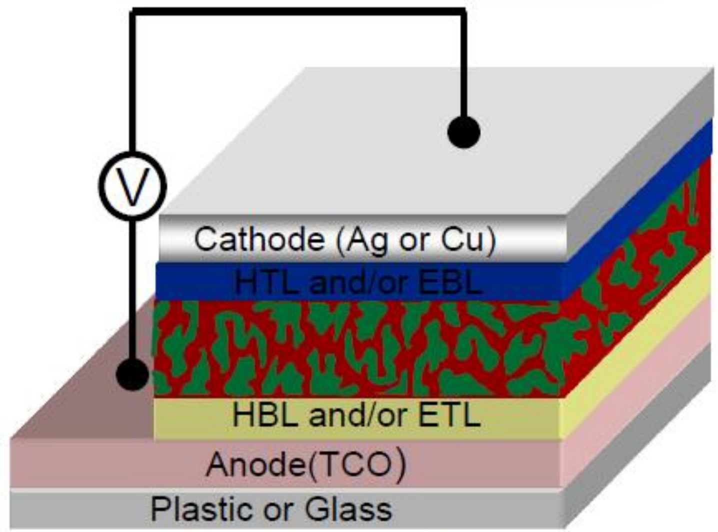
Organic Photovoltaic Architectures

“Lab” device

Commercial device

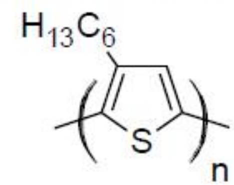


Normal stack

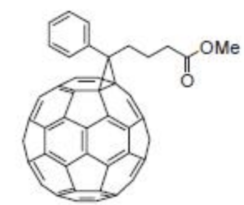


Inverted stack

Active Layer



Polymer

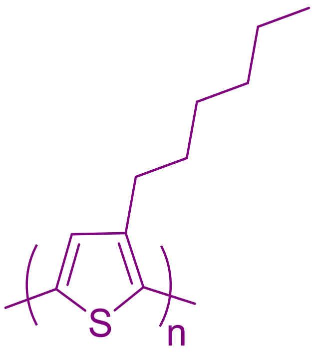


Fullerene

Development of the correct BHJ-morphology with processes (blade coating, temperature ramps ...) as close as possible to mass production tools

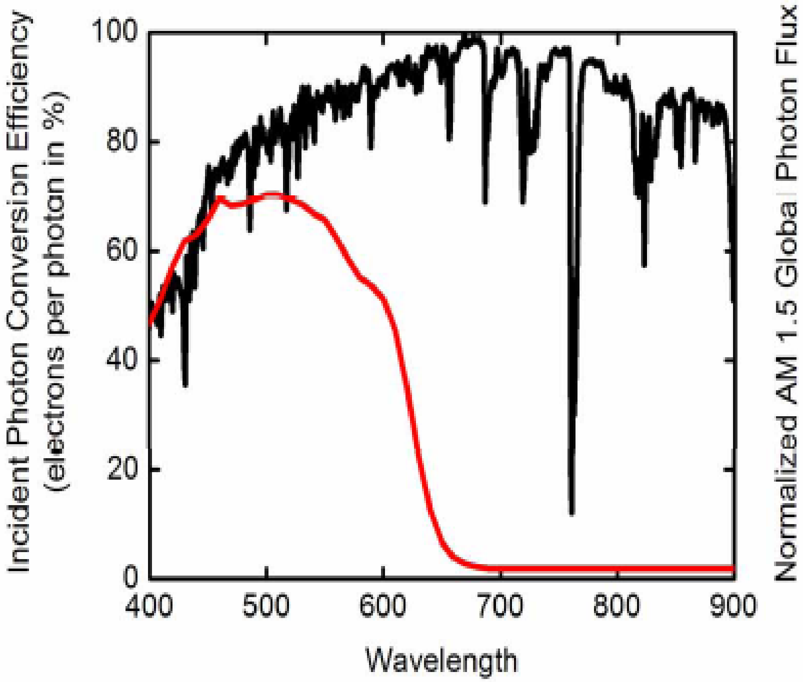
State-of-the-art P3HT:PCBM Solar Cells

Electron Donor

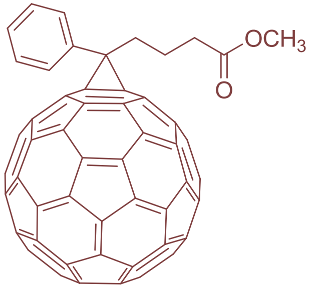


P3HT

Band gap too large ---Missing more than half the solar spectrum



Electron Acceptor



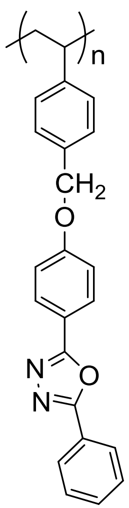
PCBM

Opportunity: Potential for > 50% improvement using polymer with smaller band gap.

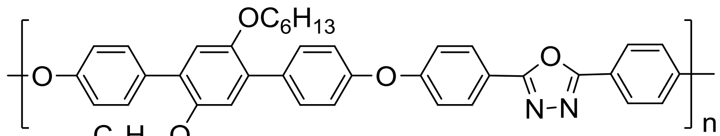
Power Conversion Efficiency: 4 – 4.5 %

N-Type Copolymers as electron acceptors in solar cells

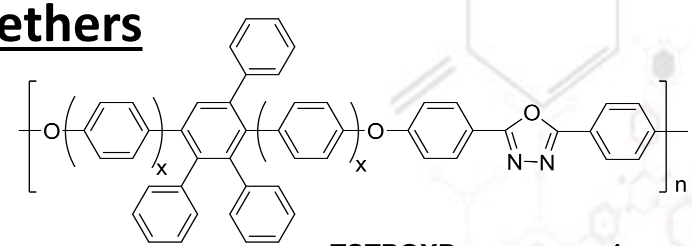
Oxadiazole based Copolyarylethers



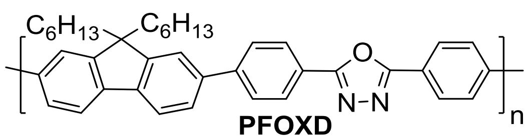
SDPOXD



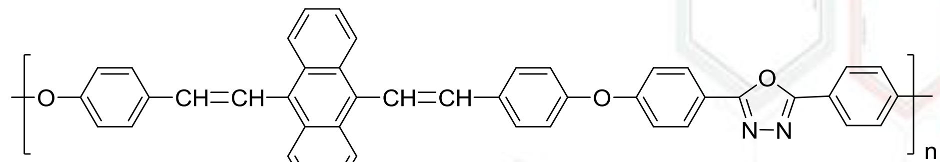
TPOXD



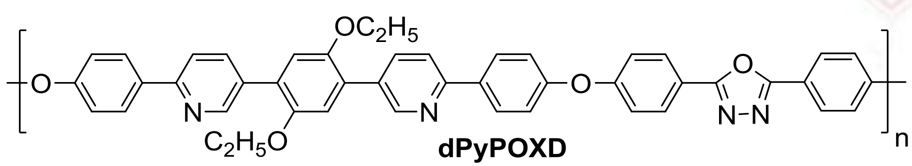
TSTPOXD : x = 1
TSQPOXD : x = 2



PFOXD



PAOXD



dPyPOXD

Active layer	Open-circuit voltage (V)	Fill factor (FF)	Power conversion efficiency ($\times 10^{-3}$%)
P3HT/TSTPOXD (1/2 w/w)	0.65	0.17	0.31
P3HT/PFOXD (1/2 w/w)	0.46	0.24	0.48

Chochos, C. L.; Govaris, G. K.; Kakali, F.; Yiannoulis, P.; Kallitsis, J. K.; Gregoriou, V. G. *Polymer* **2005**, *46*, 4654.

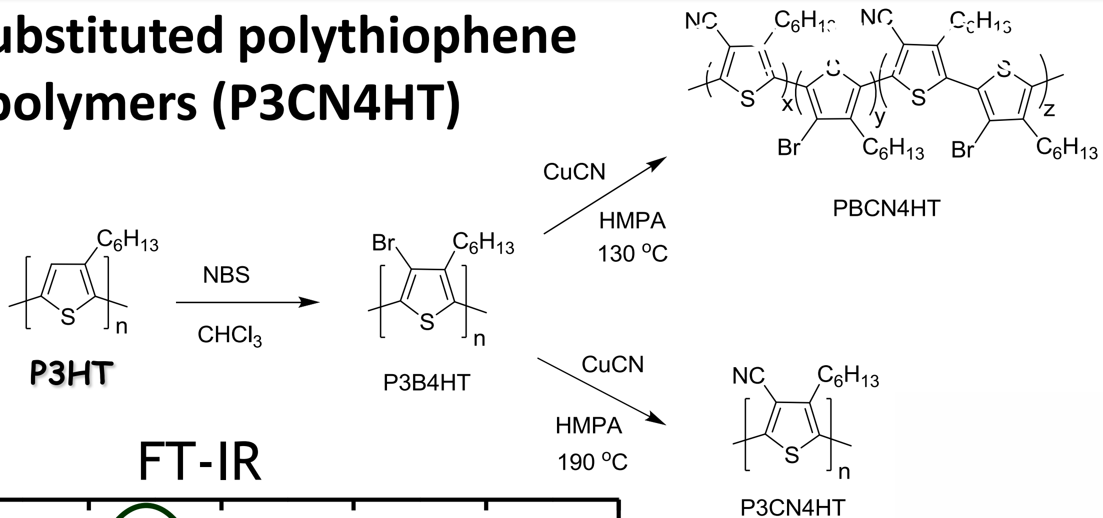
Collaboration with Konarka Technologies

ICE-HT FORTH

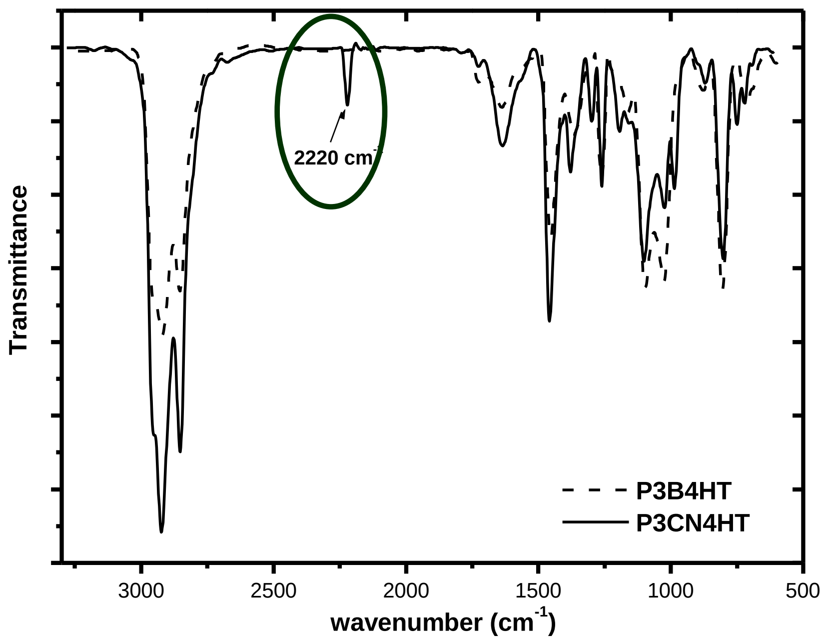
ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΑΤΡΩΝ UNIVERSITY OF PATRAS

N-Type Copolymers as electron acceptors in solar cells

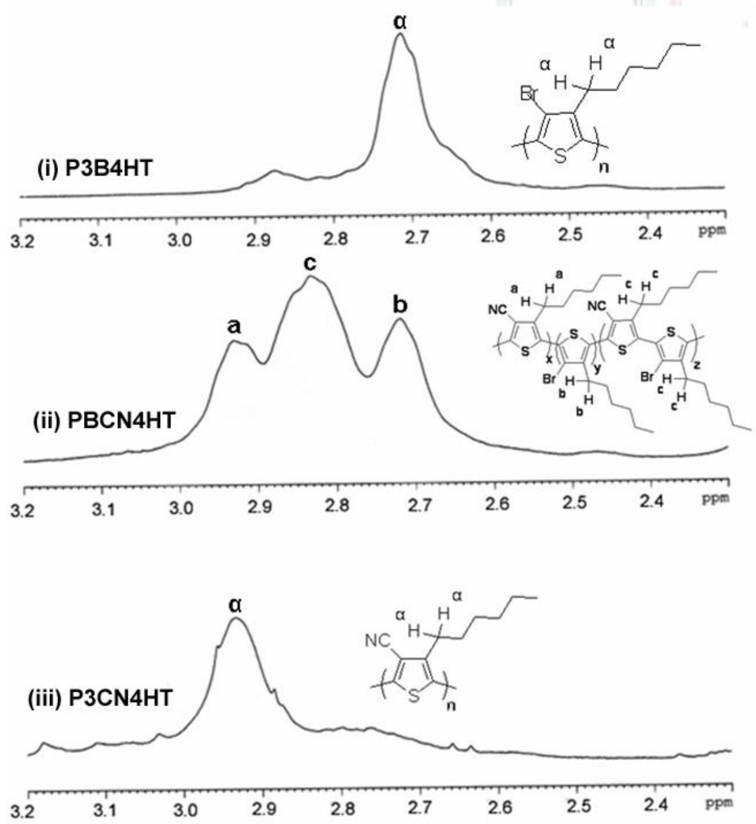
Cyano-substituted polythiophene copolymers (P3CN4HT)



FT-IR



1H-NMR

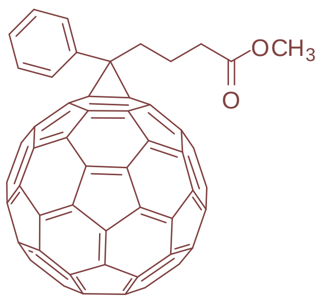


Collaboration with Konarka Technologies

N-Type Copolymers as electron acceptors in solar cells

Comparable energy levels with the state of the art PCBM

State of the Art



PCBM

3.7eV

LUMO

HOMO

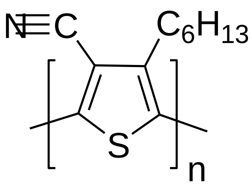
6.1eV

3.6eV

LUMO

HOMO

5.9eV



P3CN4HT

Our Material

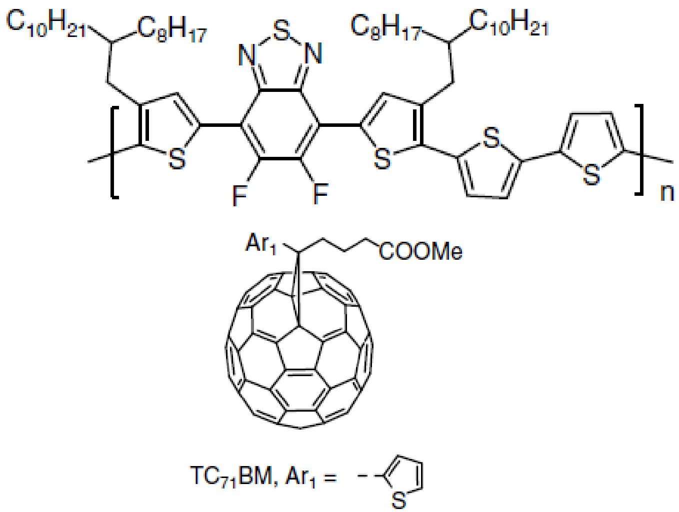
Chochos, C. L.; Economopoulos, S. P.; Deimede, V.; Gregoriou, V. G.;
Lloyd, M. T.; Malliaras, G. G.; Kallitsis, J. K. *J. Phys. Chem. C* 2007, *111*, 10732.

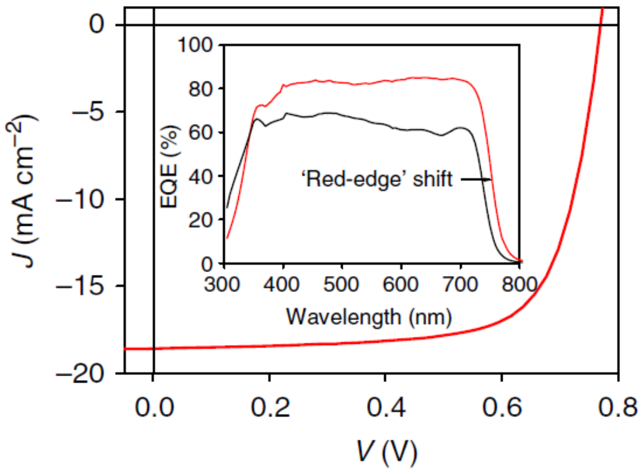
Collaboration with Konarka Technologies

State of the art in organic solar cells

Single Solar Cells: Maximum PCE of 10.8%

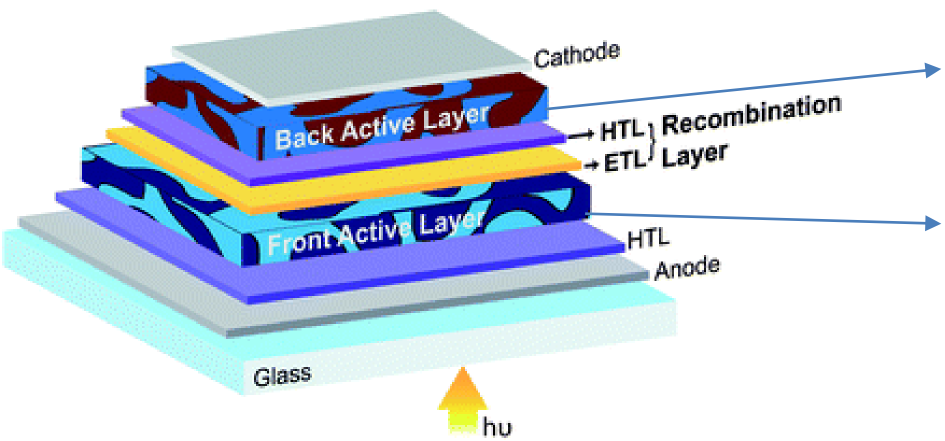
Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nature Communication* **2014**, DOI: 10.1038/ncomms6293





Tandem solar cell : Maximum PCE of 11.3%

H. Zhou, Y. Zhang, C.-K. Mai, S. D. Collins, G. C. Bazan, T.-Q. Nguyen, A. J. Heeger, *Adv. Mater.* **2015**, DOI: 10.1002/adma.201404220

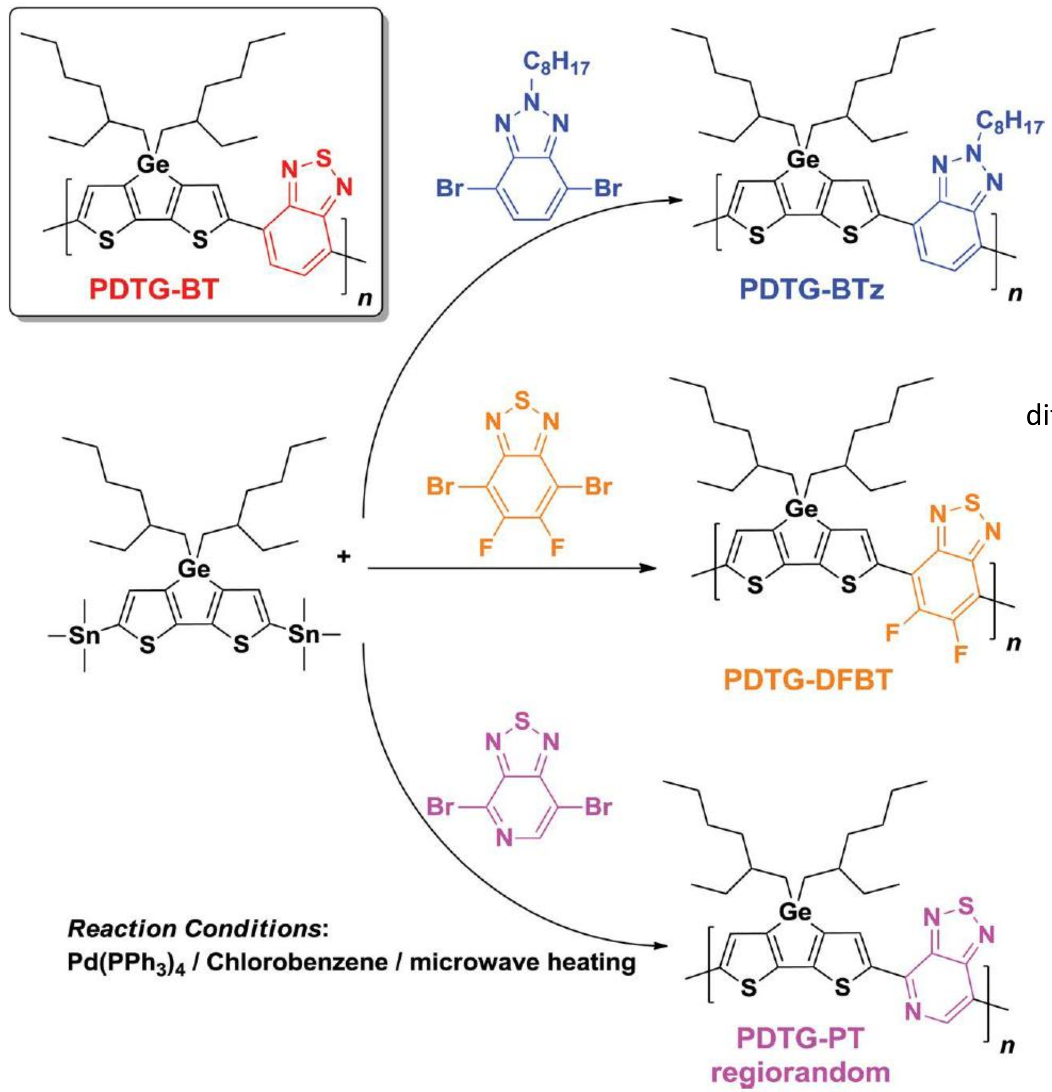


Low Band Gap polymer

High Band Gap polymer

High Performance Low Band Gap Polymer Materials in Advent

The case of Dithienogermole copolymers



benzotriazole

difluorobenzothiadiazole

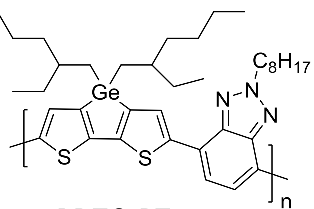
pyridinethiadiazole

Imperial College London

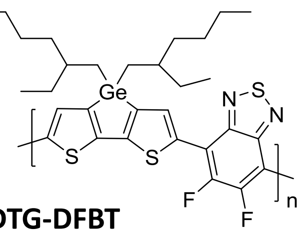
Advent

Yau, C. P.; Fei, Z; Ashraf, R. S.; Shahid, M.; Watkins, S. E.; Pattanasattayavong, P.; Anthopoulos, T. D.; Gregoriou, V. G.; Chochos, C. L.; Heeney, M. *Adv. Funct. Mater.* **2013**, *3*, 10221-10229

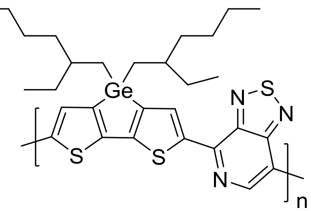
Photophysical Properties



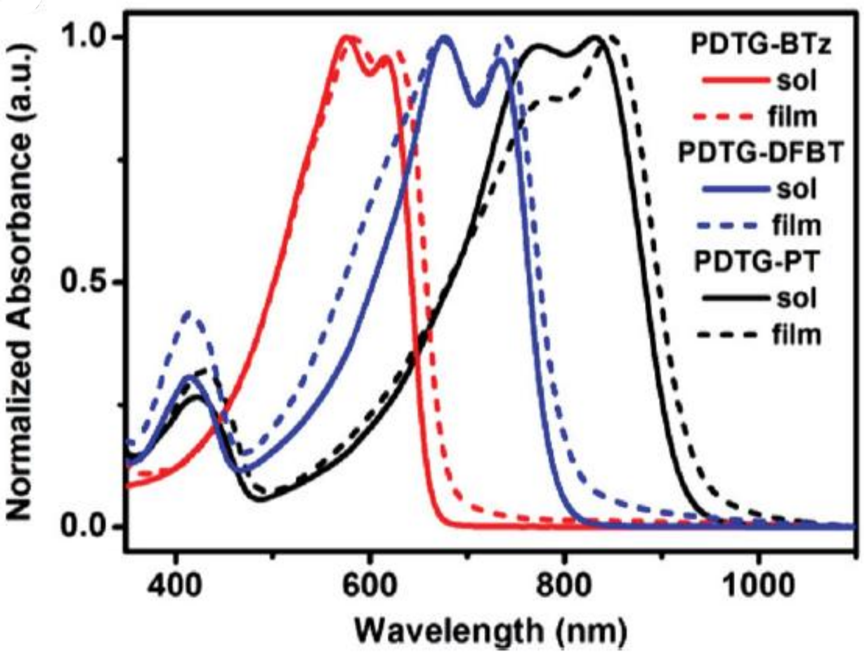
PDTG-BTz

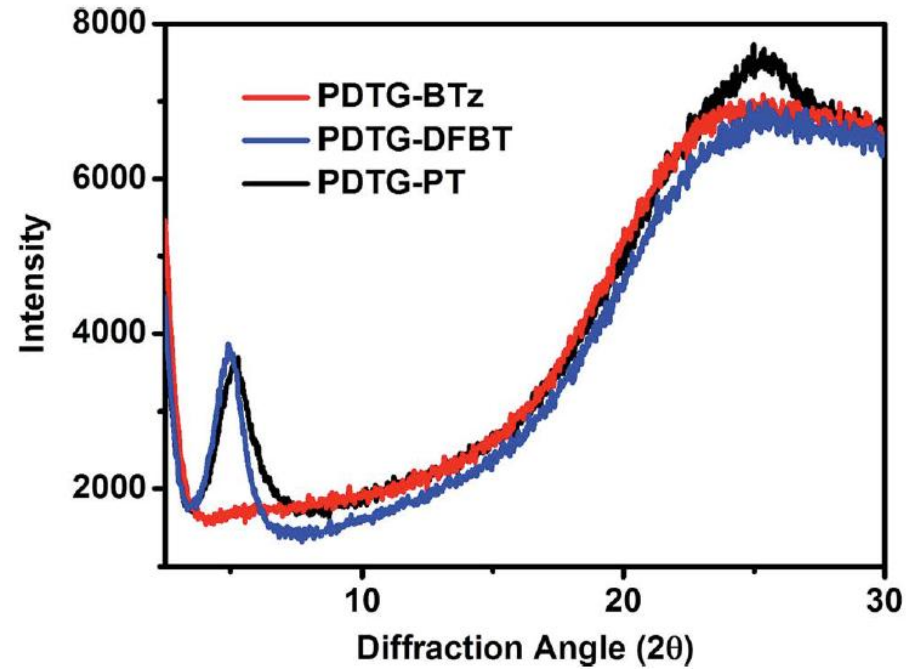


PDTG-DFBT



PDTG-PT

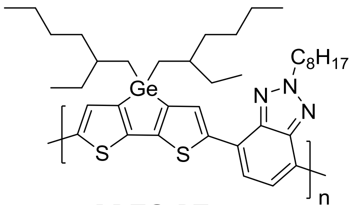




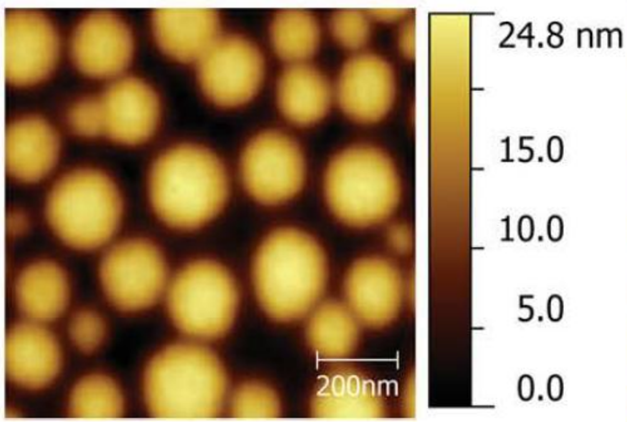
	HOMO [eV][a)]	LUMO [eV][b)]	Optical E_g [eV][c)]	Calc. HOMO [eV]	Calc. LUMO [eV]	Calc. E_g [eV]
PDTG-BTz	−4.75 ± 0.05	−2.95 ± 0.05	1.82	−4.50	−2.62	1.88
PDTG-DFBT	−5.00 ± 0.05	−3.6 ± 0.05	1.53	−4.80	−3.20	1.60
PDTG-PT	−4.90 ± 0.05	−3.6 ± 0.05	1.32	−4.79	−3.33	1.46

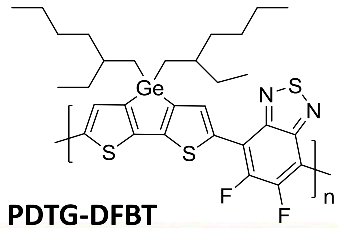
[a)]Determined as a thin film by UV-PESA; [b)]Estimated by the subtraction of the optical band gap from the HOMO; [c)] Determined by onset of optical absorption.

Morphological Characterization

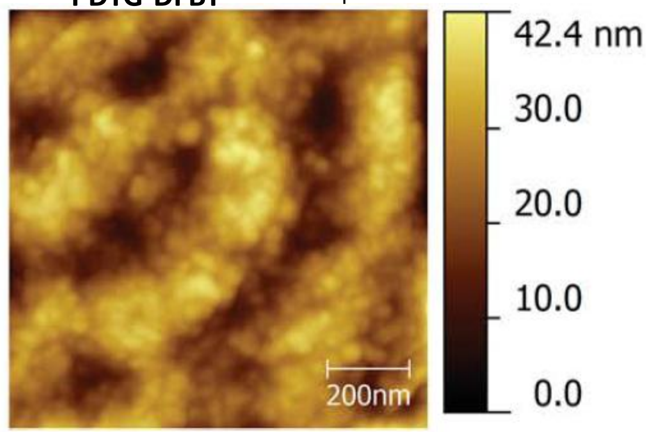


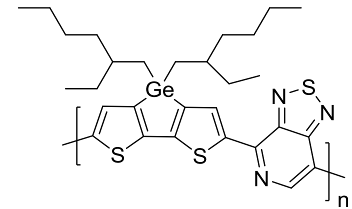
PDTG-BTz



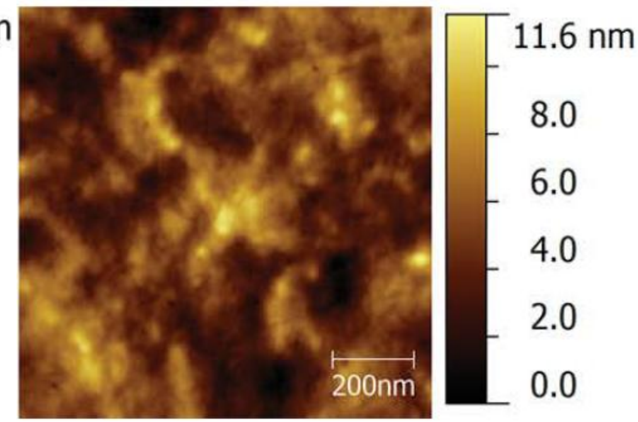


PDTG-DFBT





PDTG-PT



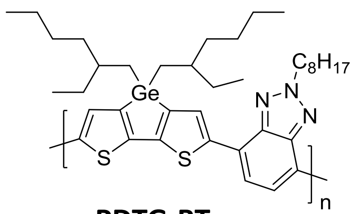
PDTG-BTz/PC$_{70}$BM blend films, rather large features on the order of 100–200 nm are apparent, with a root mean square (RMS) surface roughness of 6.70 nm

PDTG-DFBT/PC$_{70}$BM also show relatively large features on the order of 20–40 nm, and films with appreciable surface roughness (RMS of 6.77 nm)

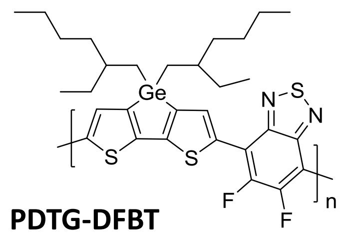
PDTG-PT/PC$_{70}$BM showed much finer mixing in addition to the lowest surface roughness (RMS of 1.78 nm)

Yau, C. P.; Fei, Z; Ashraf, R. S.; Shahid, M.; Watkins, S. E.; Pattanasattayavong, P.; Anthopoulos, T. D.; Gregoriou, V. G.; Chochos, C. L.; Heeney, M. *Adv. Funct. Mater.* **2013**, *3*, 10221-10229

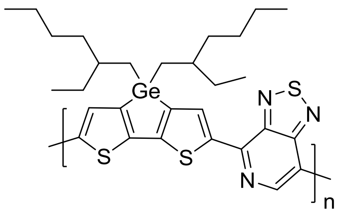
Photovoltaic Performance



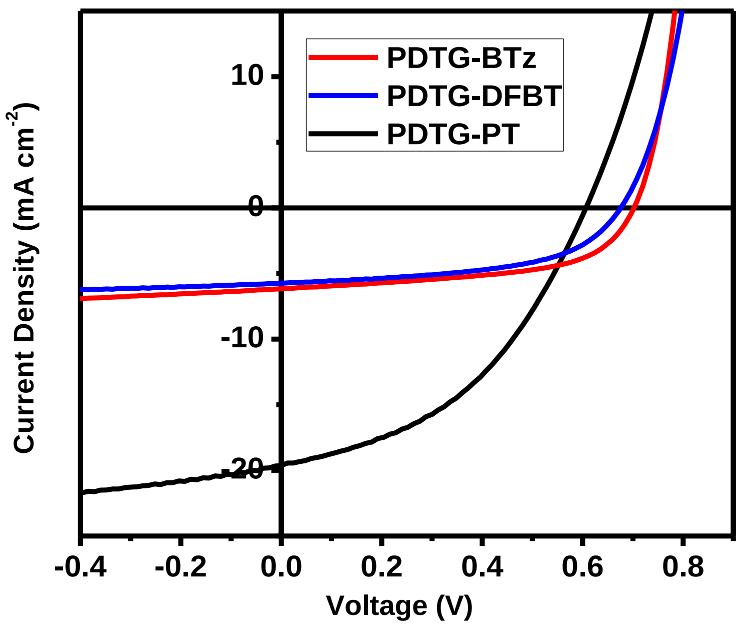
PDTG-BTz



PDTG-DFBT



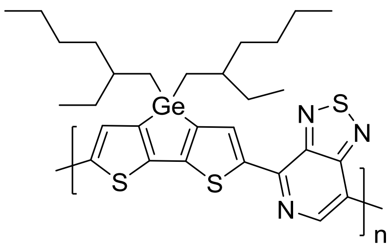
PDTG-PT



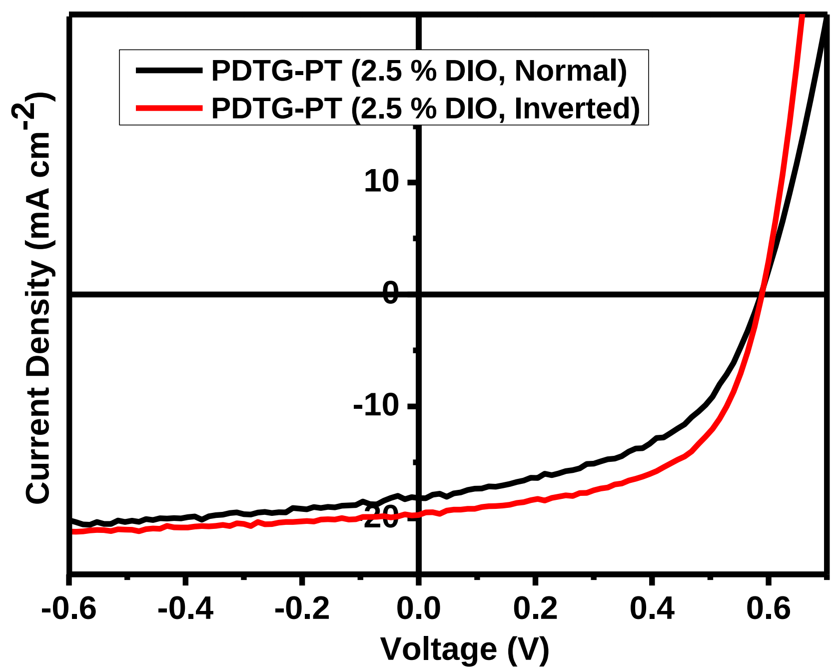
Polymer:$PC_{70}BM$ (1:2) in oDCB	**J_{SC} (mA cm^{-2})**	**V_{oc} (V)**	**FF**	**PCE (%)**
PDTG-BTz	6.17	0.70	0.56	2.4
PDTG-DFBT	5.74	0.67	0.54	2.1
PDTG-PT	17.7	0.61	0.43	4.6
PDTG-PT + 5 vol% DMF	17.5	0.60	0.44	4.6
PDTG-PT + 3 vol% CN	18.7	0.61	0.43	4.9
PDTG-PT + 2.5 vol% DIO	17.6	0.59	0.50	5.2

Yau, C. P.; Fei, Z; Ashraf, R. S.; Shahid, M.; Watkins, S. E.; Pattanasattayavong, P.; Anthopoulos, T. D.; Gregoriou, V. G.; Chochos, C. L.; Heeney, M. *Adv. Funct. Mater.* **2013**, *3*, 10221-10229

Photovoltaic Performance



PDTG-PT



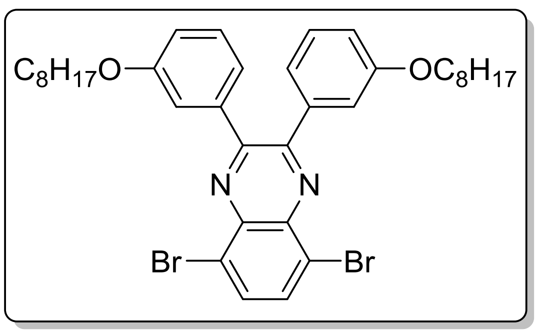
4th Highest Efficiency Worldwide for Conjugated Polymers with Band Gap below 1.4 eV

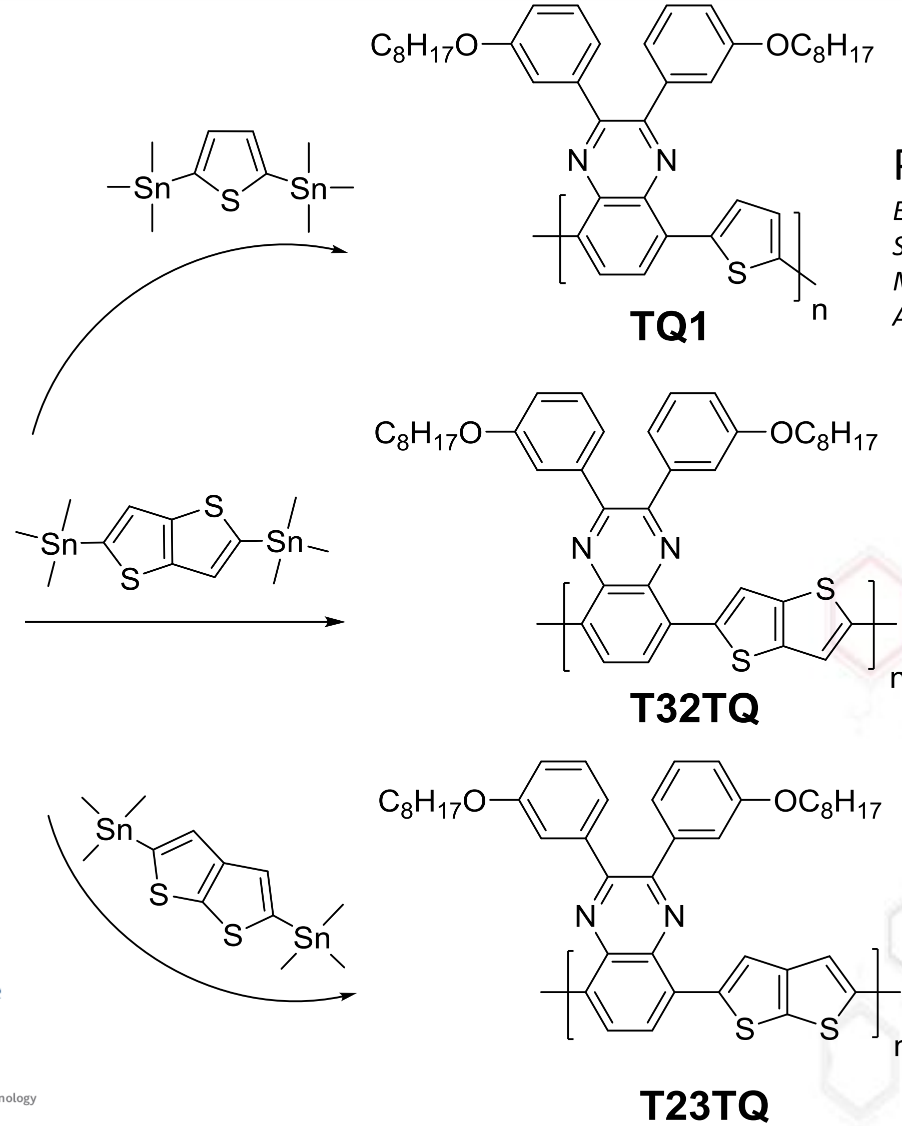
PDTG-PT:$PC_{70}BM$ (1:2) 2.5 vol% DIO	J_{SC} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
Normal	17.6	0.59	0.50	5.2
Inverted	19.6	0.59	0.57	**6.6**

Yau, C. P.; Fei, Z; Ashraf, R. S.; Shahid, M.; Watkins, S. E.; Pattanasattayavong, P.; Anthopoulos, T. D.; Gregoriou, V. G.; Chochos*, C. L.; Heeney*, M. *Adv. Funct. Mater.* **2013**, *3*, 10221-10229

New High Performance High Band Gap Copolymers as Electron Donors

Influence of thienothiophene isomeric structure on quinoxaline copolymers





PCE of 6%

E. Wang, L. Hou, Z. Wang, S. Hellström, F. Zhang, O. Inganäs, M. R. Andersson
Adv. Mater. **2010**, *22*, 5240

ΕΘΝΙΚΟ ΙΔΡΥΜΑ ΕΡΕΥΝΩΝ
National Hellenic Research Foundation

Advent

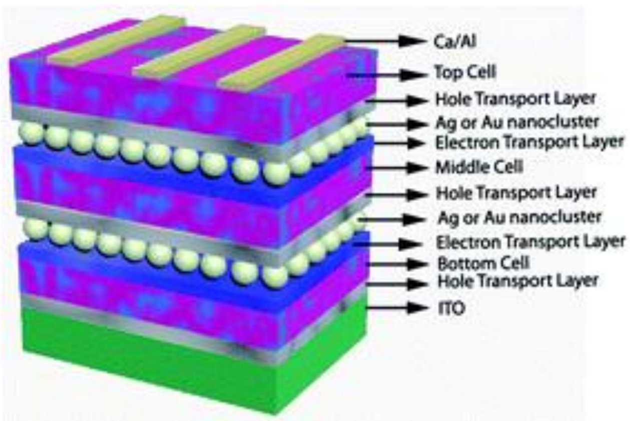
Imperial College London

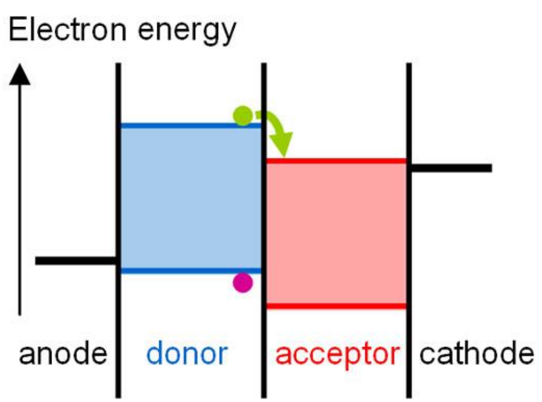
iit Center for Nano Science and Technology

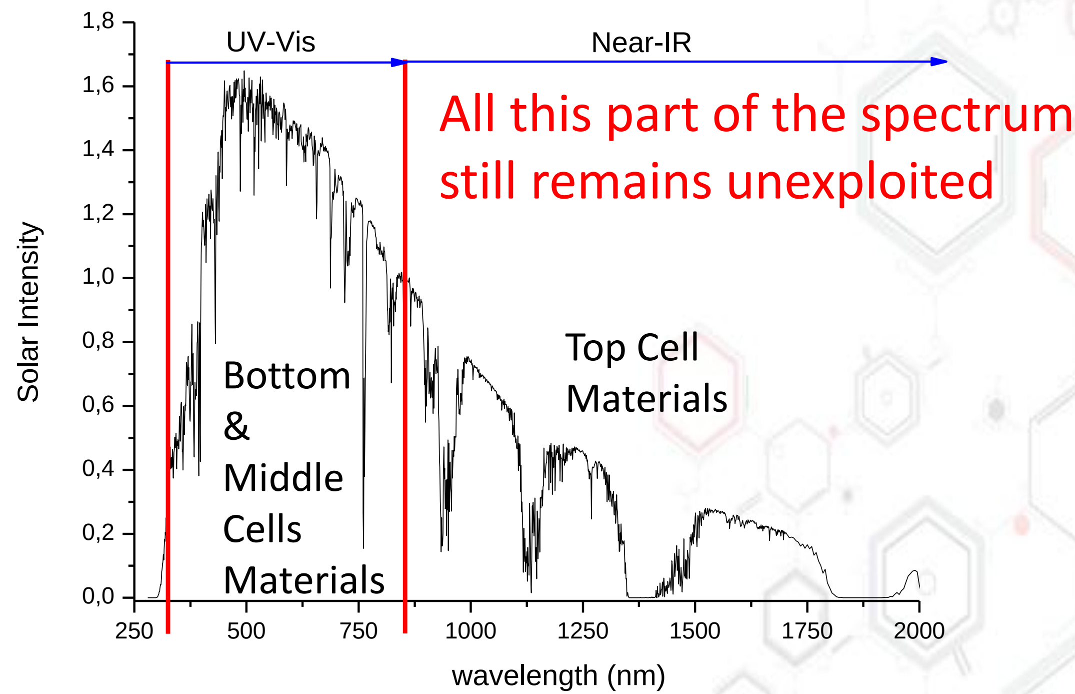
Singh, R.; Pagona, G.; Gregoriou, V. G.; Tagmatarchis, N.; Toliopoulos, D.; Yang, H.; Fei, Z.; Katsouras, A.; Avgeropoulos, A.; Anthopoulos, T. D.; Heeney, M.; Keivanidis, P.; Chochos, C. L.* **2014,** submitted

Emerging need for Near Infrared (NIR) Organic Materials

Triple Junction Solar Cells are consider the final optimization step towards higher efficiencies





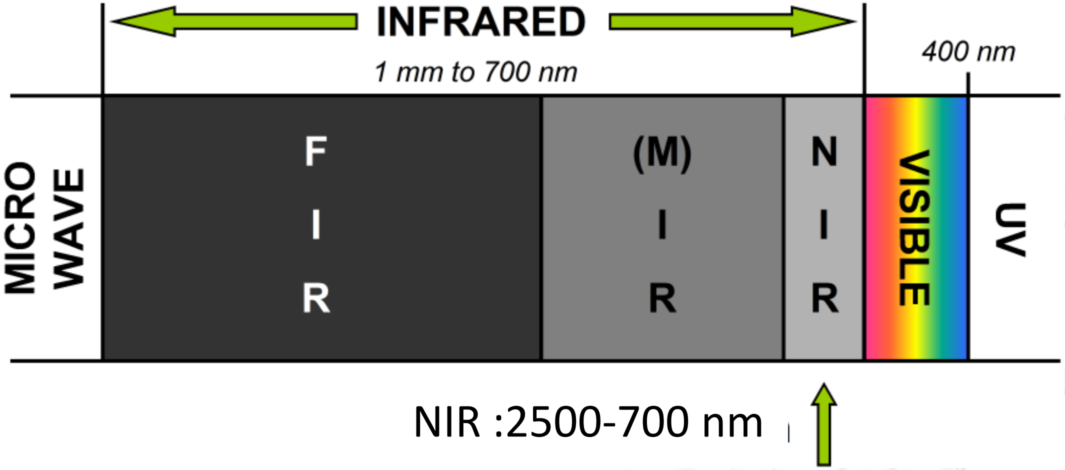


- New conjugated polymers absorbing in the NIR region
- New Electron accepting materials with higher efficiencies than fullerenes

Near Infrared (NIR) Materials

Near-infrared materials are defined as the substances that interact with NIR light, such as absorption and reflection, and emit NIR light under external stimulation such as photoexcitation, electric field, and chemical reaction.

The near-infrared (NIR) fall in the region of spectrum between 700 and 2500 nm.

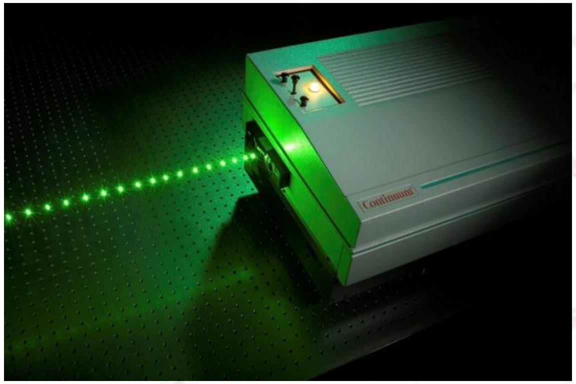


NIR materials find application in:

- Energy
- Communication
- Bio-imaging
- Sensing
- Advanced optoelectronics

Near Infrared (NIR) Inorganic Materials

The inorganic materials are the most common materials for NIR applications, especially in lasers and photodiodes.

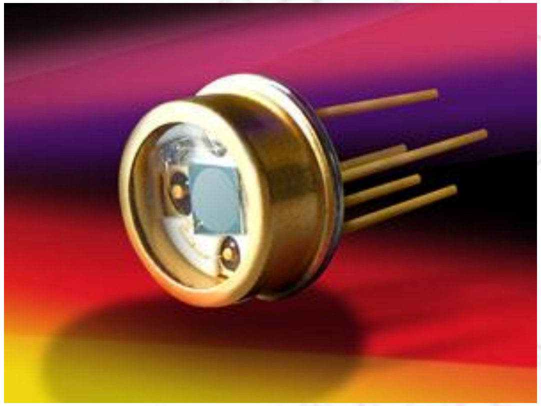


The commonly used materials as active components are:

- YLF ($YLiF_4$),
- YAG ($Y_3Al_5O_{12}$),
- LISAF ($LiSrAlF_6$),
- LICAF ($LiCaAlF_6$),

glasses from silicate (SiO_2) and phosphate (P_2O_5) doped with transition metals and rare earth elements like:

- Neodymium [Nd:YAG] (emitting@ 1064 nm)
- Erbium [Er: YAG] (emitting@ 1640 or 2940 nm)
- Yitterbium [Yb:Er:YAG] (emitting@ 1540 nm)



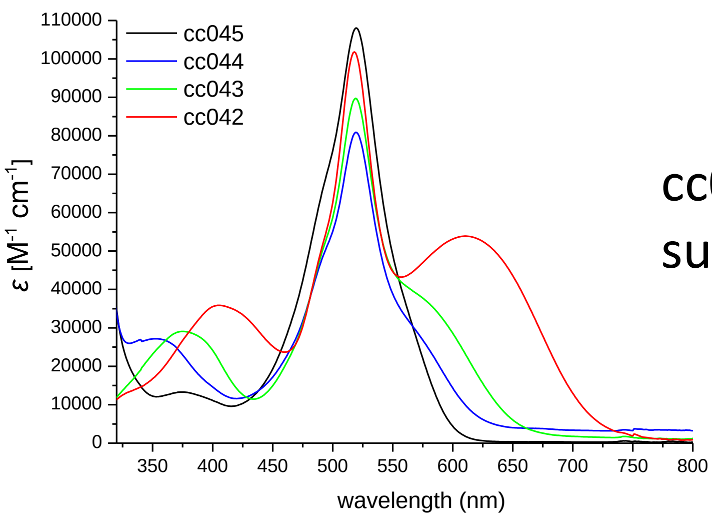
As regard absorber NIR, the most used in photodiodes and similar device are compounds of III-V elements (Al, Ga, In ... – N, P, As, Sb ...), like InGaAs.

Byer R.L ., *Science* **1988**, *233*, 742-747

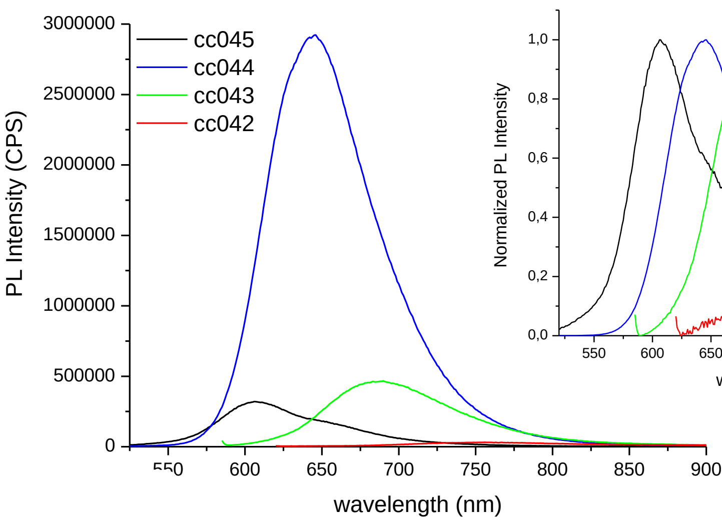
Li N. et al., *Appl. Phys. Lett.* **2003**, *82*, 2175 -2177

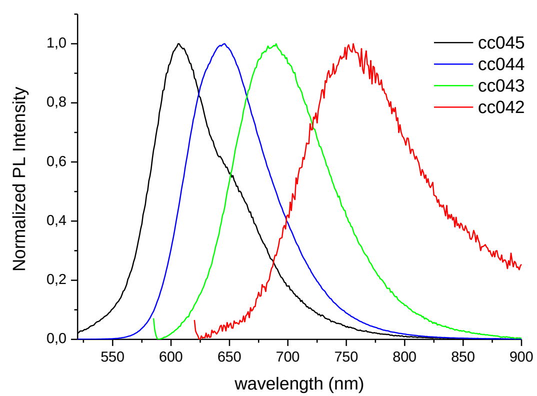
NIR Organic Small Molecules

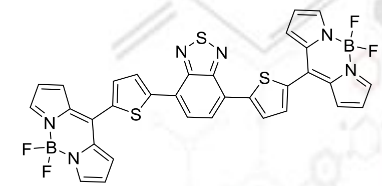
Absorption and Emission Spectra

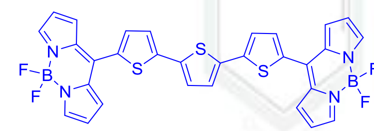


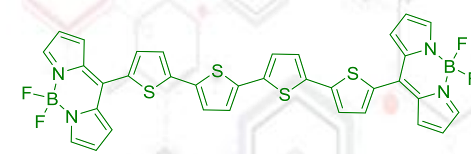
cc042 emits at the NIR region suitable for NIR OLEDs

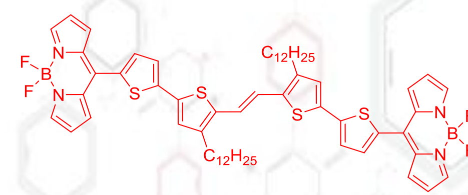






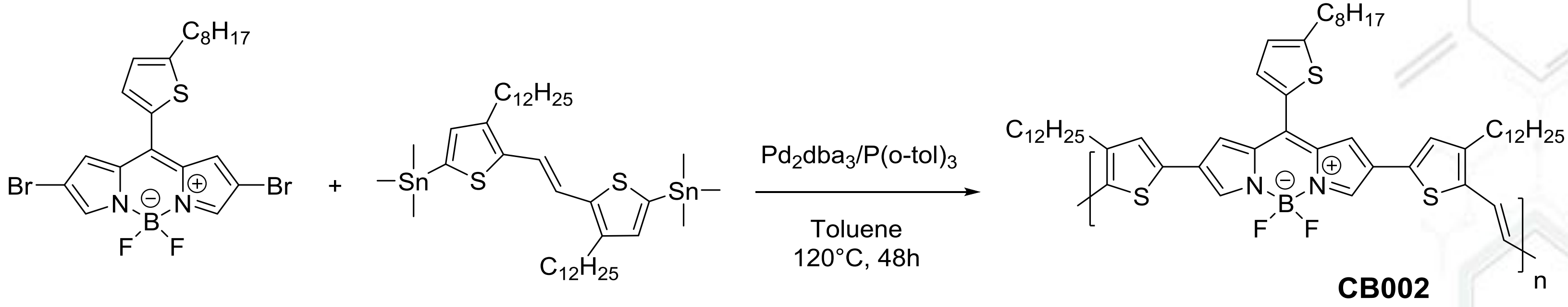




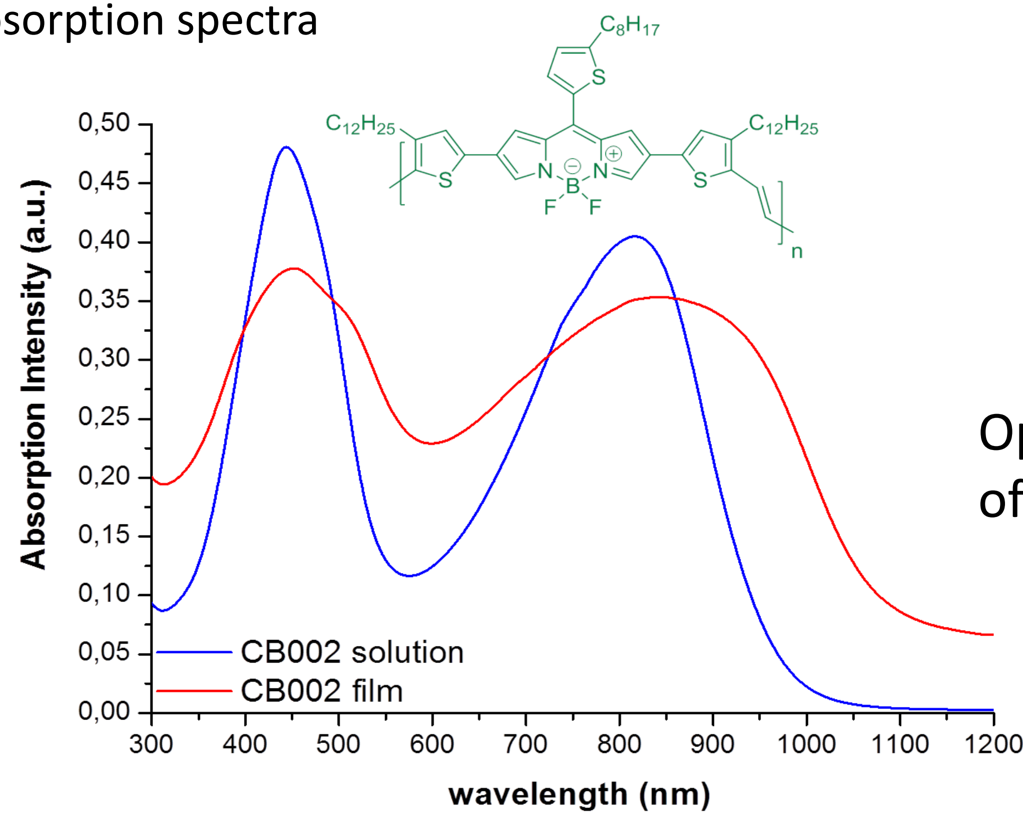


New conjugated polymer for NIR absorption

Synthesis of NIR absorbing copolymer



Absorption spectra



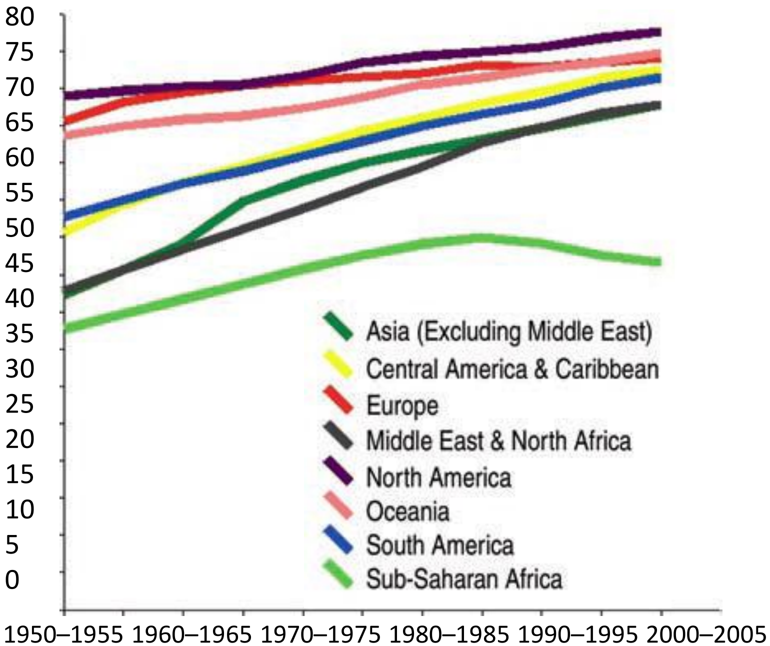
Advent

Optical Bandgap of 1.15 eV

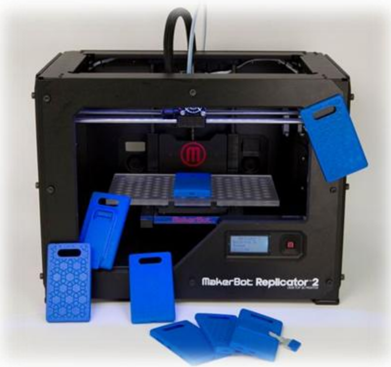
Future Biomaterials trends

- Life expectancy over the years has increased significantly. During the last five decades, life expectancy has risen by 15% (from 69 to 80 years). More importantly, not only are we living longer but our quality of life has dramatically improved thanks to the many advances in medicine, biology, and materials.
- Recent advances and developments include: cornea tissue regeneration, artificial skin, artificial heart valves (e.g., mitral valve), coronary stents, drug eluting stents, hip joints, artificial knees, spinal cord fusion devices etc
- The difficult issues we will face in the future are not technological ones, but rather ethical and societal:
  - -health care
  - inequalities across the globe?
  - a person's propensity for disease a-priori?

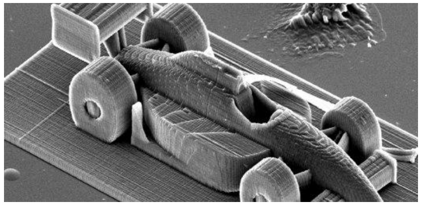
Life expectancy



3D Printing Technology



From small

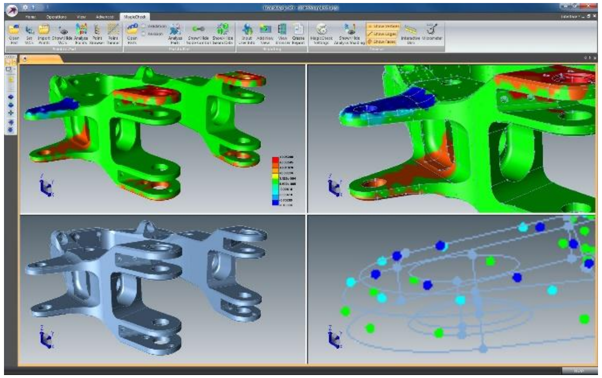


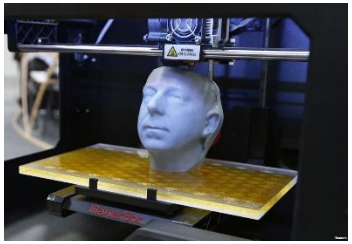
To Large

From Fashion

To Medicine

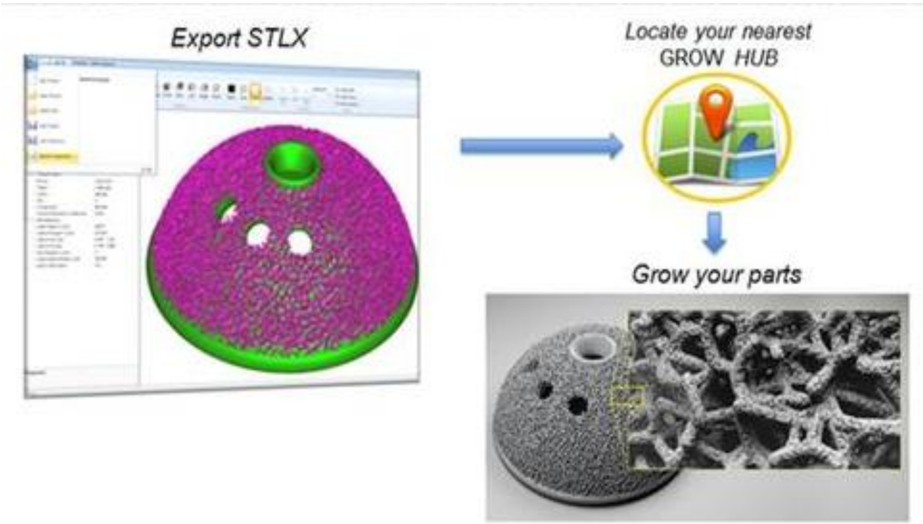
How 3D Printing Works ?

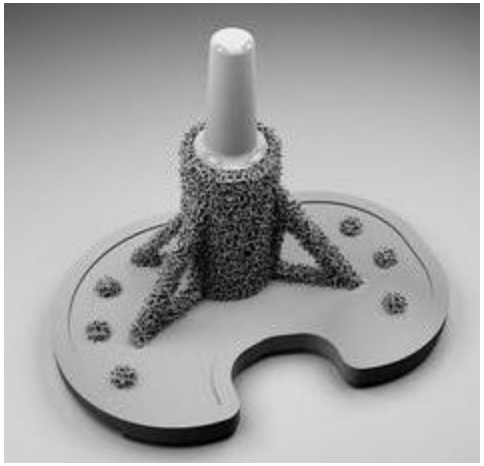




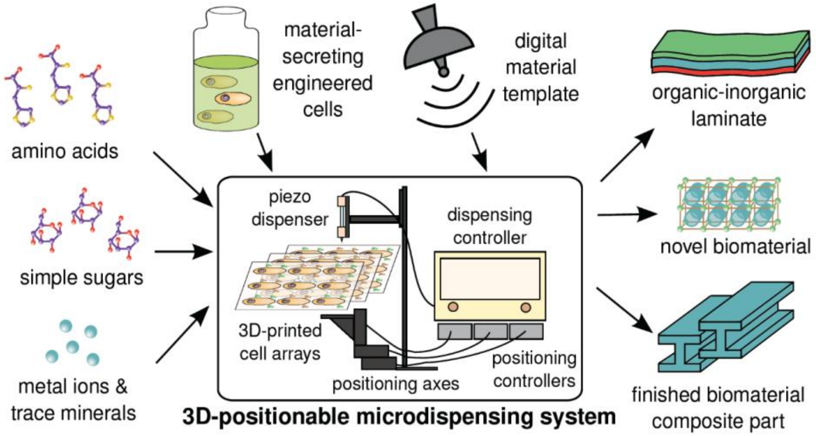
Bioimplants using 3D printing

Personalized medicine





Plastic surgery

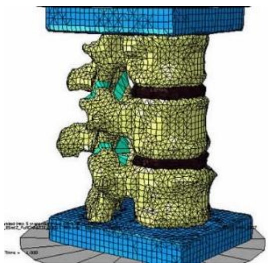


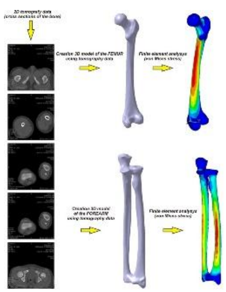
Dental implants

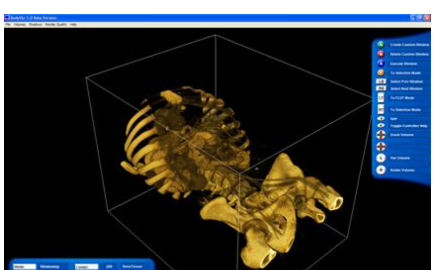
Orthopedic implants

3D Printing Technology

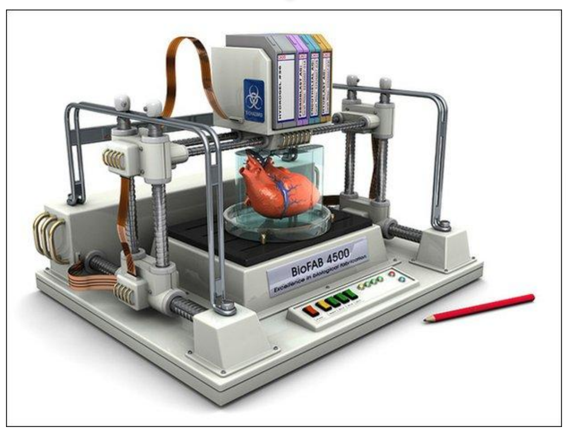
From Medical
C-Scan
and MRI 3D files





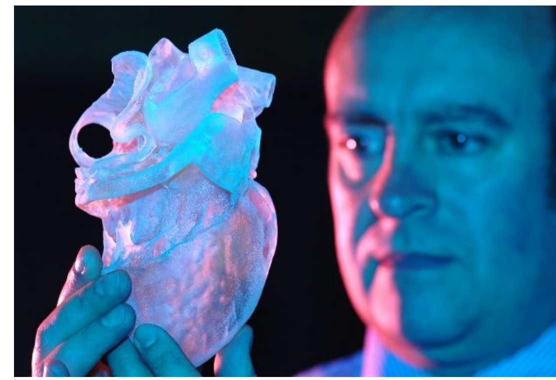


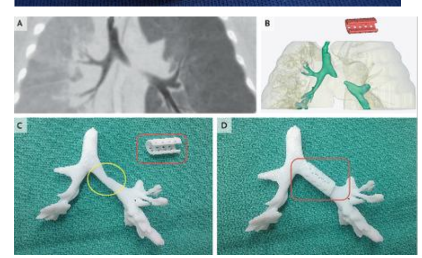
Addition to matrix polymer of
Angiomatic agents and special proteins
e.g. bone growth (BMP) proteins
And/or cell cultures



Bio-3d Printer

To ready-for use
Personalized Implants





Final thoughts

- We live in a society that is market driven and therefore coupled to the realities of capital markets.

- Material developments take far too long and in the eyes of capital markets and the return on the investment is difficult to justify in the early stages.

- Future material science developments will need to happen in an accelerated fashion to attract investments of capital and resources. For the adoption of a new material class, 20 years are needed.

- A culture change should occur that fosters innovation, rapid development, and accelerated technology transition with the help on agency funding.

As Antoine de Saint-Exupery said:
“When it comes to the future, our task is not to foresee it, but rather to enable it to happen.”

Acknowledgment – Collaborators

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Christos L. Chochos
George Paloumbis

Dionysis Mouzakis

Organic Semiconductors for NIR Optoelectronics

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Arkema