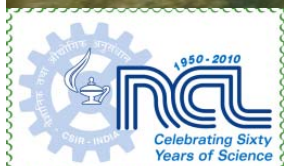


BEYOND SILICON: CHALLENGES IN EMERGING PHOTOVOLTAIC TECHNOLOGIES

Short Course on Flexible Electronics

IIT-Kanpur, July 4, 2016



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National Chemical Laboratory,
Pune, 411 008, INDIA**

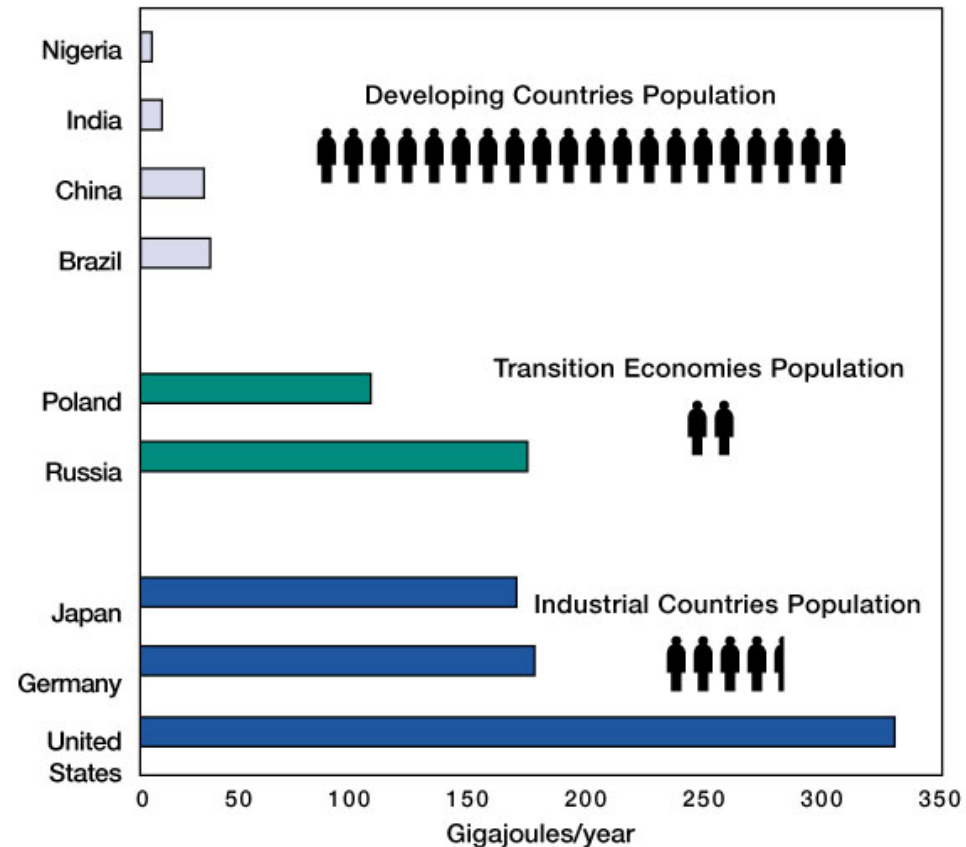
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Email : s.sivaram@ncl.res.in

www.swaminathansivaram.in

THE ENERGY ASYMETRY



One = 200 million people.

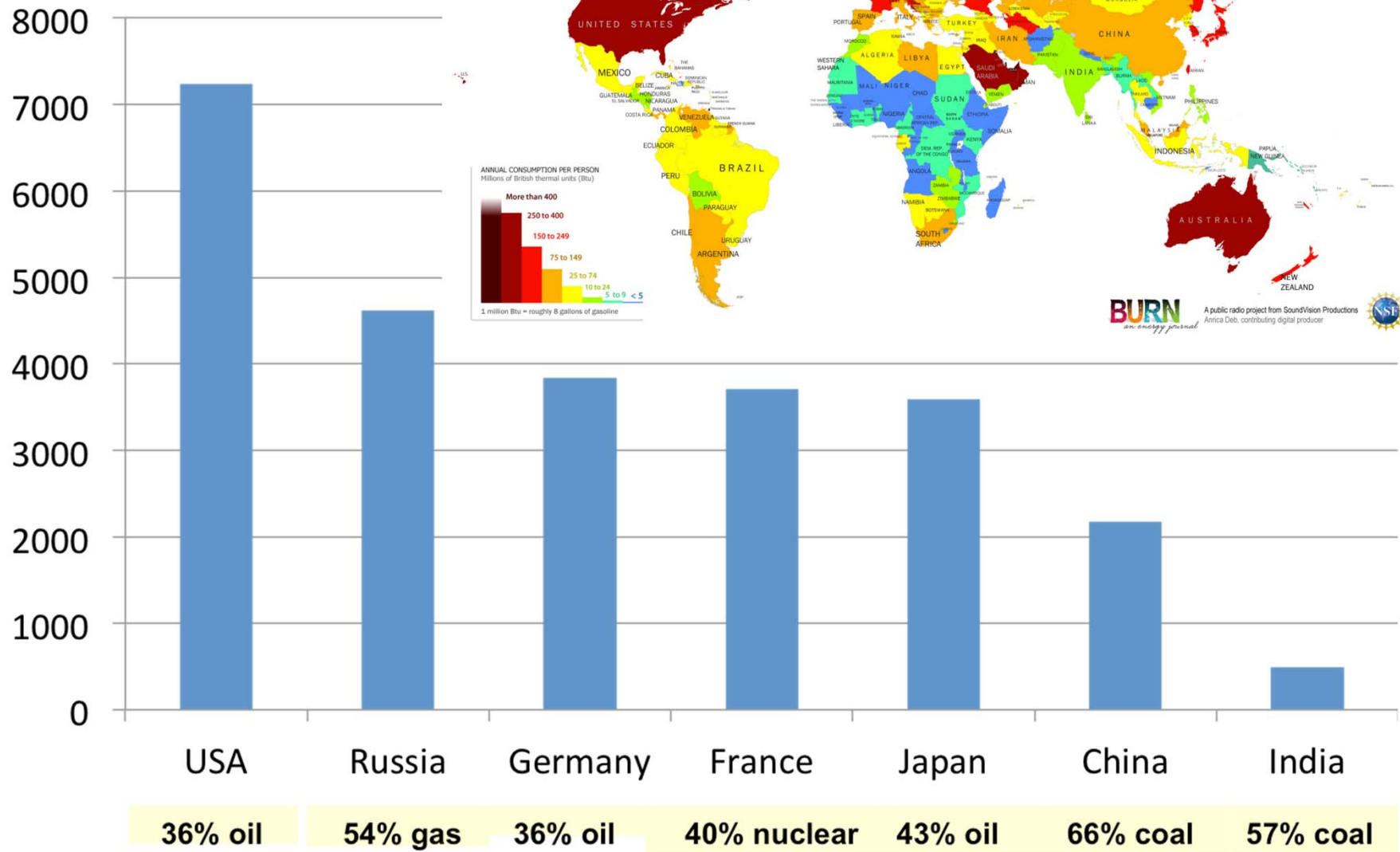
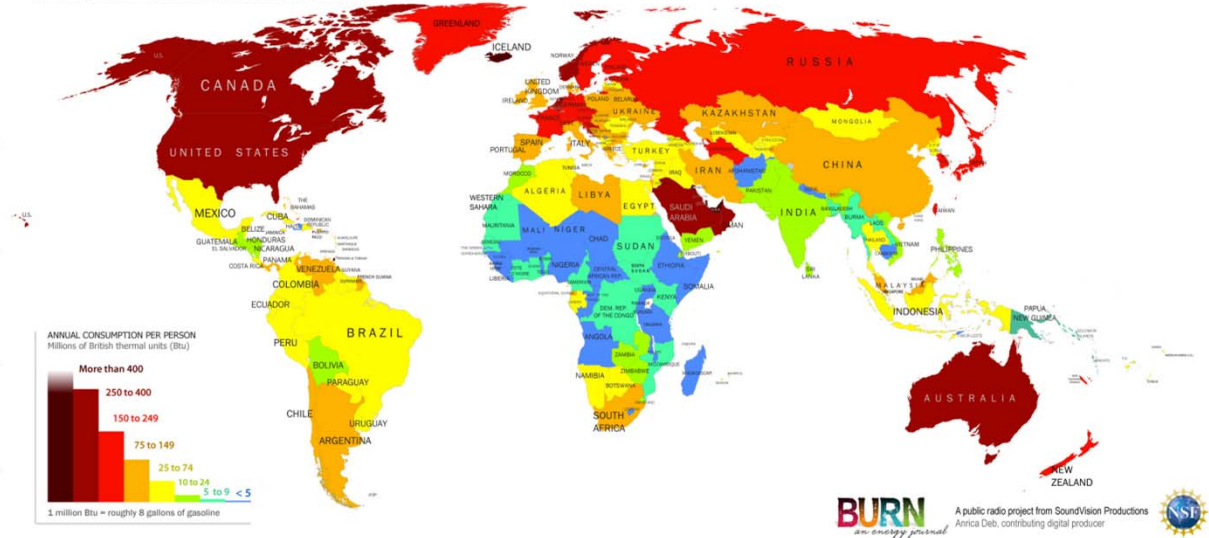
Data: World Bank

Half the world's population subsists on agrarian or lower levels of energy access. Their population density generally exceeds the carrying capacity of their environment

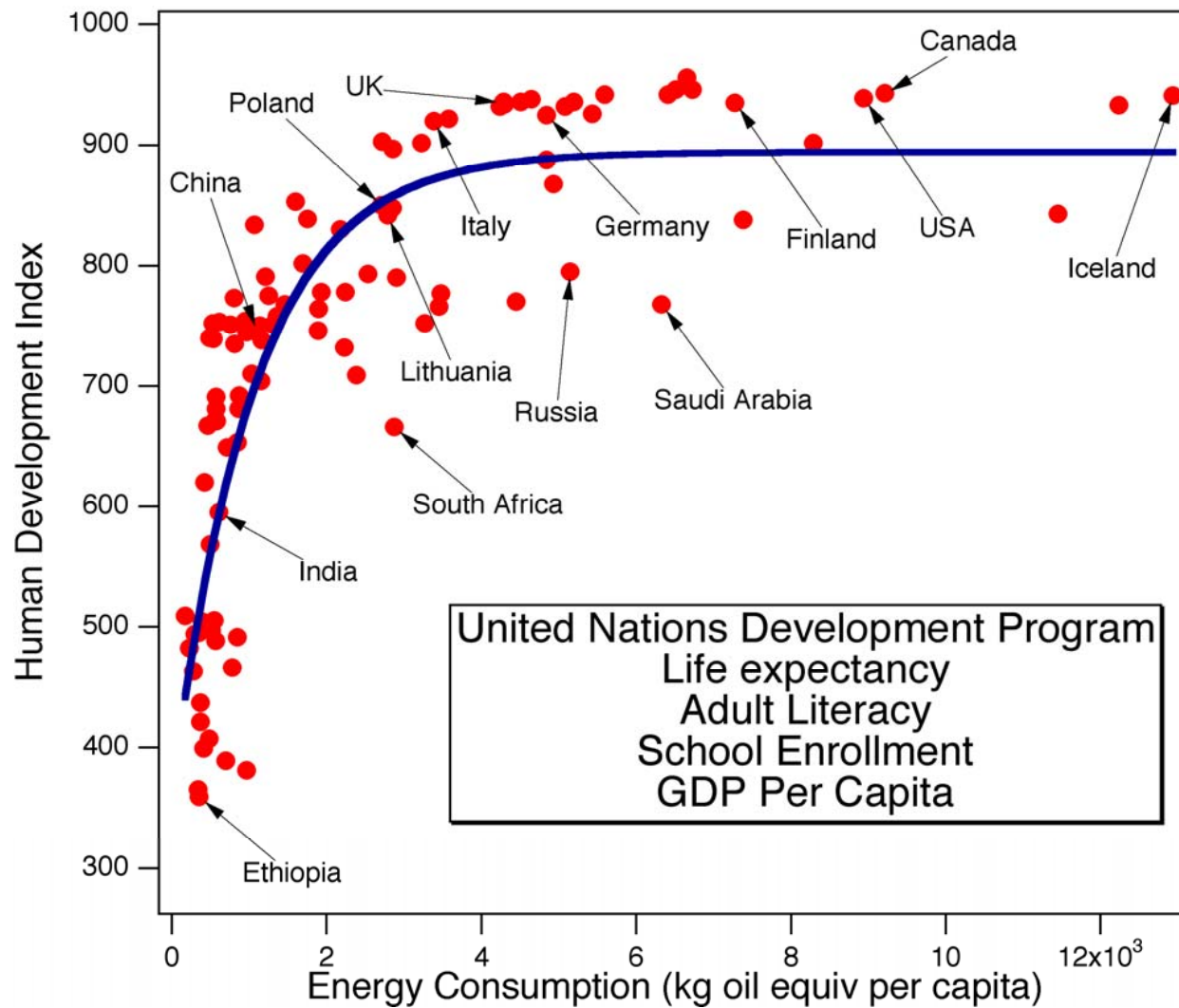
PRIMARY ENERGY CONSUMPTION, KG OF OIL EQUIVALENT, PER CAPITA, 2014

Energy Consumption Per Person, by country, 2010.

SOURCE: U.S. Energy Information Administration, International Energy Agency, UN World Population, U.S. Dept. of Commerce and Social Science



A NATION'S HUMAN DEVELOPMENT INDEX IS RELATED TO PER CAPITA ENERGY CONSUMPTION





Conversion

Photovoltaic, solar cell
Solar thermal
Solar fuel
Thermoelectric

Energy

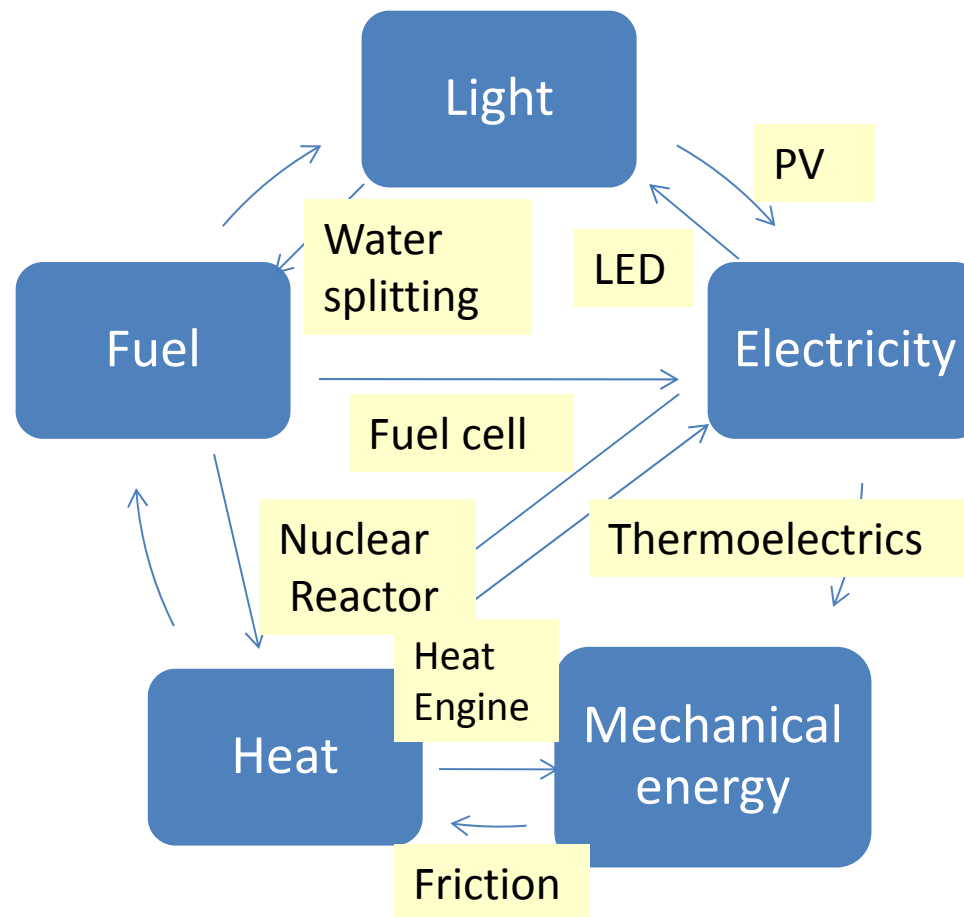
Conservation

LEDs
OLEDs
Field emission
Energy saving architectures

Storage

Supercapacitors
Batteries
Thermal storage

ENERGY INTERCONVERSIONS



If you want to find out the secrets of the universe, think in terms of energy, frequency and vibration

Nikolas Tesla

SOLAR ENERGY SCENE IN INDIA

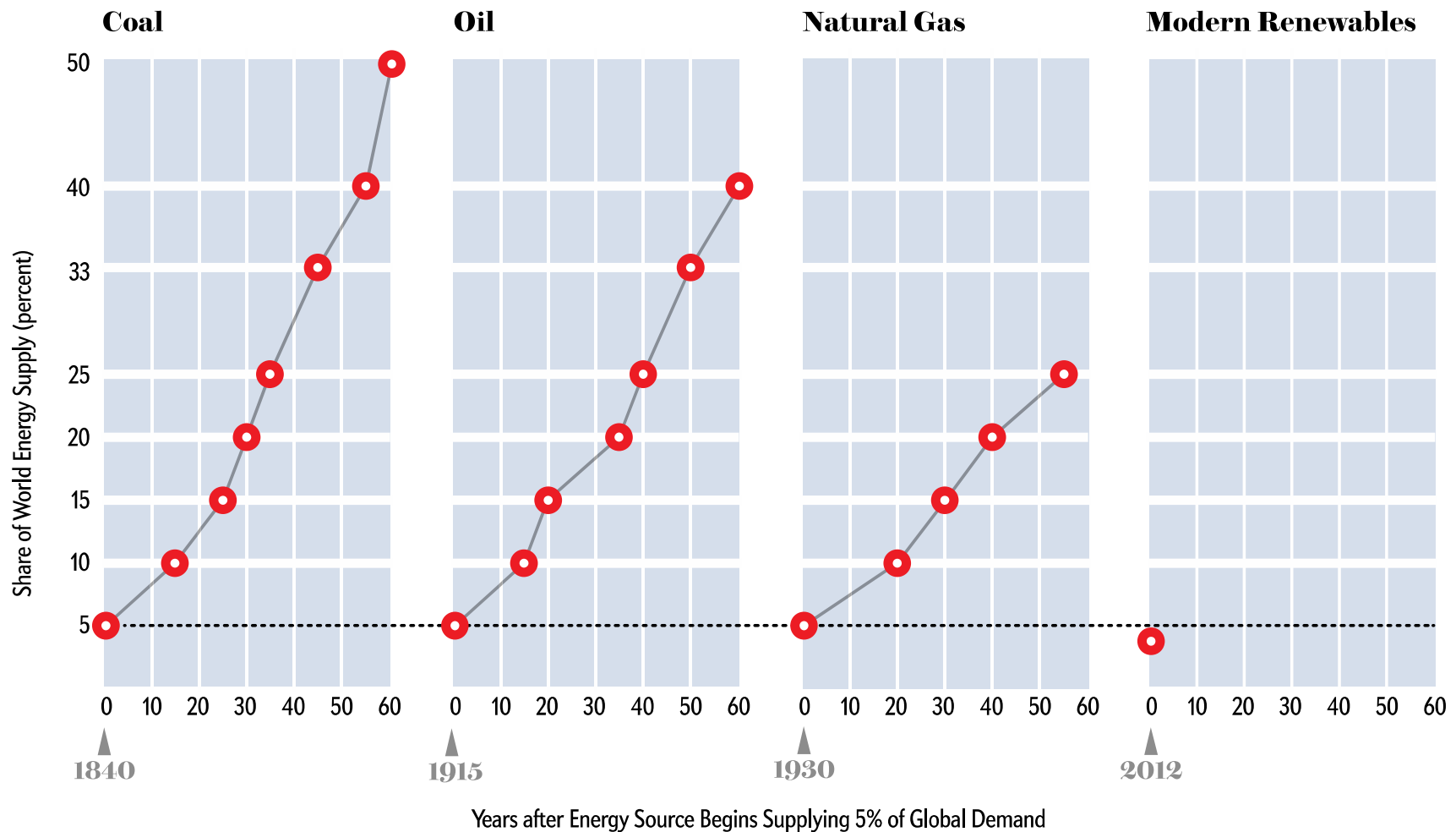
- 100 GW by 2022; 60% utility scale and balance roof top; 4 GW actual capacity in 2015
- If achieved 25 % of total electricity capacity by 2020
- Capital investment needed \$ 160 billion
- One of the top three markets in the world
- 500 MW project by Sun Edison at Ghani Solar Park, Kurnool, AP at Rs 4.63 per kWh (Reverse Auction, 3 November 2015, Economic Times)

LAG BETWEEN DISCOVERY AND ITS MATERIAL IMPACT ON ENERGY INFRASTRUCTURE

- Thomas Edison illuminated the office of J. P. Morgan in Manhattan in 1882 with an incandescent bulb. However, electricity displaced steam power only in the mid thirties. The reason for this slow diffusion was the design of the factories. They had been built vertically to accommodate the pulley system used with steam power and electric motor could not be accommodated within this structure. The factories had to be ultimately destroyed before they could be electrified
- Discovery of photoelectric effect was in 1880; On 25 April 1954, Chapin, Fuller and Pearson in Bell Labs demonstrated that electricity can be produced from sunlight using a diffused silicon crystal. It was a serendipitous discovery. Silicon solar cells were a technical success, but a financial failure ! It would have cost an average homeowner in the US \$ 1.5 million to power his house in 1956. Until 2000, the installed solar energy capacity in the world was only 1 GW !

The lag is a result of inherent physical and psychological limits to quick acceptance of new ideas as well as the need for a multidimensional and coordinated approach to bring technology to markets

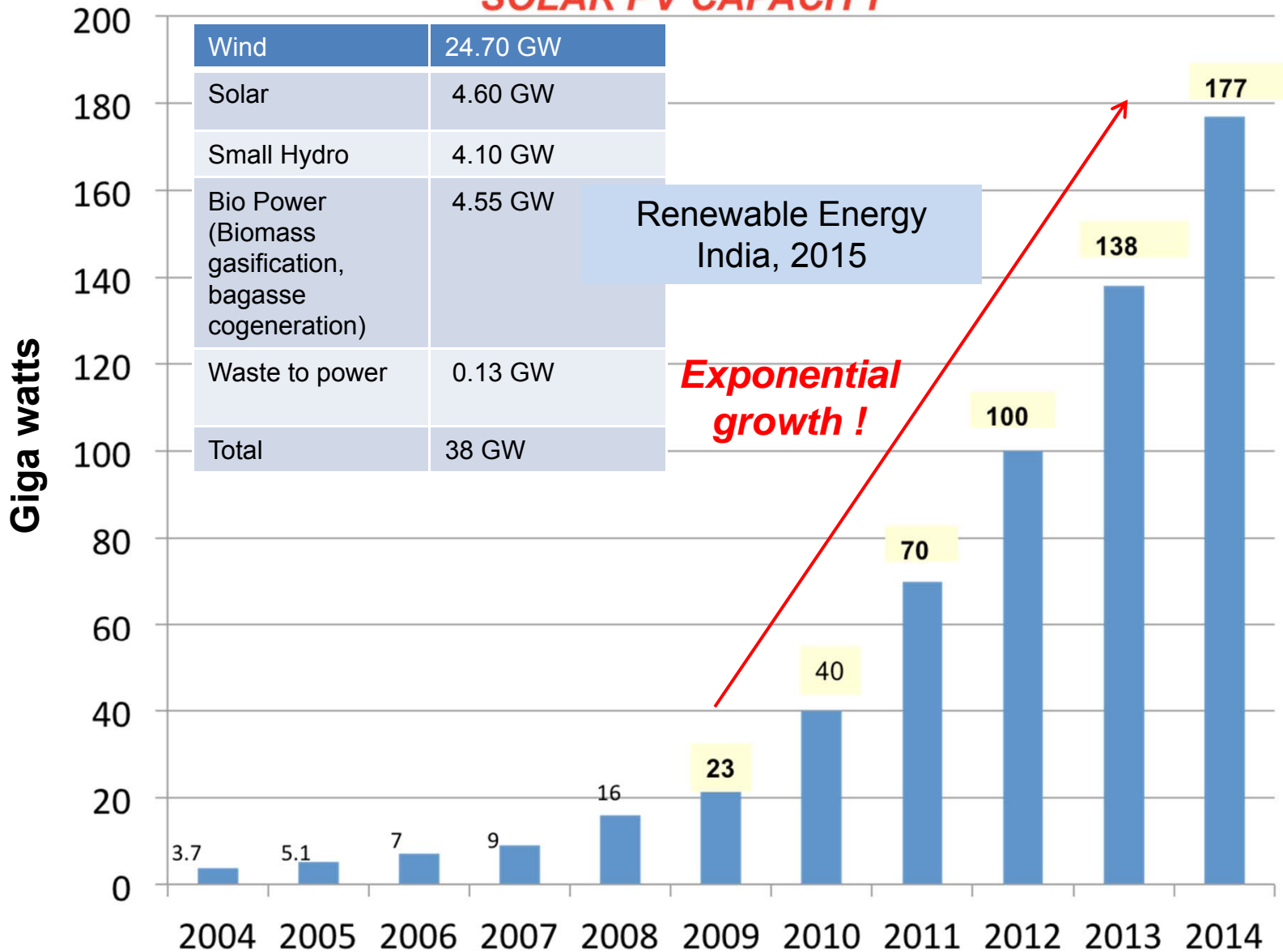
TRANSITIONS IN ENERGY : ALWAYS SLOW !



Disruptive technology or revolutionary policy needed; otherwise the transition of renewables is likely to be equally slow

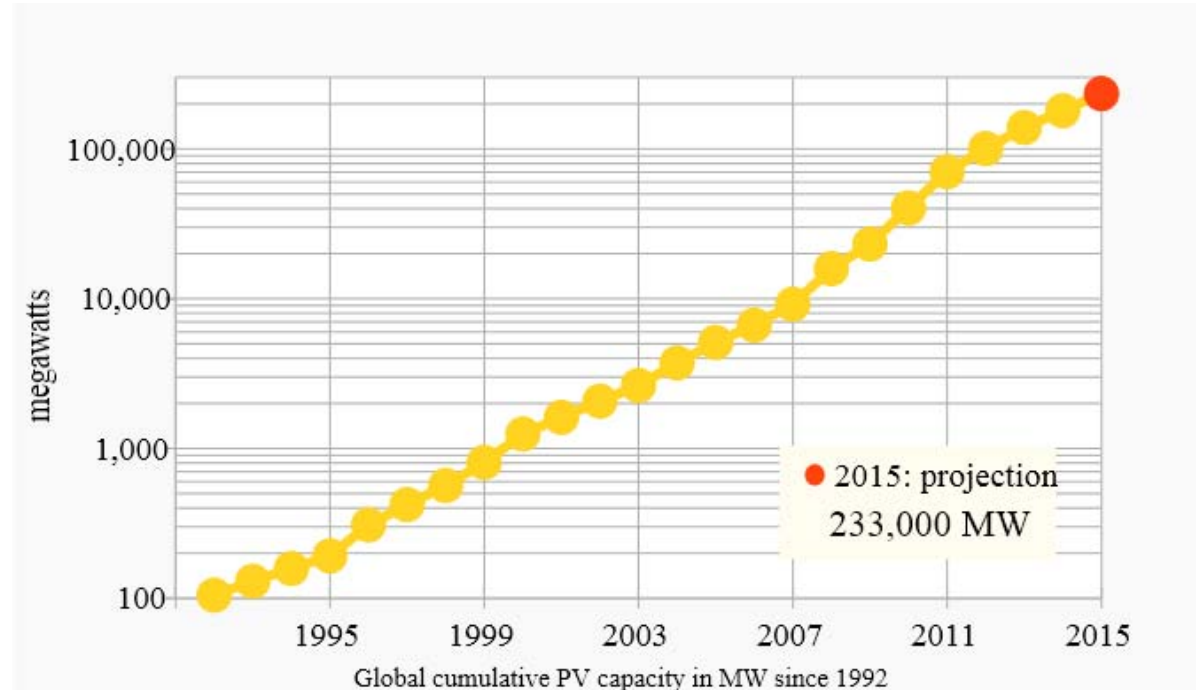
V. Smil, Scientific American, January 2014

RENEWABLE ENERGY :GLOBAL SOLAR PV CAPACITY



WHY IS THE PRICE OF SOLAR PV POWER SO LOW ?

- Global PV power Capacity : 177 GW
- PV contributes today to 1 % of the total power capacity
- Solar silicon : 60 % capacity in China; Four of the five largest PV module suppliers are Chinese companies
- Current price : 60 cents / Wp

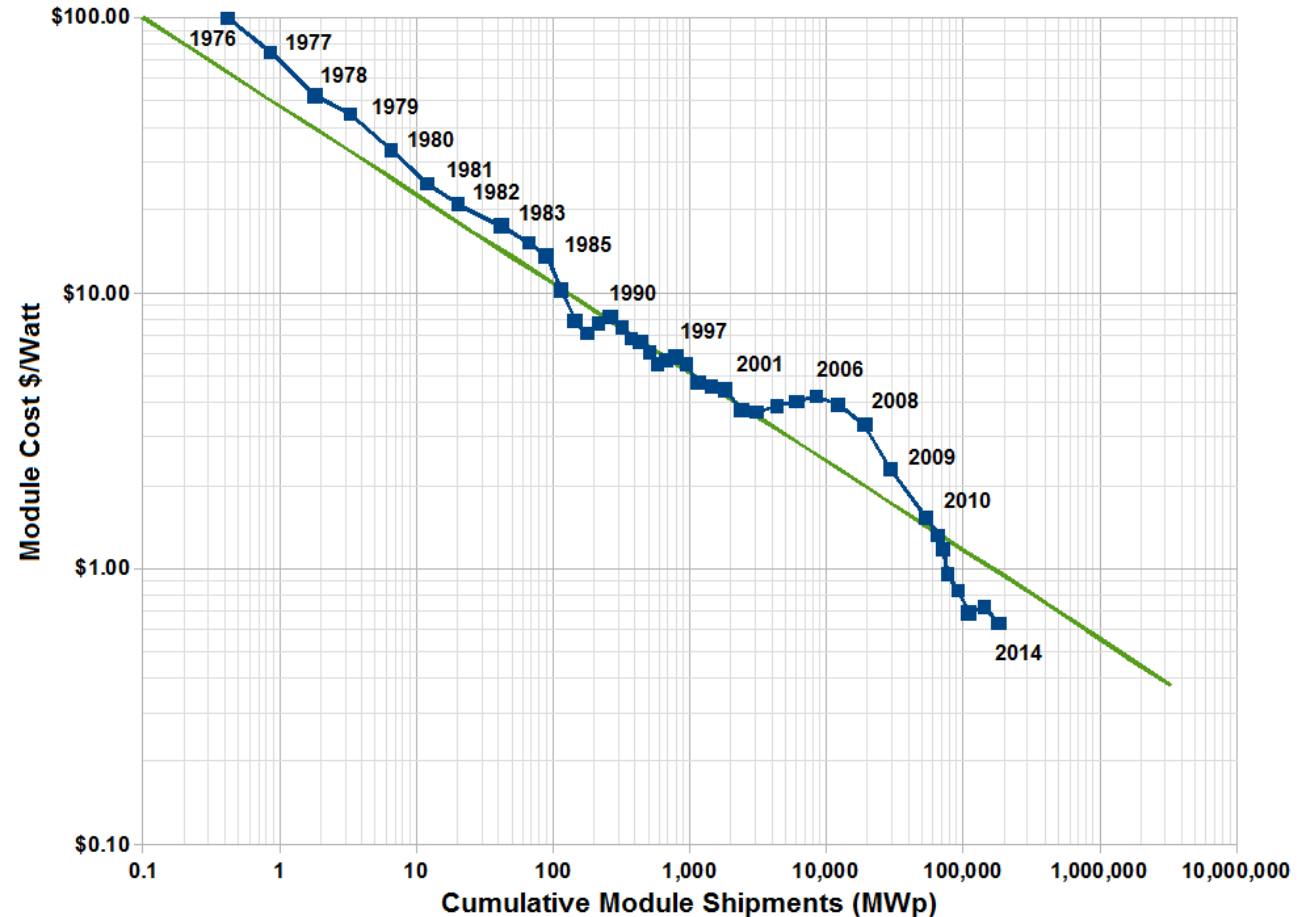


Price reductions due to unsustainable pricing or distress sale ?

HAS THERE BEEN TECHNOLOGY DISRUPTIONS IN SOLAR PV ?

Swanson's Law

- Is there an equivalent of a Moore's Law in Solar PV ?
- Has there been significant new innovations by industry ?
- Solar cell prices fall 20% for every doubling of industry capacity



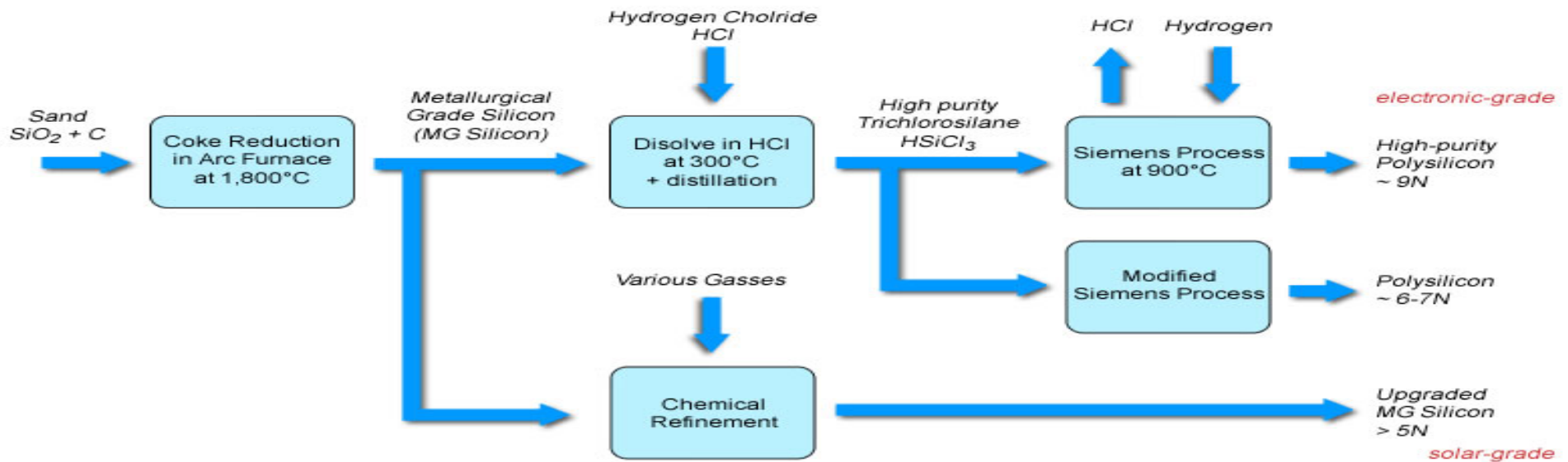
The Economist, 18 November 2012

Cost reductions not driven by advances in technology

IS SILICON PV GREEN ENERGY ?

Consider the following facts

- Solar PV manufacturing processes involve converting quartz to metallurgical grade silicon and then to polysilicon ingots which are sliced to form wafers



- Every ton of metallurgical grade silicon production results in 4 tons of silicon tetrachloride; Material utilization efficiency is a mere 30%
- 1 ton of crude silicon production results in 10 t of carbon dioxide; Purification process results in additional 45 t of carbon dioxide
- 99.999% pure silicon requires energy intensive crystal growth and vapor deposition methods

IS SILICON PV GREEN ENERGY ?

- Silicon solar cells use 1000 times more light absorbing materials than organic PV cells, because silicon does not absorb light strongly
- Silicon is intrinsically brittle and must be supported on glass making panels heavy
- Solar cell fabricated with Siemen's process needs 6 years of operation to recover the energy used to make it
- Silicon production uses sulfur hexafluoride, HF, 1,1,1 trichloroethane and large quantities of strong acids
- Silver that is used for making panels at 5 % of current power demand will consume 50 % of current silver produced
- Little or no recycling of silicon in process waste or end of life panels

Ironic that we consider silicon PV as a clean and sustainable form of energy !

India has no domestic silicon production capacity

D. Mulvaney, IEEE Spectrum, 26 August 2014

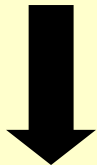
THE CHALLENGE OF SOLAR CELL FABRICATION

- 5 TW of solar power generation



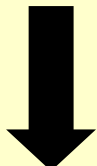
***15% efficiency
250 w/sq m***

- 250,000 sq km



30 year replacement

- 25 sq km of cells per day



- 1 billion cells (15x15 cm) each day

The current method of fabrication of silicon wafers from ingots is incapable of achieving this scale of operation ; clearly, there is a technology gap

IS THERE ANOTHER WAY TO HARVEST ENERGY BEYOND SILICON ?

The promise of organic photovoltaics

Bottoms approach from molecules to devices

MOLECULES TO MATERIALS & DEVICES

CHEMISTRY

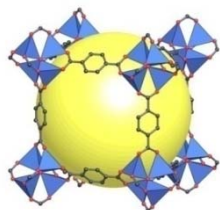
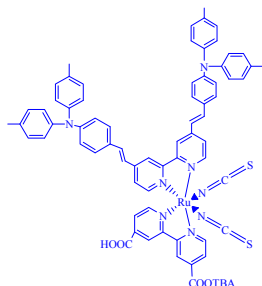
Molecular Design and Engineering

Architecture through Assembly

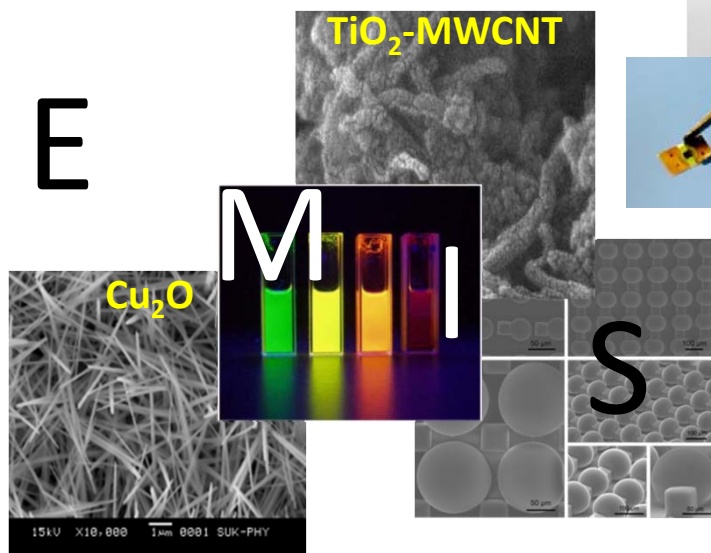
Economy through scalability

C H E M I S T R Y

Magic of molecules



Functionality through Design



Novelty of Response

Energy : Solar Cells, Batteries, Fuel Cells, LEDs

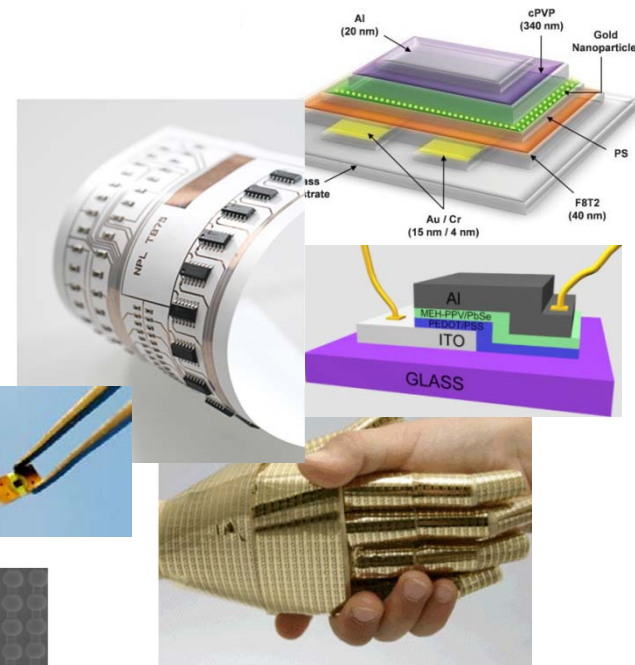
Environment: Sensors, Adsorbants

Health: Biosensors, Controlled Drug Delivery

Water: Filters, Purifiers

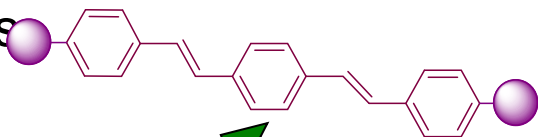
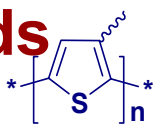
Food: Smart Packaging

Electronics: Computers, Robotics (Flexible Electronics)



Organic compounds

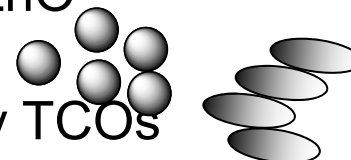
- Conducting polymers
- Small light harvesting dye molecules
- Oligomers
- Dendrimers
- Polymers



Materials

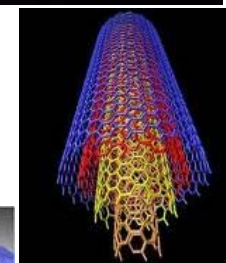
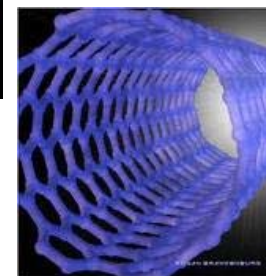
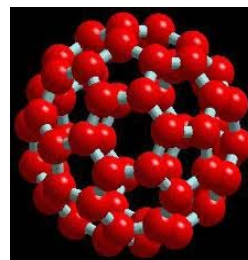
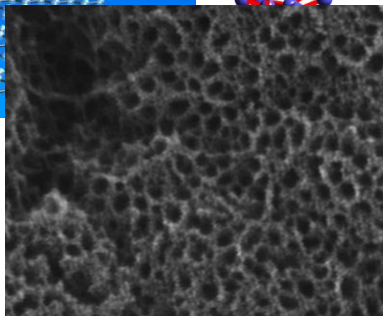
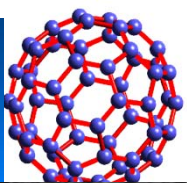
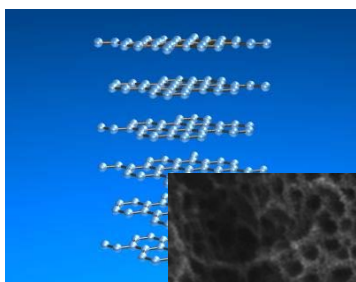
Inorganic compounds

- TiO_2 , ZnO
- SiO_2
- Ternary TCOs
- Zn_2SnO_4 etc.
- Other metal oxides
- Metal sulfides
- Quantum dots



Carbon Family

- SWCNT
- MWCNT
- Graphene
- Fullerene
- Amorphous carbon

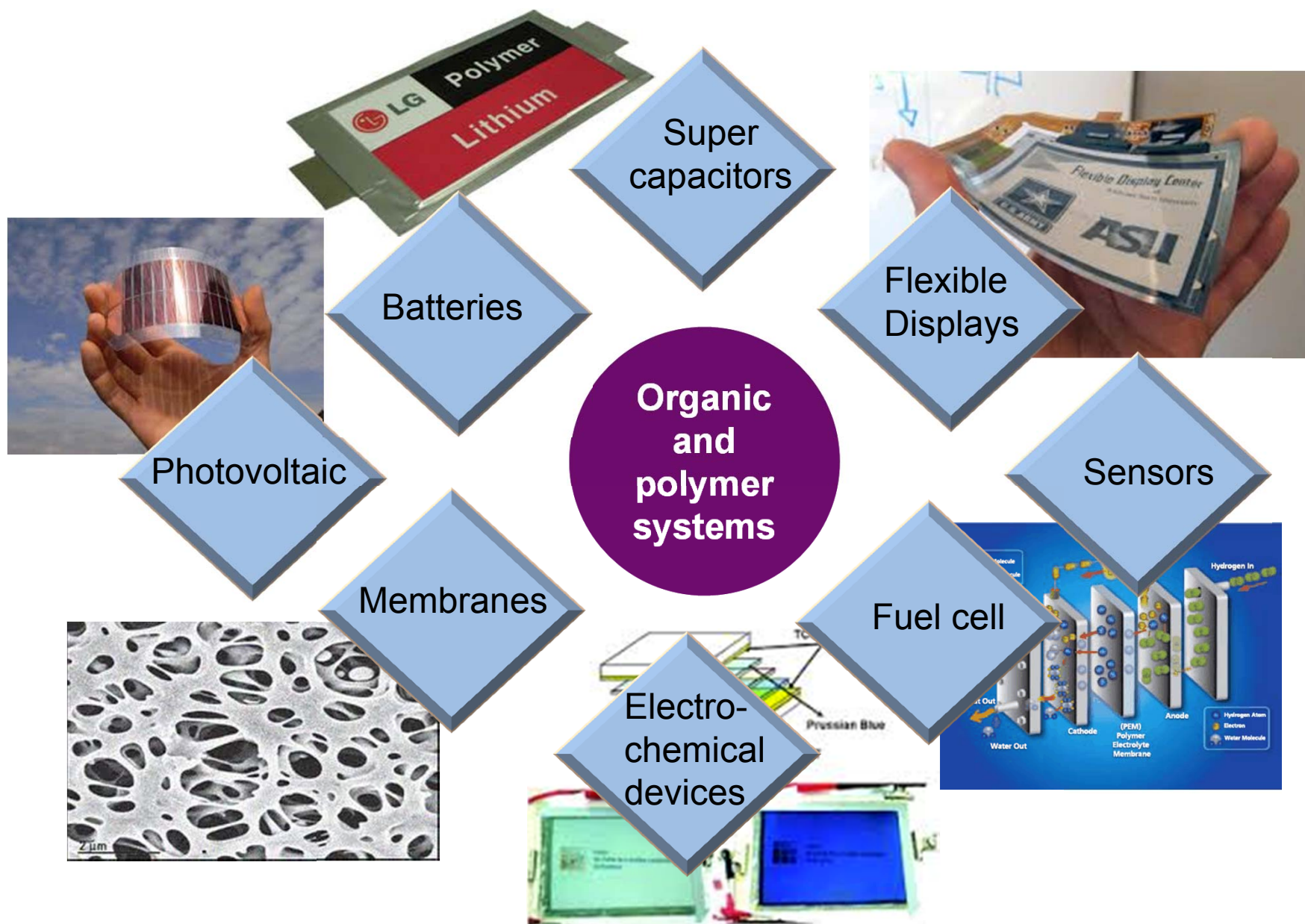


BEYOND SILICON: EMERGING PHOTOVOLTAIC TECHNOLOGIES

- Organic photovoltaics
- Dye sensitized solar cells
- Perovskite Photovoltaics
- Inorganic quantum dots

Thinner, amenable to a wide range of lighting conditions, can be fabricated on flexible supports using solution phase techniques or roll to roll processing, common to plastic processing and the promise of being less expensive

POLYMERS IN ENERGY APPLICATIONS



EMERGING PHOTOVOLTAIC TECHNOLOGIES

- Are they academic curiosities?
- When can we expect large scale manufacturing?
- What are the technology challenges
- What applications will drive their demand?
- How relevant are they for the Indian environment?
- Do they have a place for legacy energy infrastructure such as grid or distributed power?

POWER CONVERSION EFFICIENCY

(Source : NREL)

Material	PCE, %
Ga-As	46
Single crystal silicon	25
Perovskites	22
Multicrystalline silicon	21
DSSC, OPV and QD's	12

Is lower price enough to offset lower performance ?

Solar Cell Efficiencies



Silicon Solar Cell Efficiencies:

Theoretical Maximum: 26%

Best in Lab: 25% (Green, UNSW)

Modules: 15-22%



Thin Film Solar Cell Efficiencies:

Theoretical Maximum: >22%

Best in Lab: 20% (Noufi, NREL)

Modules: 9-12%



Dye-Sensitized Solar Cell Efficiencies:

Theoretical Maximum: 14-20%

Best in Lab: 12% (Grätzel, EPFL)

Modules: 6-9%

PV DEVICES : PRINCIPLES

Three events

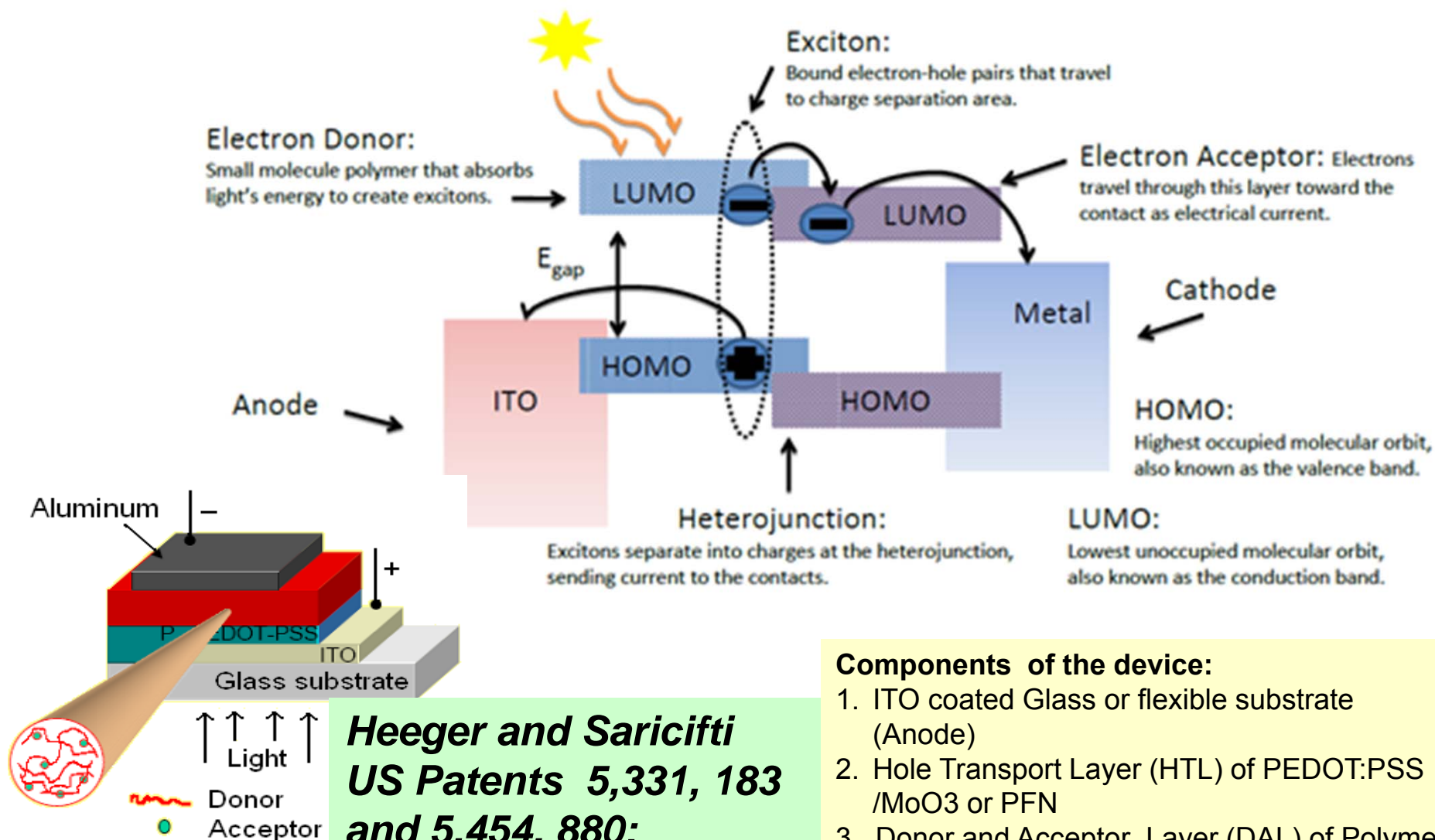
Light absorption

Electronic excitation

Charge separation

These events occur in a single layer in silicon , whereas in organic PV they occur in separate molecular layers

Operation of Organic Solar Cell

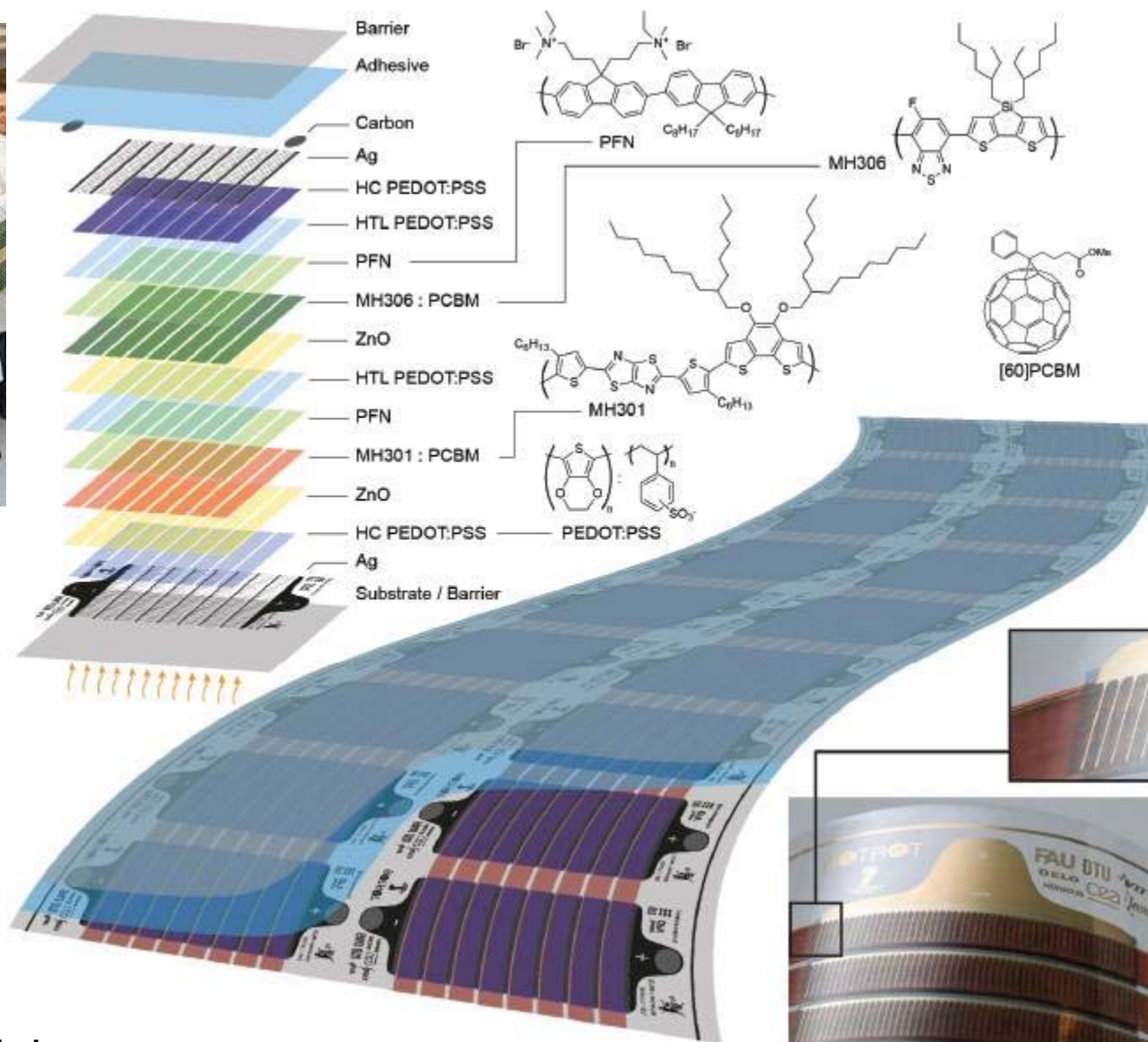
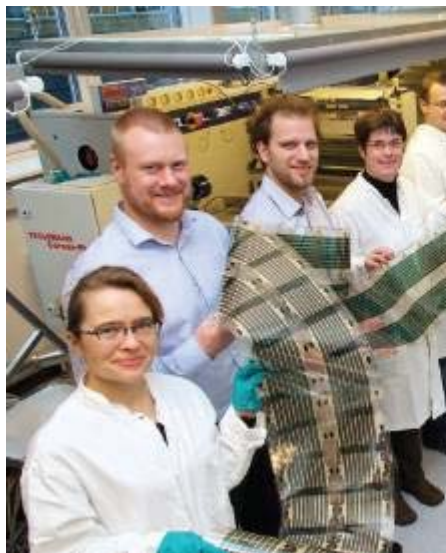


Heeger and Saricifti
US Patents 5,331, 183
and 5,454, 880;
Science,
258, 1474, 1992

Components of the device:

1. ITO coated Glass or flexible substrate (Anode)
2. Hole Transport Layer (HTL) of PEDOT:PSS /MoO₃ or PFN
3. Donor and Acceptor Layer (DAL) of Polymer : PC60BM/PC70BM
4. Electron Transport Layer (ETL)
5. Cathode Electrode of Al/Ag

ORGANIC PHOTOVOLTAICS



**Maximum certified
efficiency : 11.5 %**

Konarka, USA

Heliatic, Germany

Solarmer

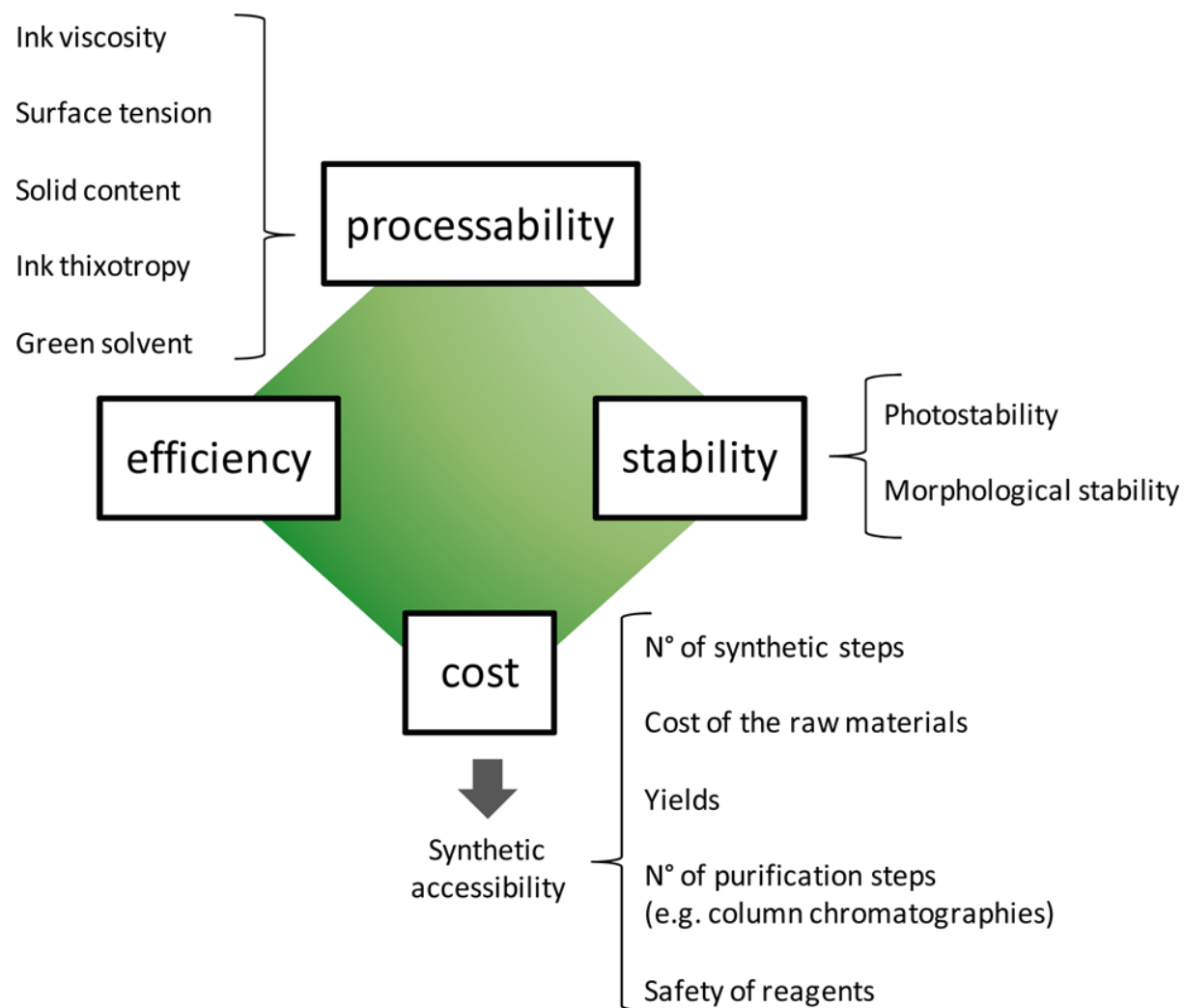
819, UK

Infinity PV(Denmark)

Plextronics(Solvay) : inks

Chemistry World, August 2014, p.24

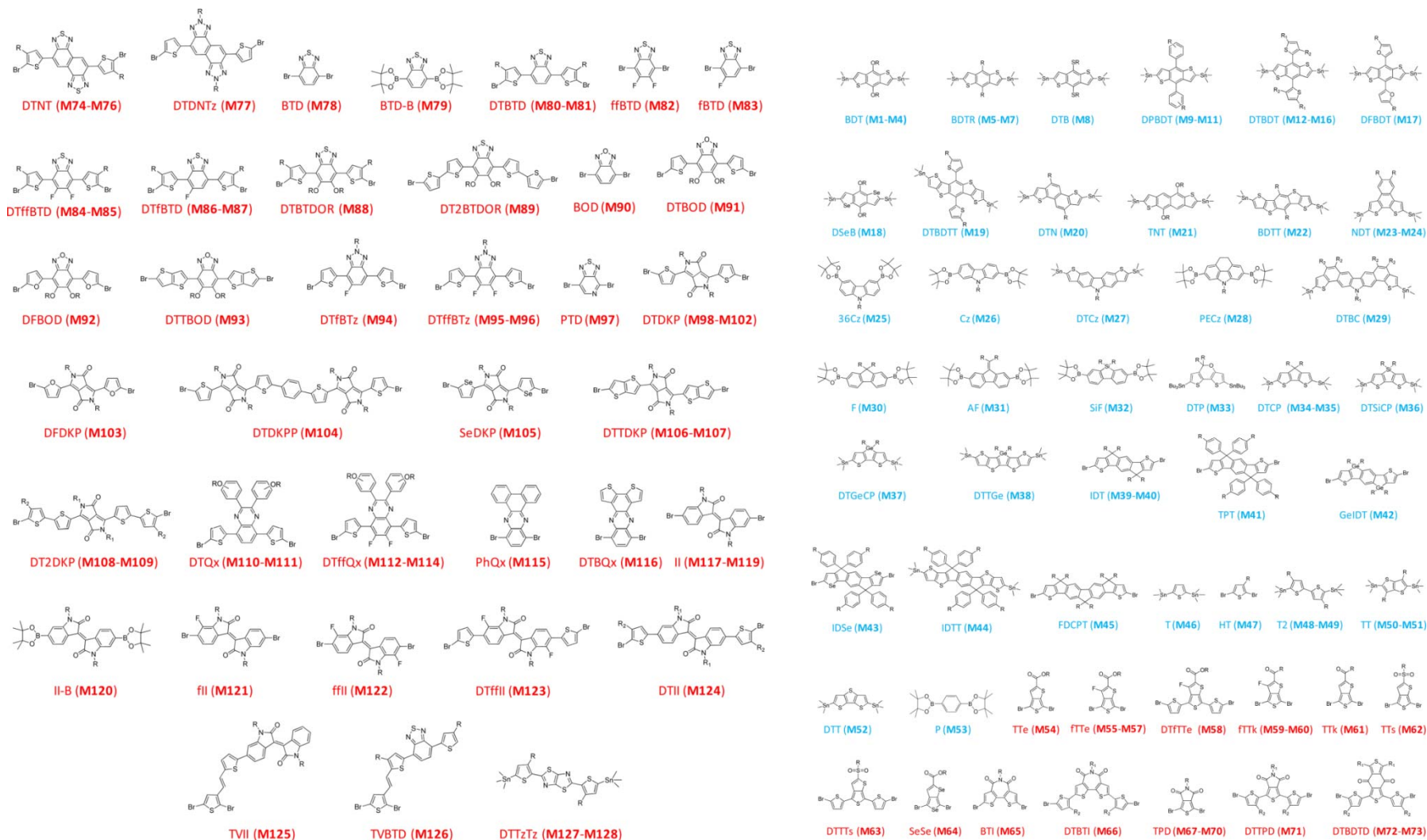
OPV: PERFORMANCE OPTIMIZATION



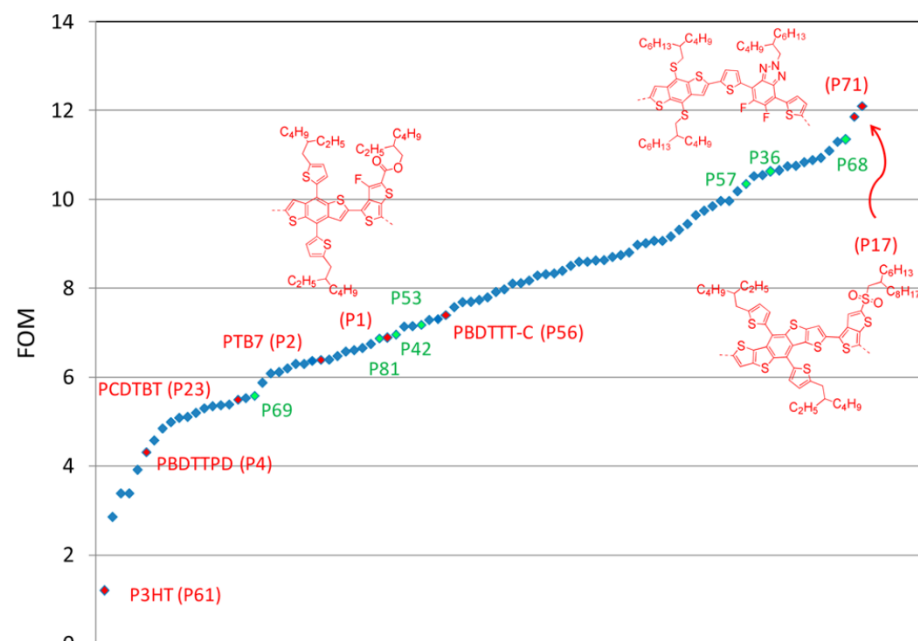
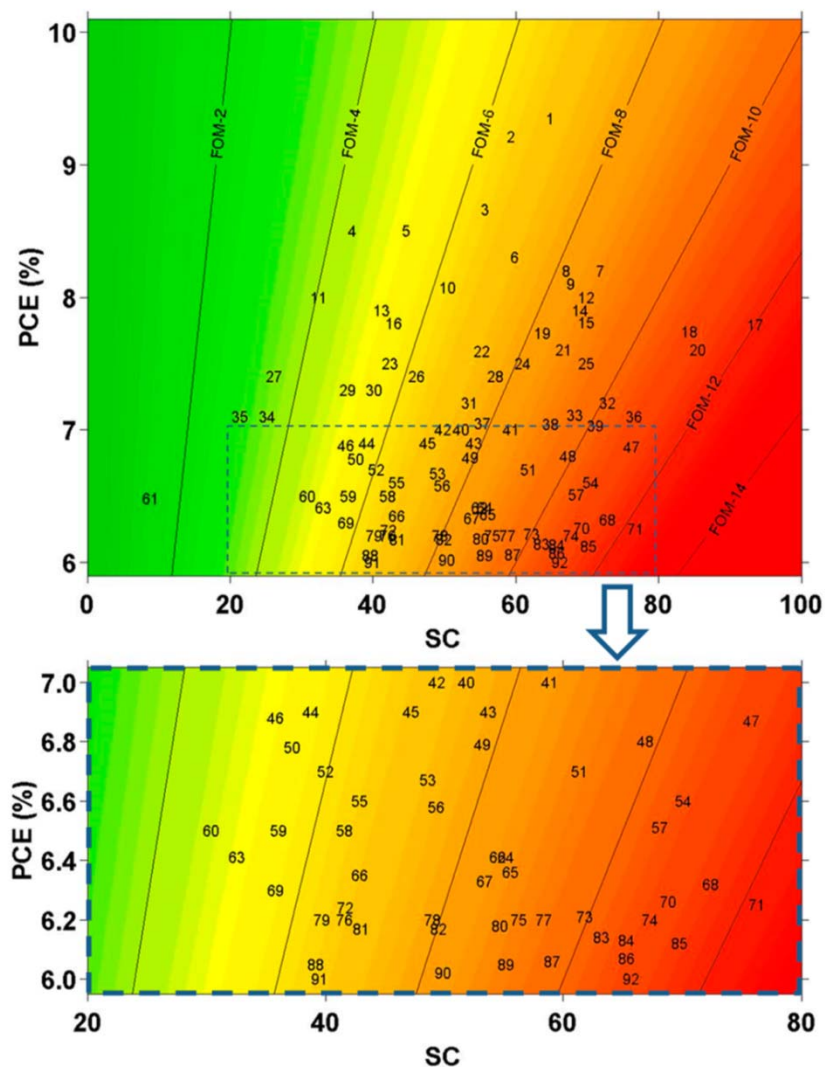
Macromolecules, 48, 453, 2015

DONORS AND ACCEPTORS REPORTED IN 2013

(Macromolecules, 48, 453, 2015)



COMPLEXITY IN THE SYNTHESIS OF EFFICIENT POLYMER DONORS



Synthetic complexity (SC)

- Number of steps
- Yields
- Unit Operation
- Purification
- Safety and toxicity

$$\text{Figure of Merit} = \text{SC} / \text{PCE}$$

Macromolecules, 48, 453, 2015

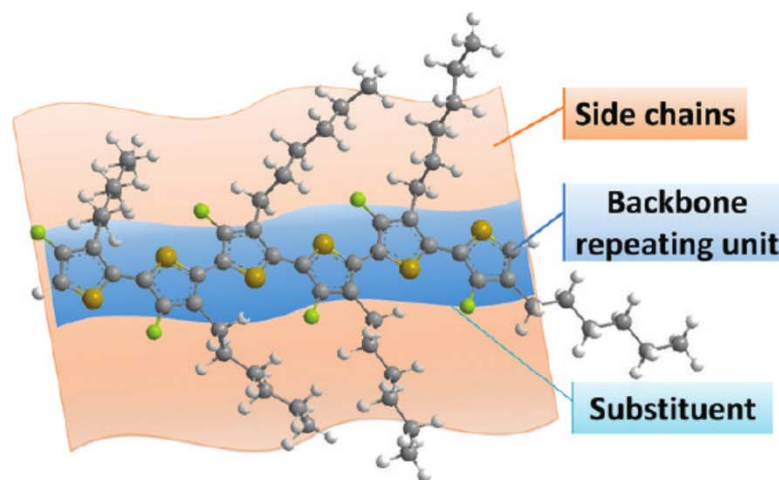
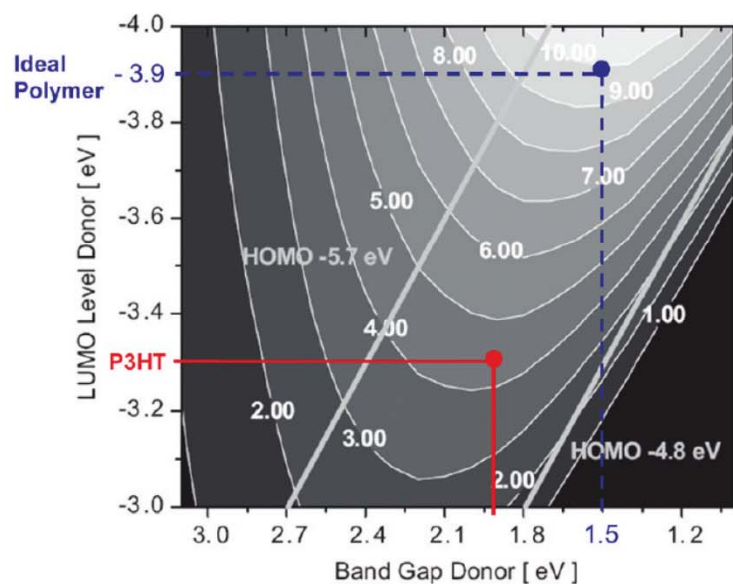
Rational Design of High Performance Conjugated Polymers for Organic Solar Cells

Huaxing Zhou,[†] Liqiang Yang,[‡] and Wei You^{*,†,‡}

[†]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

[‡]Curriculum in Applied Sciences and Engineering, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3287, United States

Macromolecules, 45, 607, 2012



PCE of 10 % can be achieved by an ideal polymer with a band gap of 1.5 eV and HOMO level of -5.4 eV

KEY CHALLENGE : OPV STABILITY

(*Chem. Soc. Rev.*, 45, 2544, 2016)



Water



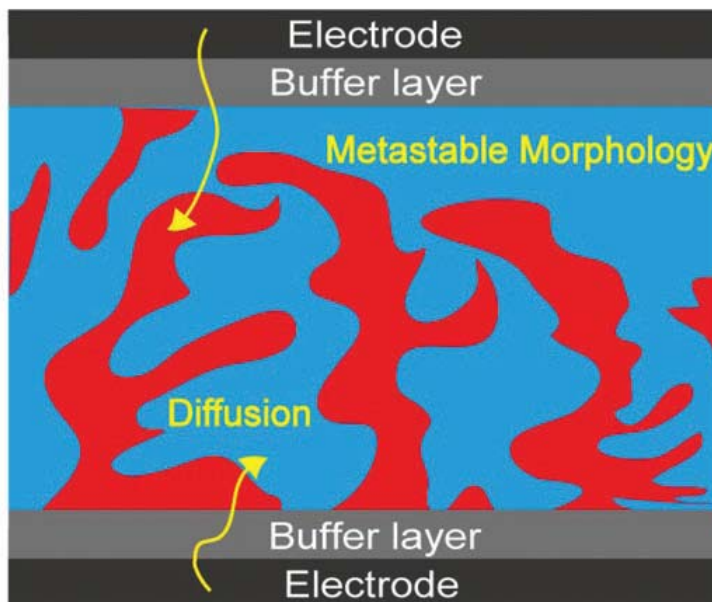
Irradiation



Oxygen

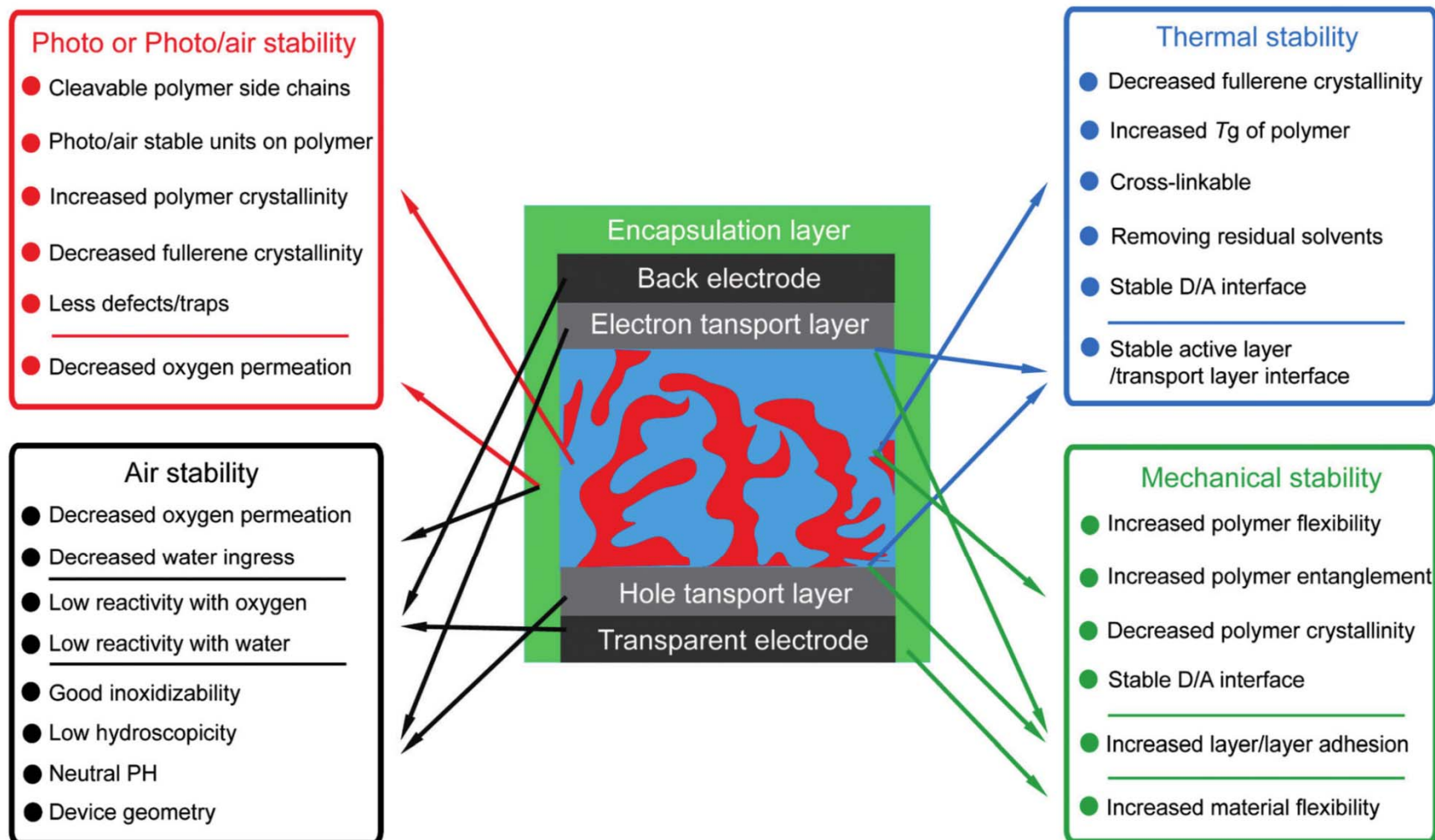


Mechanical
Stress



Heating

IMPROVING OPV STABILITY : STRATEGIES



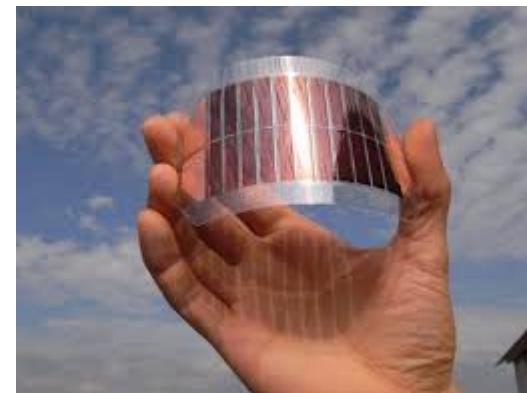
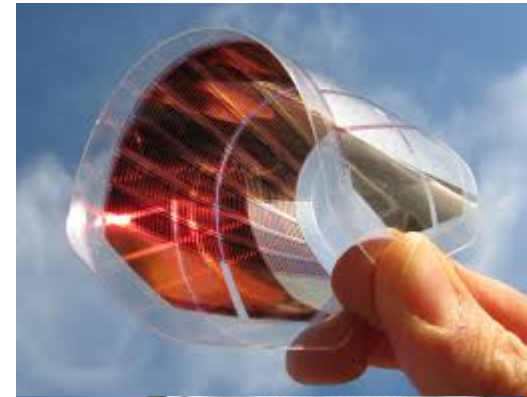
ORGANIC PHOTOVOLTAICS: CURRENT STATUS

- Theoretical Limit 20%
- Desirable : 10%, Lifetime 10> Years,
- Konarka Corporation ~ 3%, 2000 hours certified; 1 GW capacity created
- 1c/Wp appear possible
- Deposition techniques and scaling up : Roll-to-roll deposition; current capabilities: 10,000 to 20,000 m² per year; Minimum viable capacity : 1 million m² per year
- Materials
 - *Inks and solvents (polymers and small molecules)*
 - *Substrates (glass, plastics, aluminum)*
 - *Electrodes (ITO, alternative TCOs)*

Organic Photovoltaics: Technology and Manufacturing

Y. Galagan and R. Adriessen, TNO, Netherlands

www.intechopen.com



SOLAR PARKS FREDERIK KREBS, TECHNICAL UNIVERSITY DENMARK



Installation

<https://www.youtube.com/watch?v=o425pMjZL1Y>

De-Installation

<http://www.youtube.com/watch?v=K2REgwwxrac>

Manufacture of Polymer Solar cell: 1 m min^{-1}

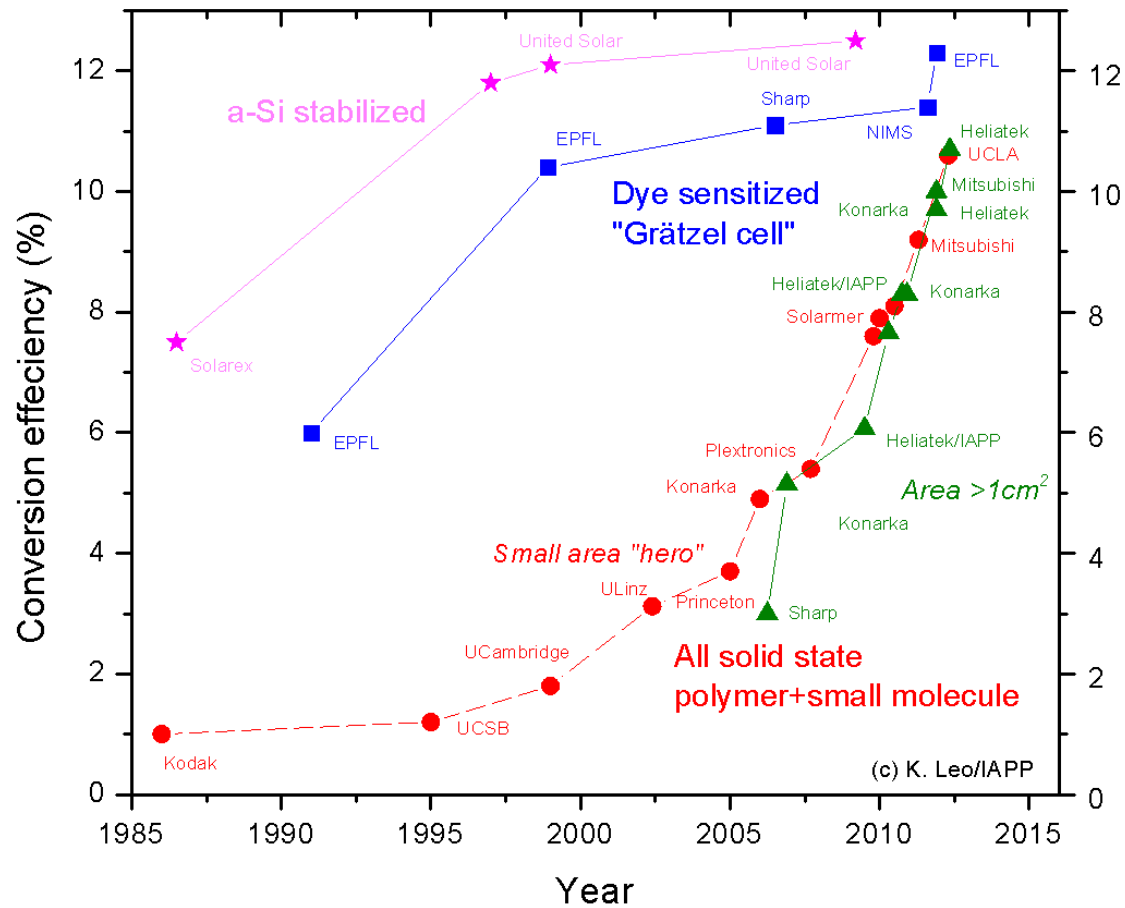
Installation De-installation: 100 m min^{-1}

Initial efficiency 2% stabilizes at 1.6-1.8%

Target : 4% efficiency
10 year stability

*Rise to power - OPV based solar parks.
Advanced Materials. 2014, 26, 29-39*

IMPROVEMENTS IN PCE



WEARABLE ORGANIC SOLAR CELLS

(*Solar Energy Materials and Solar Cells*, 144, 438, 2016)

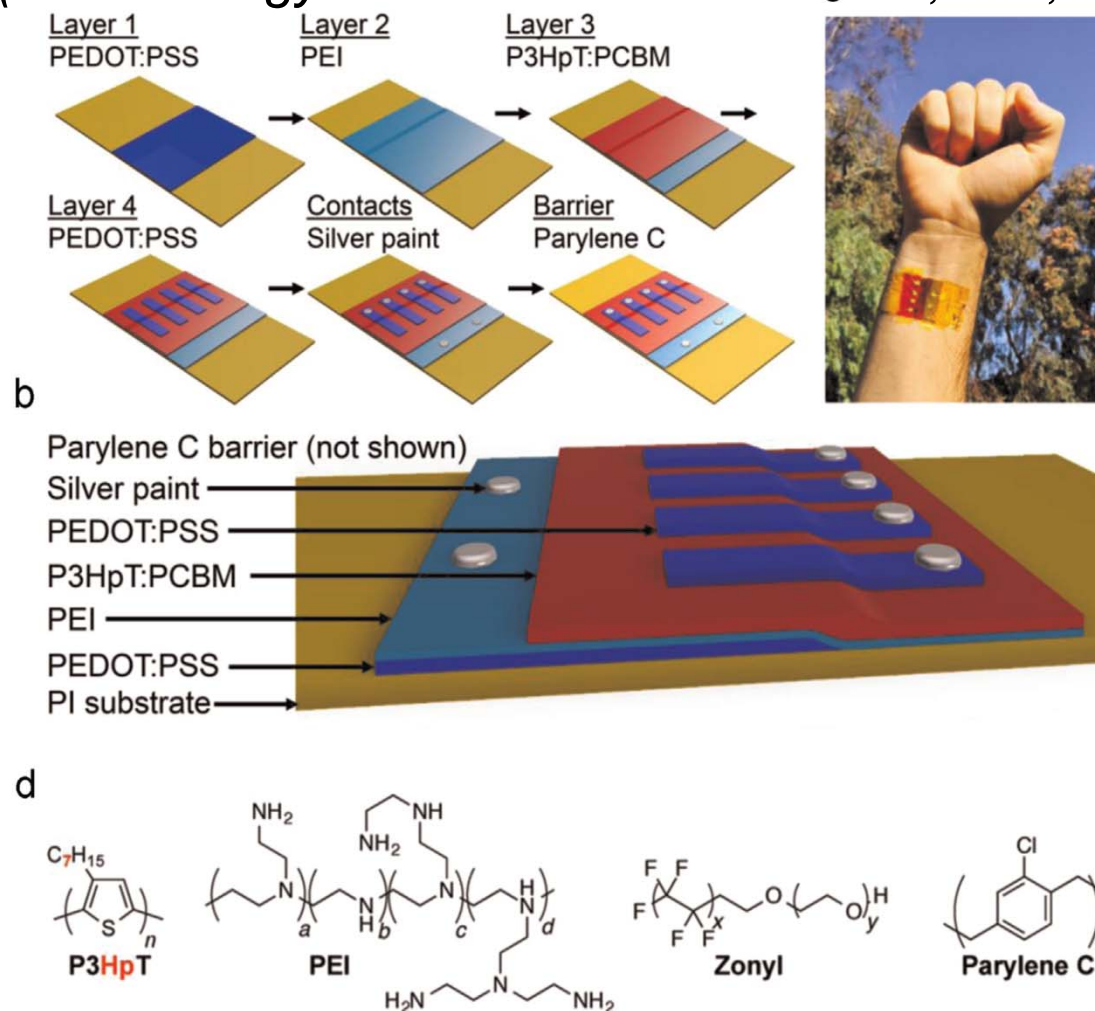


Fig. 1. Fabrication of ultra-flexible, wearable OSCs. (a) Schematic summary of the process used to fabricate wearable OSCs. Thin ($13\ \mu\text{m}$) PI adhesive substrates were spin-coated with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), polyethyleneimine (PEI), and P3HpT:PCBM. PEDOT:PSS top-contacts are then transferred on top of the device using thermal release tape, and a strip of the active layer was wiped away to expose the bottom electrode. Silver paint was then applied to make electrical contact. (b) Schematic diagram of the cross section of a wearable OSC. (c) A photograph of the wearable solar cell on skin. (d) Chemical structures of the critical materials used in this study.

CAN OPV REPLACE THIN FILM TECHNOLOGIES ?

Organic photovoltaics are similar to thin films in many respects

Technology	Efficiency, %	US \$ per W_p
Amorphous silicon	5-8	1-2
CdTe	9-11	2.5
CIGS	12	2
OPV	3	11-12

Impossible to compete with thin films at the current level of technologies; no data yet on levelized cost of electricity based on organic materials which takes into account the operational lifetime

MATERIAL +PROCESSING COST OF OPV

Material	Cost (Euro)
PET-ITO	2.819
ZnO	0.225
P3HT-PCBM	0.616
PEDOT-PSS	0.398
Silver	0.579
Barrier	0.489
Pressure sensitive adhesive	0.224
TOTAL	5.35

Cost of manufacture of one 16x13 mm module with an active area of 360 cm²; power output : 660 mW; processing time : 90 sec

J. Materials Chem, 19, 5442, 2009

OPPORTUNITIES FOR COST REDUCTION

- Lower cost replacement for transparent conductor, ITO
- Opportunity to reduce cost of active material by improved process chemistry
- Reduce or eliminate use of silver
- Increasing processing speed by 10 x
- Print electrode directly on the barrier material; eliminate one adhesive layer

PROGRESSION OF MARKET SEGMENTS AND APPLICATIONS

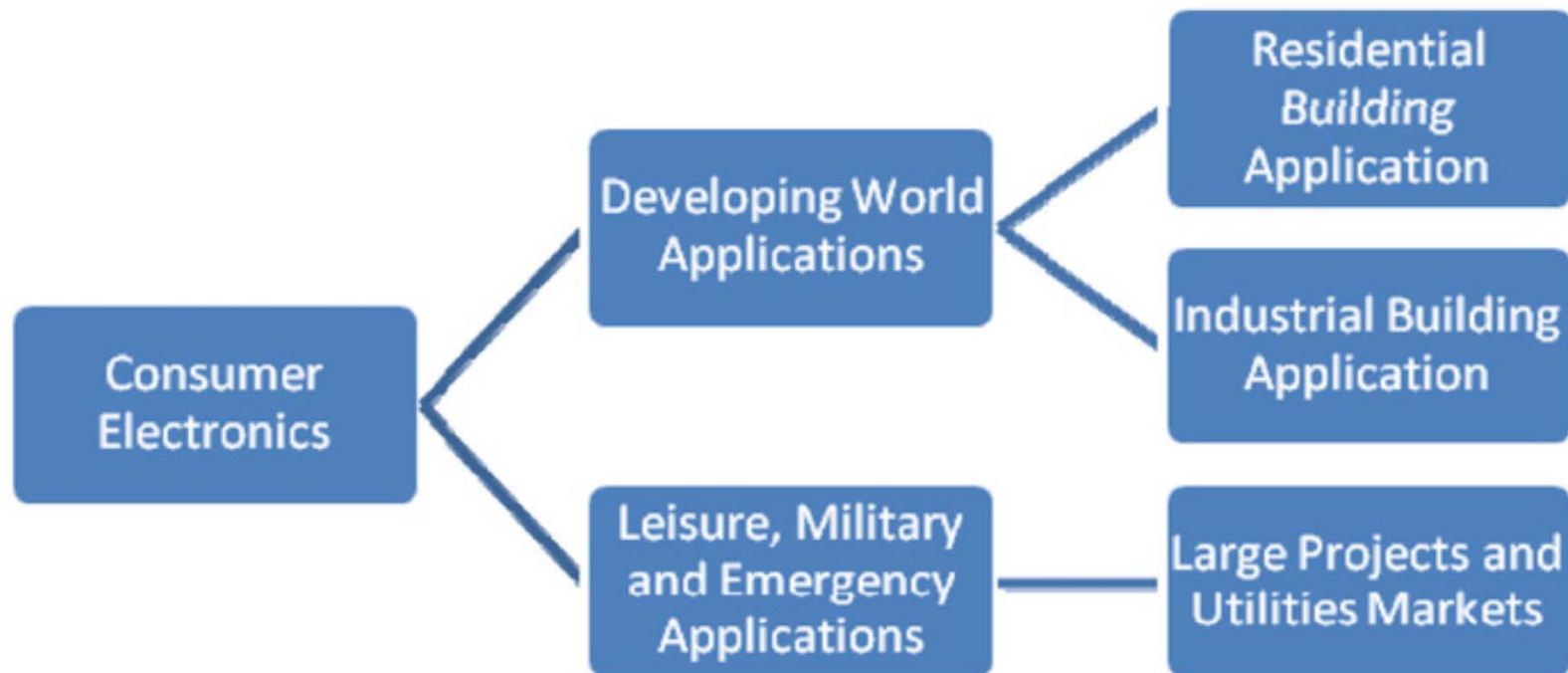


Fig. 2. Increasing solar cell performance leads to increasing market size. Each market segment represents a jump forward in technology maturity and market size increase with the addition of each market segment to the previous segments.

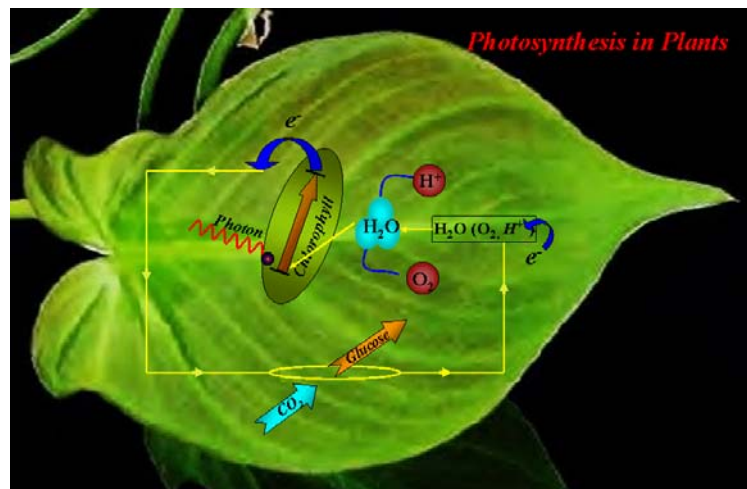
Technology driver : Power conversion efficiency and lifetime
Cost driver : scale and market size

COST TO PERFORMANCE RATIO AND APPLICATIONS

Performance	Expected Applications
1-3% PCE, 1-2 year lifetime, 8-12 US\$ per W, small area modules, T(80): 2500 h; capacity : 1 GW	Consumer electronics, toys, smart cards and low power devices (current)
4-6 % PCE, 3-5 year life time, 1 US \$ per W, medium area modules, T(80) : 12,000 h; Capacity : 5 GW	Solar curtains for indoor use, solar active films for windows, low power demand application such as distributed power and lighting (2020 +)
6-9% PCE, 5-7 year lifetime, below 0.5 \$ per W, large area modules, T(80) : 20,000 h; capacity : 60 GW	Building integrated applications (2015 +)

Cost to performance ratio : Product of PCE and lifetime divided by cost per W

DYE SENSITIZED SOLAR CELL : TAKING A LEAF OUT OF NATURE



Dye-Sensitized Solar Cell Components

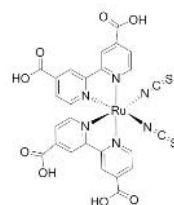
Sensitizing Dye



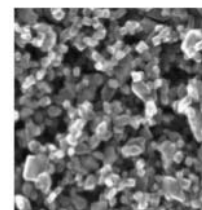
Titania Nanoparticles



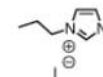
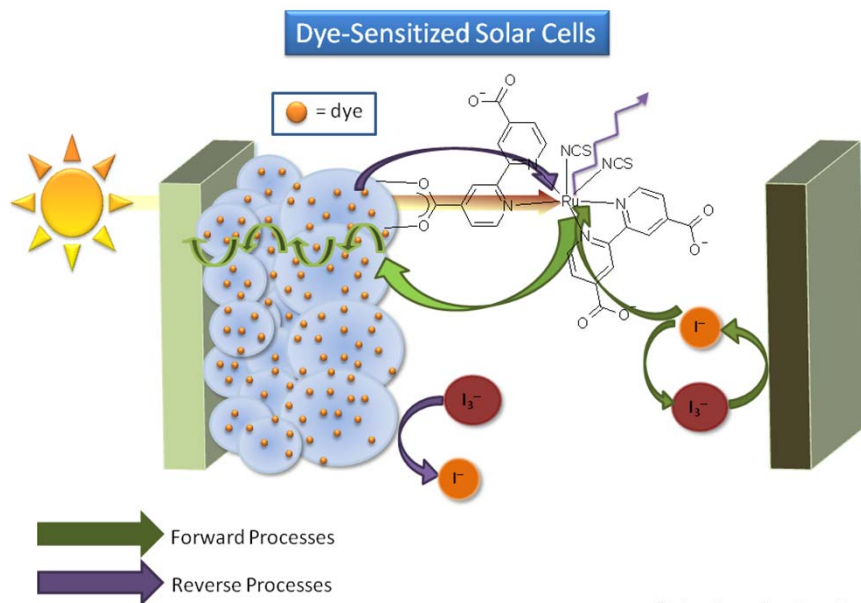
Electrolyte



Chemical Structure of N3 Dye



20 nm Titania nanoparticles

Iodide/Tri-iodide
Redox Couple

Max. Certified Efficiency : 11.9 %

Gratzel and O'Regan, Nature, 353, 737 (1991)(cited over 10,000 times); US Patent, 1988 (a patent classic)

Applications of DSSC

(a) 200 m² of DSSC panels installed in Newcastle (Australia)– the first commercial DSSC module



60

- Flexible
- Wearable
- Paintable
- Can harvest diffuse light

Building Integrated Photovoltaics IoT applications

Solar Powered Solar Panel Sun Glasses

The SIG, or "Self-Energy Converting Sunglasses" are quite simple. The lenses of the glasses have **dye solar cells**, collecting energy and making it able to power your small devices through the power jack at the back of the frame. "Infinite Energy: SIG"



Courtesy: Sony Corp.

67



Dye-Sensitized Solar Cells are 12% Efficient. What can we do to make them better?

- Develop dyes to absorb more photons
- Create new electrolytes that provide higher voltages. *Iodide/ triiodide redox couple is corrosive, volatile and leaks*
- Develop Dye-Sensitized Solar Cells that can last for 30 years

Design Near-Infrared Absorbing Dyes

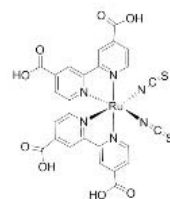
- Can increase power conversion efficiency from 12% to 14% by absorbing light out to 900 nm.
- Probably can't make DSCs >14% using liquid electrolytes.



Stanford/EPFL collaboration through the Center for Advanced Molecular Photovoltaics (CAMP)



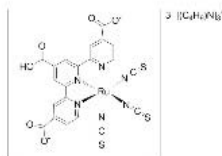
Design dyes that broadly absorb light



N3

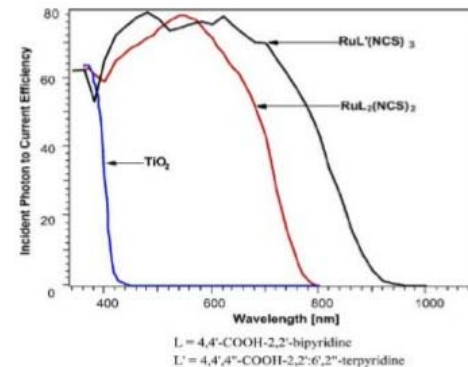
cis-Ru(SCN)₂L₂

(L = 2,2-bipyridyl-4,4-dicarboxylate)

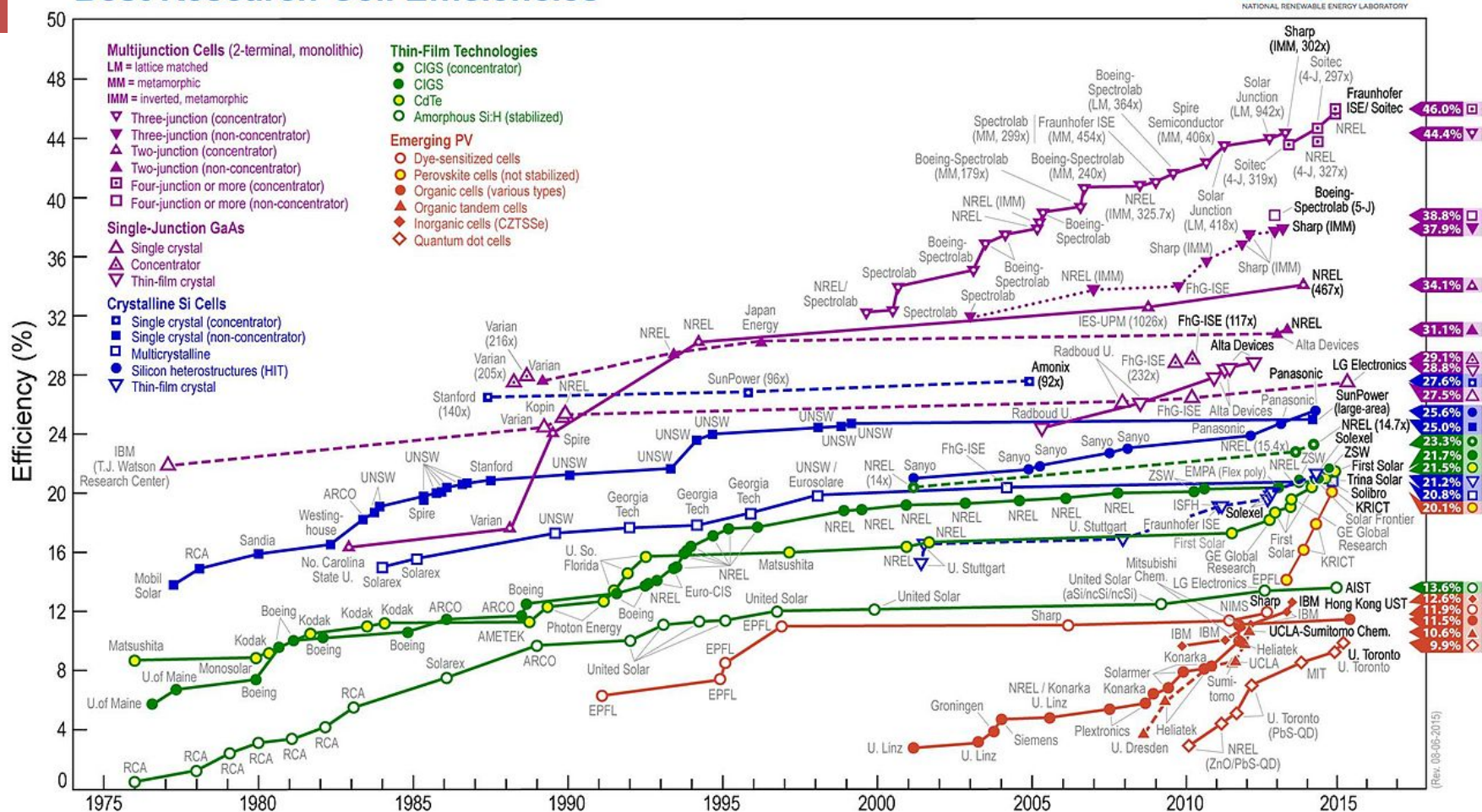


N749

tri(cyanato)-2,2,2-terpyridyl-4,4,4-tricarboxylate)Ru(II)

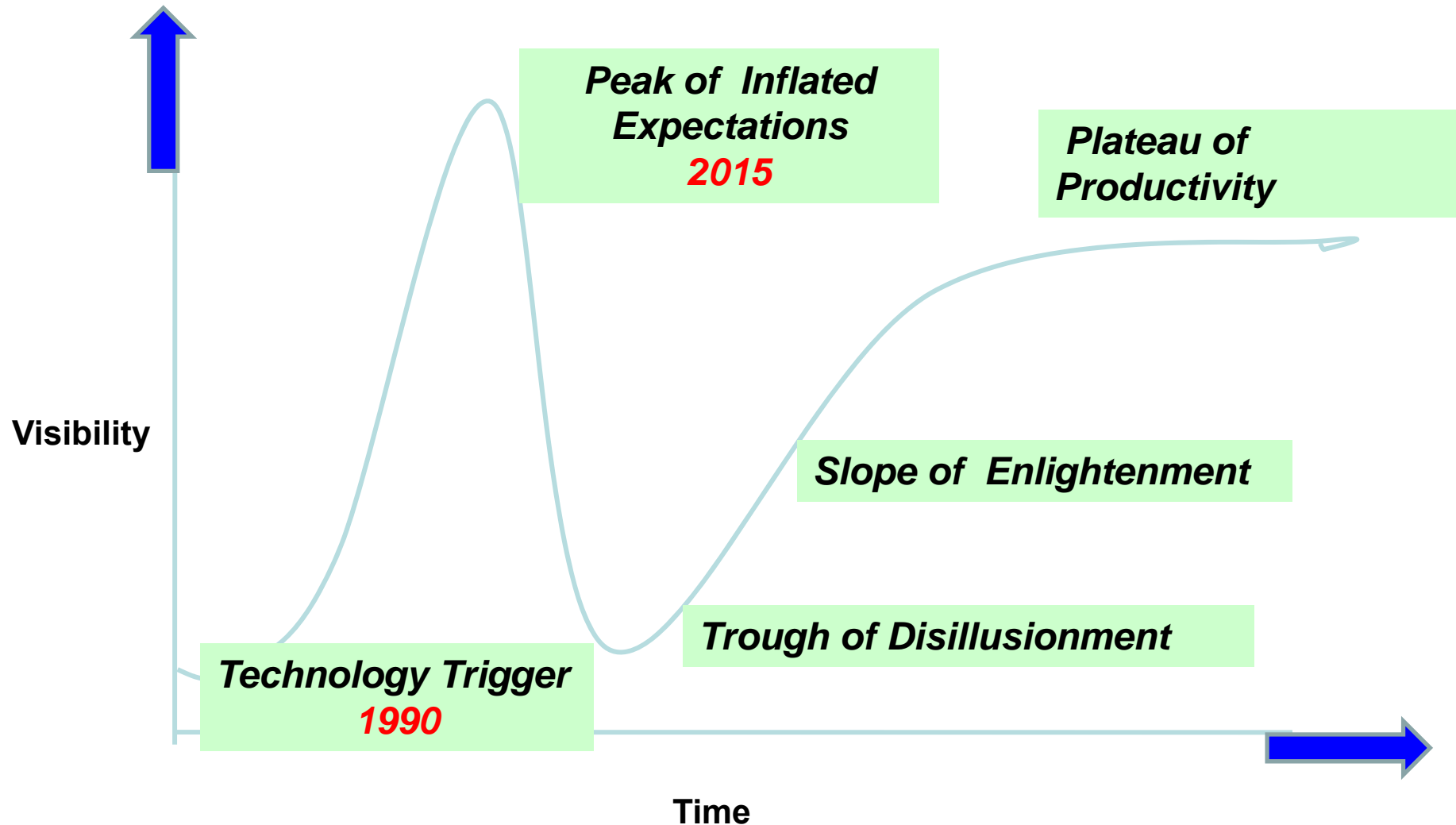


Best Research-Cell Efficiencies



EVOLUTION OF TECHNOLOGIES : THE HYPE CYCLE

(http://en.wikipedia.org/wiki/Hype_cycle)



WHAT IS DRIVING THE HYPE?

- Increasing focus on renewable energy, environment and climate change
- Large availability of Government research funds/ philanthropic funding/ start up funding
- The accelerating pace of digital revolution, large data analytics and internet of things

Large scientific data in the open literature, more academic spin offs, large number of small companies trying to optimize product performance

CAN WE LEAP FROG WITH LOW COST SOLAR ENERGY ?

(Carl Pope Sierra Club)

- 1.4 billion people without electricity
- Bottom 20% pay 9-18% of world's lighting bills, receiving only 0.1% of benefits
- Over 10 years, a poor family spends 1500 US \$ on kerosene
- Kerosene: Single day's supply in a bottle; Solar power: cost needs amortization over 20 year period
- However, LED lighting powered by solar energy appears to be eminently appropriate in this area of application
- 66% of India's households will need to be served off grid; wiring a remote village adds 0.02\$/kwh/km
- Governments pays only for grid power infrastructure; Who will bear the cost of small distributed power or building /home power solutions?
- Renewables are not competitive for big central power plants; However, emerging market investments in renewables is devoted to this sector

STRATEGIES FOR PRODUCT INNOVATION

- Product design for BoP (Frugal Innovation) or ToP application segment
- BoP customer is increasingly demanding higher functionality at lower price
- Value to a customer is defined as the ratio of functionality to price; discerning customers place importance on value rather than price
- Should a new product entry maximize functionality to achieve a niche or high end application or create a low functionality product at a price that is affordable?

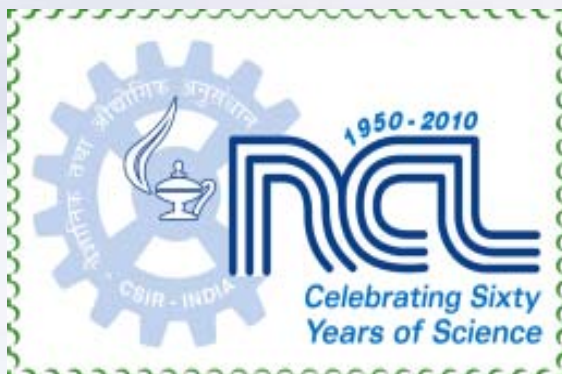
STRATEGIES FOR PRODUCT INNOVATION

- Is it possible to create cutting edge innovation in high technology products focusing only on BoP segment?
- Most successful innovations began as products with high functionalities (at high price) and low volumes for niche applications. Building scale and learning/experience curve brought the price down and made it affordable to a larger segment of customers
- Most products developed by advanced countries enter application in emerging markets at appropriate price points

“ Cell phones, computers, refrigerators and colour TV’s did not start off by making a low end product for masses; they were relatively expensive when they were first introduced and only few could afford them” Martin Eberhard, Founder , Tesla Motors, later acquired by Elon Musk

SUMMARY

- The world is in the midst of unprecedented change
- Population growth, rural to urban migration, unique demographics (very young and very old), shrinking urban space, increasing mobility
- Broader access to energy is essential to face the challenge of “climate change”.
- This will require the transformation of what still remains a “Paleolithic” global energy economy. The technology portfolio to enable this transformation is feasible but lacks the needed priority and resources.
- Focus too much on supply side; Need to focus on demand side
- Three risks for India: ability to prioritize and identify optimal solutions for India, risk of solutions imposed on us by technology providers, risk of Government and policy driven adoption of sub optimal technologies
- Risk management : Geopolitical (oil), economic (renewable), psychological and perception (nuclear)
- Need to articulate tangible value proposition to all stakeholders



THANK YOU

