Nanotechnology and Materials Chemistry in New and Emerging Solar Cell and Lighting Technologies-I

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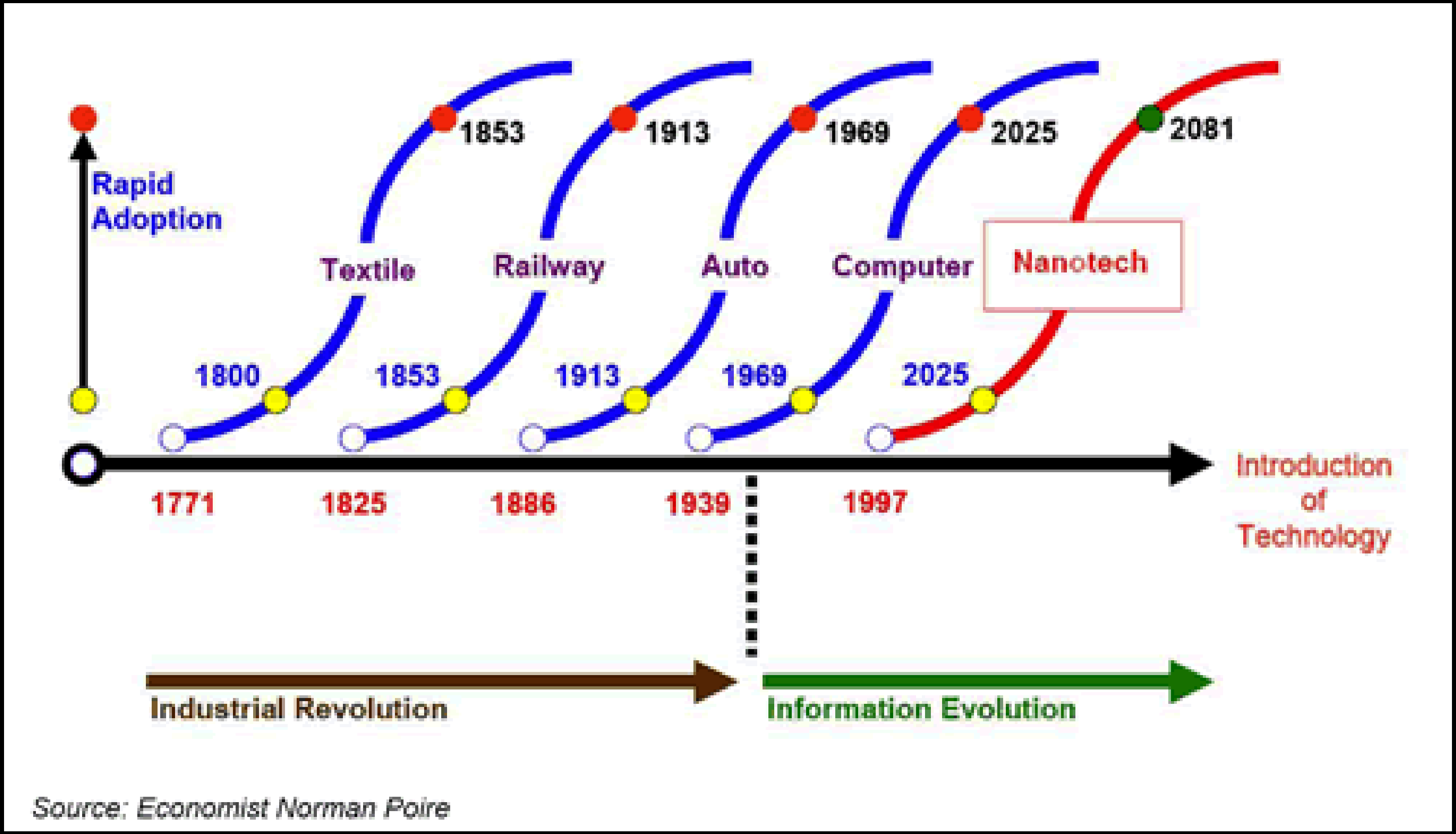
PV Systems Engineering & the other Renewable Energy Systems
through the Entrepreneurship spirit
3 July, 2013; 10:30-11:00

Nanotechnology Drives the Next Growth Cycle



http://www.nanotechnologyresearchfoundation.org/nanohistory.html

What is Nanotechnology?

A *basic definition*: Nanotechnology is the engineering of functional systems at the molecular scale.

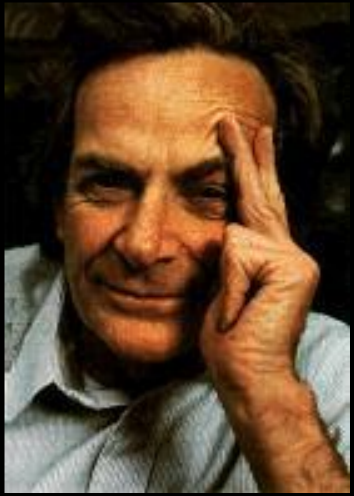
The *Meaning of Nanotechnology*:

1980's popularized the word 'nanotechnology'

building machines on the scale of molecules

motors, robot arms, and even whole computers, far smaller than a cell.

K. Eric Drexler



Richard P. Feynman
1918-1988 (1965 Nobel Prize winner)

traditional sense, building things from the bottom up, with atomic precision.
theoretical capability was envisioned in 1959

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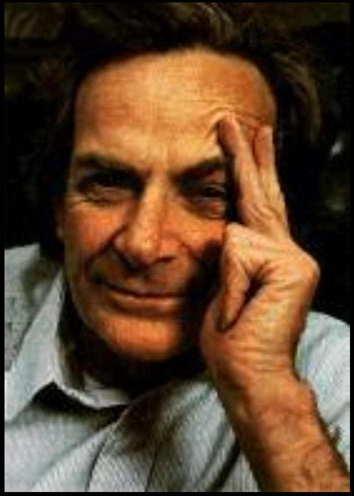
K. Eric Drexler
1955-



I want to build a billion tiny factories, models of each other, which are manufacturing simultaneously. . . The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big. — Richard Feynman

«plenty of room at the bottom»

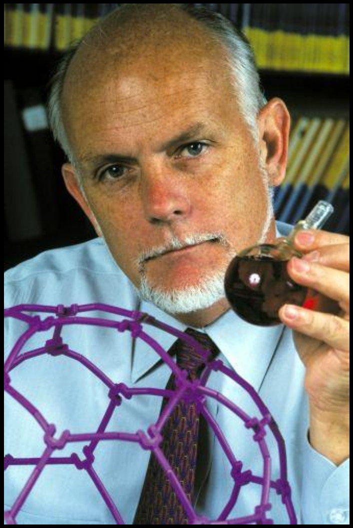
Richard P. Feynman
1918-1988 (1965 Nobel Prize in Physics)

Productive Nanosystems:

From molecules to superproducts

Version 1.1

Is this science fiction?



Richard Errett Smalley
1943-2005
(1996 Nobel Prize in Chemistry)

The "Fat Fingers" Problem

"Chemistry is the concerted motion of at least 10 atoms."

"In an ordinary chemical reaction five to 15 atoms near the reaction site engage in an intricate three-dimensional…"

The "Sticky Fingers" Problem

"…the atoms of the manipulator hands will adhere to the atom that is being moved. So it will often be impossible to release this minuscule building block in precisely the right spot….these problems are fundamental…."

exchange of letters which were published in Chemical & Engineering News
Nanotechnology: Drexler and Smalley make the case for and against 'molecular assemblers'

Ho and Lee [3] physically bound a CO molecule to an iron atom on a silver substrate using an STM.

[3] Wilson Ho, Hyojune Lee, "Single bond formation and characterization with a scanning tunneling microscope," Science 286(26 November 1999):1719-1722; http://www.physics.uci.edu/~wilsonho/stm-iets.html

www.mrs.org/publications/bulletin

MATERIAL MATTERS

Future Global Energy Prosperity: The Terawatt Challenge

Richard E. Smalley

412 MRS BULLETIN • VOLUME 30 • JUNE 2005

the most critical problems we will have to confront as we go through this century

Richard Errett Smalley's list

1. Energy
2. Water
3. Food
4. Environment
5. Poverty
6. Terrorism and war
7. Disease
8. Education
9. Democracy
10. Population

World population	2009	≅ 6.8 billion
	2025	≅ 8.0 billion
	2050	≅ 9.4 billion

United Nations Population Division

"new oil" for 10 billion people!..

In 2004, we consumed on average the equivalent of **220 million barrels of oil** per day to run the world.

Or, if we convert that into watts, what ran the world was about **14.5 terawatts**.

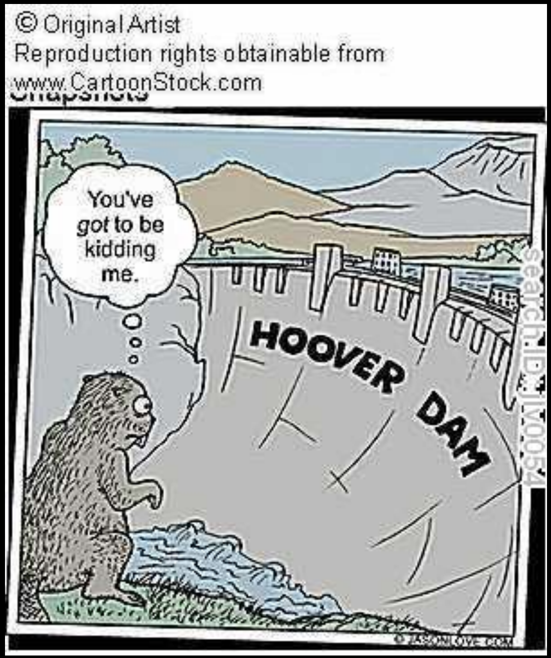
The vast majority of this energy was from

oil,

gas, and

coal.

Fission, biomass and hydro power were significant players.



≅3.0 billion people
cow dung, vegetation, etc.

most of it already traped

0.5 % of 14.5 terawatts was from
(≅ 72.500 gigawatts)

solar
wind and
geothermal

10 billion people in 2050

According to Smalley,

60 terawatts around the planet

900 million barrels of oil / day

According to Salzburg Global Seminar

(July 10, 2008)

40 terawatts

&

25 terrawatts of clean energy

The structure of technologic development

Conservative development

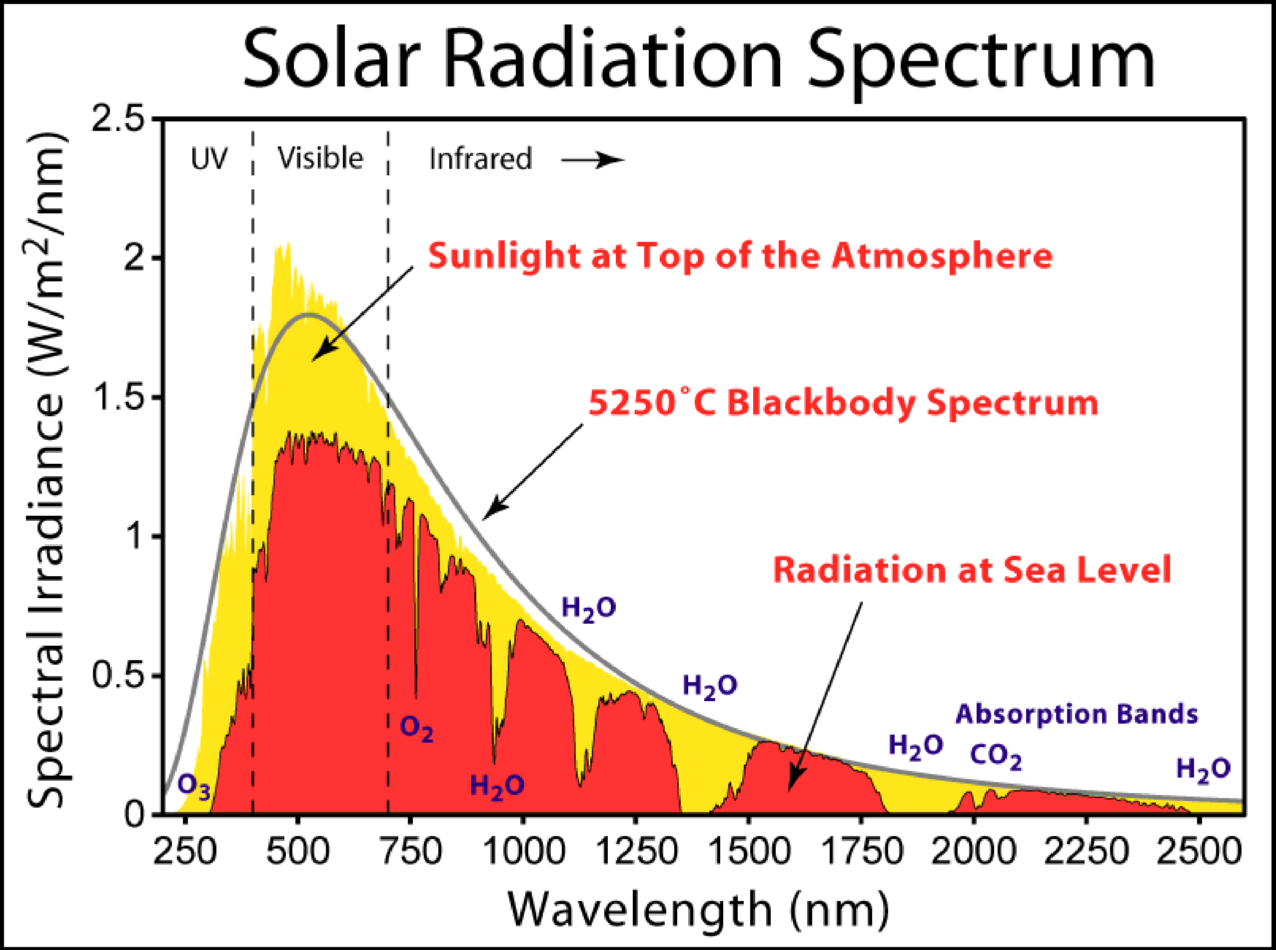
deals with improvement and dissemination of present technology

Radical development

brings new technologic system

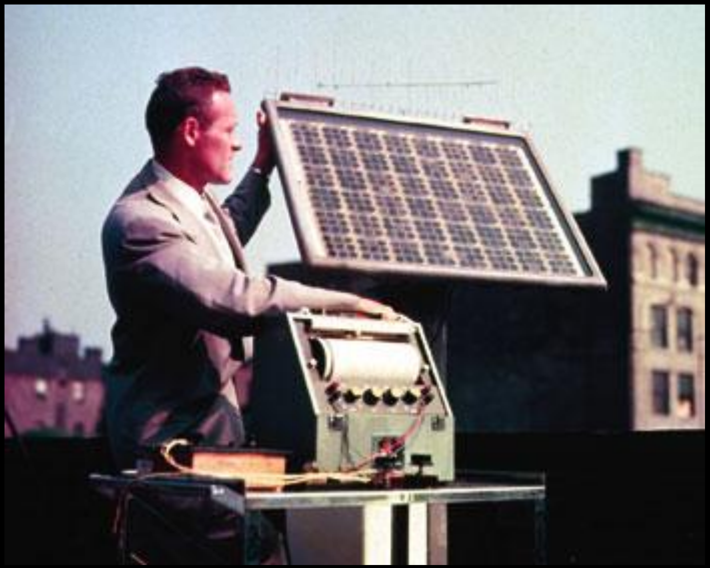
Energy sources	Energy change	Energy distribution	Energy storage	Energy usage
Regenerative	**Gas Turbines**	**Power Transmission**	**Electrical Energy**	**Thermal Insulation**
Photovoltaics: Nano-optimized cells (polymeric, dye, quantum dot, thin film, multiple junction), antireflective coatings **Wind Energy:** Nano-composites for lighter and stronger rotor blades, wear and corrosion protection nano-coatings for bearings and power trains etc. **Geothermal:** Nano-coatings and -composites for wear resistant drilling equipment **Hydro-/Tidal Power:** Nano-coatings for corrosion protection **Biomass Energy:** Yield optimization by nano-based precision farming (nanosensors, controlled release and storage of pesticides and nutrients)	Heat and corrosion protection of turbine blades (e.g. ceramic or intermetallic nano-coatings) for more efficient turbine power plants	**High-Voltage Transmission:** Nanofillers for electrical isolation systems, soft magnetic nano-materials for efficient current transformation **Super Conductors:** Optimized high temperature SC's based on nanoscale interface design for loss-less power transmission **CNT Power Lines:** Super conducting cables based on carbon nanotubes (long term) **Wireless Power Transmission:** Power transmission by laser, microwaves or electromagnetic resonance based on nano-optimized components (long term)	**Batterries:** Optimized Li-ion-batteries by nanostructured electrodes and flexible, ceramic separator-foils, application in mobile electronics, automobile, flexible load management in power grids (mid term) **Supercapacitors:** Nanomaterials for electrodes (carbon-aerogels, CNT, metall(-oxides) and elektrolytes for higher energy densities)	Nanoporous foams and gels (aerogels, polymer foams) for thermal insulation of buildings or in industrial processes
	Thermoelectrics			**Air Conditioning**
	Nanostructured compounds (interface design, nanorods) for efficient thermoelectrical power generation (e.g. usage of waste heat in automobiles or body heat for personal electronics (long term))			Intelligent management of light and heat flux in buildings by electrochromic windows, micro mirror arrays or IR-reflectors
	Fuel Cells		**Chemical Energy**	**Lightweight Construction**
	Nano-optimized membranes and electrodes for efficient fuel cells (PEM) for applications in automobiles/mobile electronics		**Hydrogen:** Nanoporous materials (organometals, metal hydrides) for application in micro fuel cells for mobile electronics or in automobiles (long term) **Fuel Reforming/Refining:** Nano-catalysts for optimized fuel production (oil refining, desulphurization, coal liquefaction **Fuel Tanks:** Gas tight fuel tanks based on nano-composites for reduction of hydrocarbon emissions	Lightweight construction materials using nano-composites (carbon nanotubes, metal-matrix-composites, nano-coated light metals, ultra performance concrete, polymer-composites)
	Hydrogen Generation			
	Nano-catalysts and new processes for more efficient hydrogen generation (e.g. photoelectrical, elektrolysis, biophotonic)			
Fossil Fuels		**Smart Grids**		**Industrial Processes**
Wear and corrosion protection of oil and gas drilling equipment, nanoparticles for improved oil yields		Nanosensors (e.g. magneto-resistive) for intelligent and flexible grid management capable of managing highly decentralised power feeds		Substitution of energy intensive processes based on nanotech process innovations (e.g. nano-catalysts, self-assembling processes etc.)
	Combustion Engines		**Thermal Energy**	
	Wear and corrosion protection of engine components (nano-composites/-coatings, nano-particles as fuel additive etc.)		**Phase Change Materials:** Encapsulated PCM for air conditioning of buildings **Adsorptive Storage:** Nano-porous materials (e.g. zeolites) for reversible heat storage in buildings and heating nets	
Nuclear	**Electrical Motors**	**Heat Transfer**		**Lighting**
Nano-composites for radiation shielding and protection (personal equipment, container etc.), long term option for nuclear fusion reactors	Nano-composites for superconducting components in electro motors (e.g. in ship engines)	Efficient heat in- and outflow based on nano-optimized heat exchangers and conductors (e.g. based on CNT-composites) in industries and buildings		Energy efficient lighting systems (e.g. LED, OLED)

*www.hessen-**nanotech**.de/mm/Nano**Energy**_web.**pdf***



Solar Cell Technology : convert solar energy to electricity

Lighting Technology : bring sunlight where nature fails to

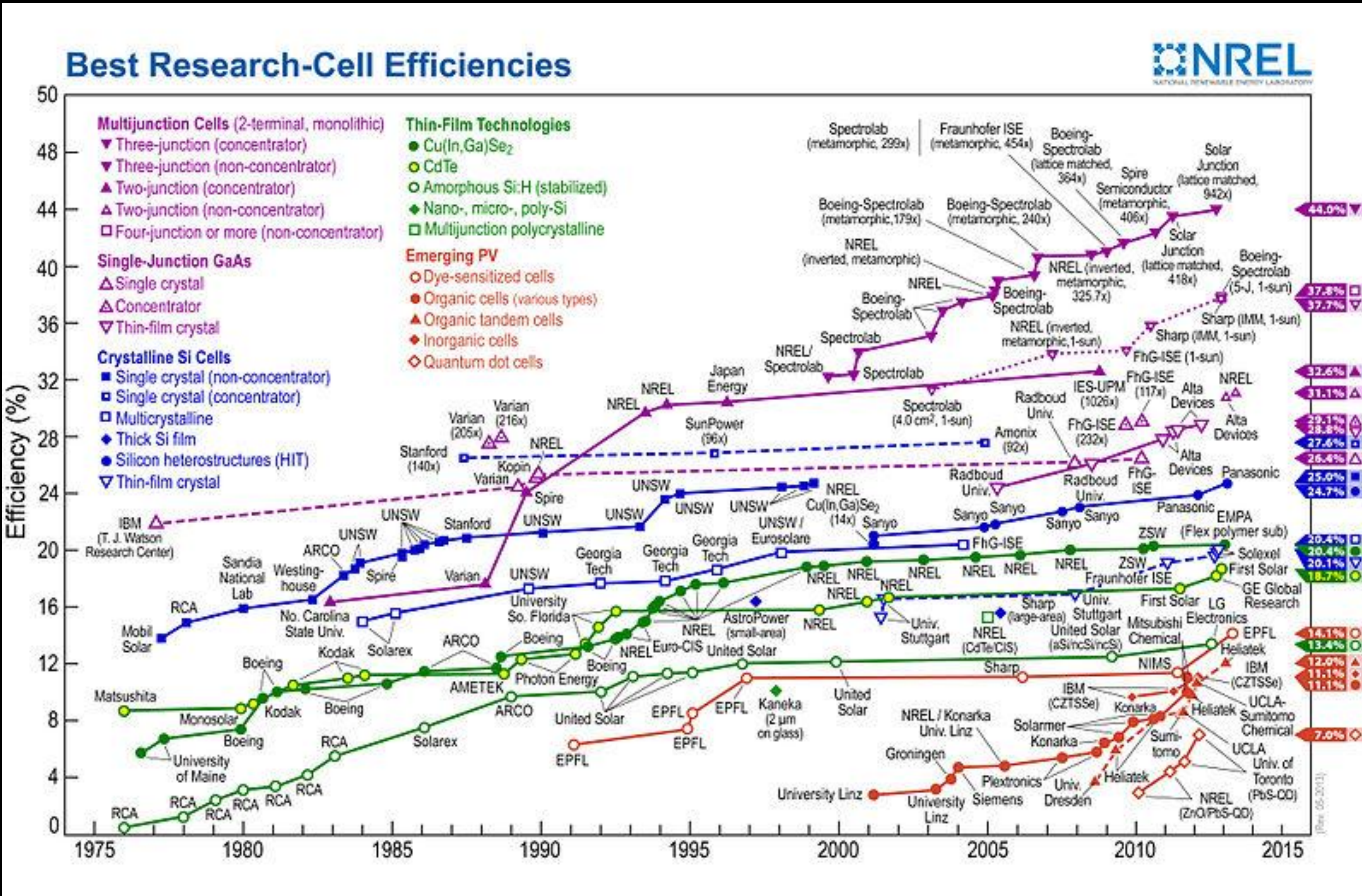


Bell Labs engineer testing solar cells in 1954

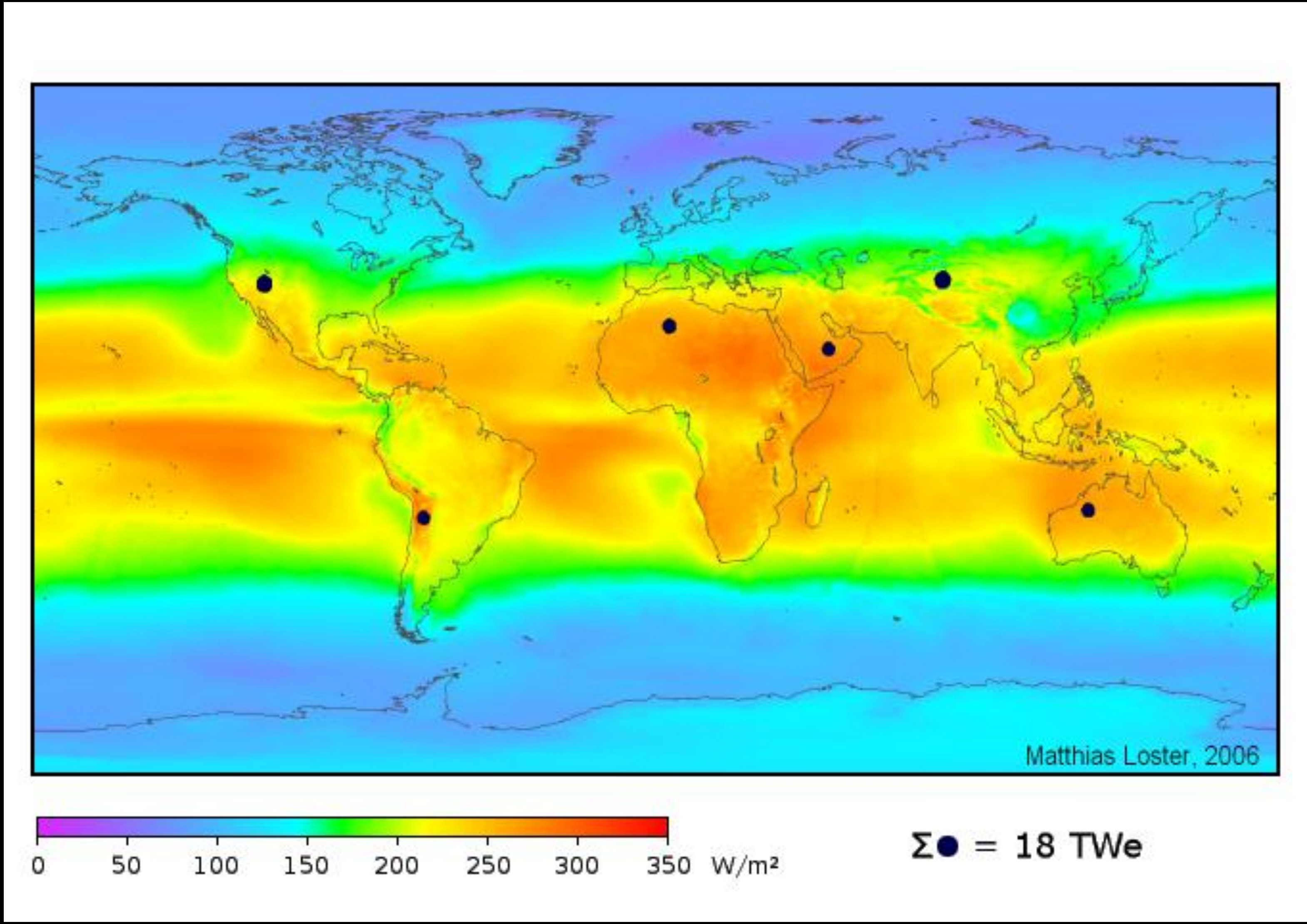
The original Bell Solar Battery (photovoltaic panel) is used in an early test in 1945

In the early 1950s **R.S. Ohl** discovered that sunlight striking a wafer of silicon would produce unexpectedly large numbers of free electrons. In 1954, **G.L. Pearson**, **C.S. Fuller, and D.M. Chapin** created an array of several strips of silicon (each about the size of a razor blade), placed them in sunlight, captured the free electrons and turned them into electrical current.

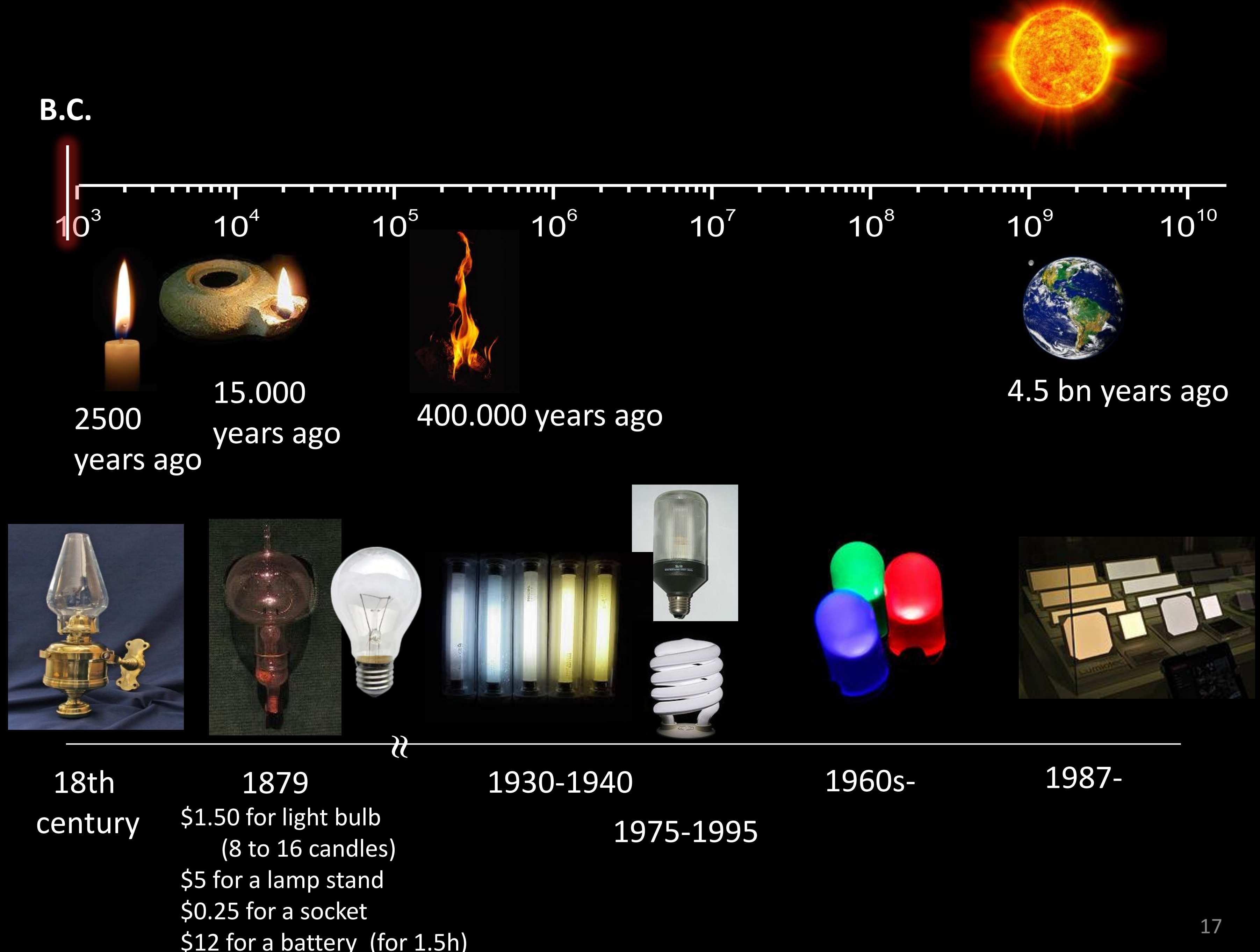
It could convert only **six percent** of the sunlight into useful energy



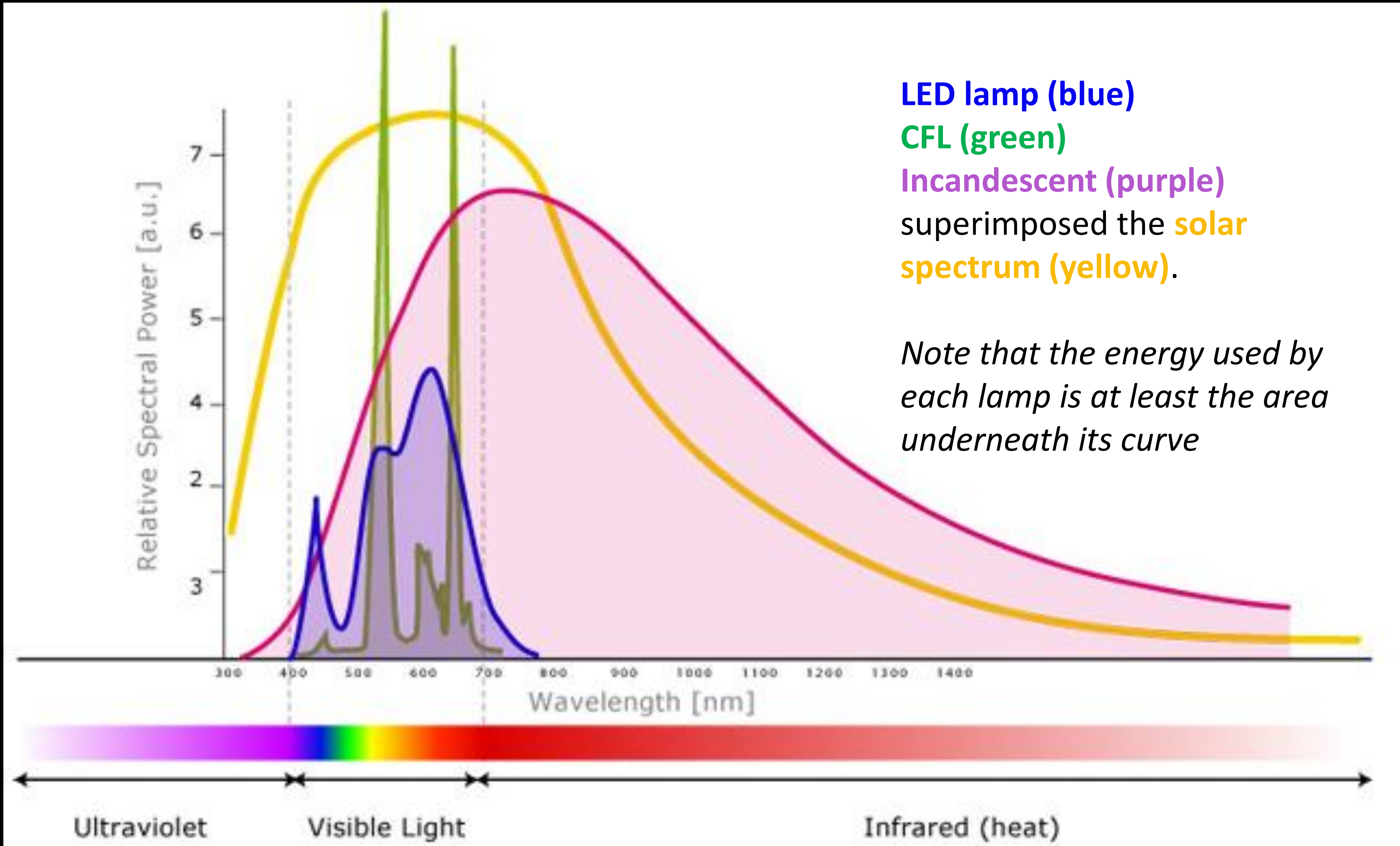
http://en.wikipedia.org/wiki/Solar_cell



Average solar irradiance, watts per square metre. Note that this is for a horizontal surface, whereas solar panels are normally mounted at an angle and receive more energy per unit area. The small black dots show the area of solar panels needed to generate all of the world's energy using 8% efficient photovoltaics.



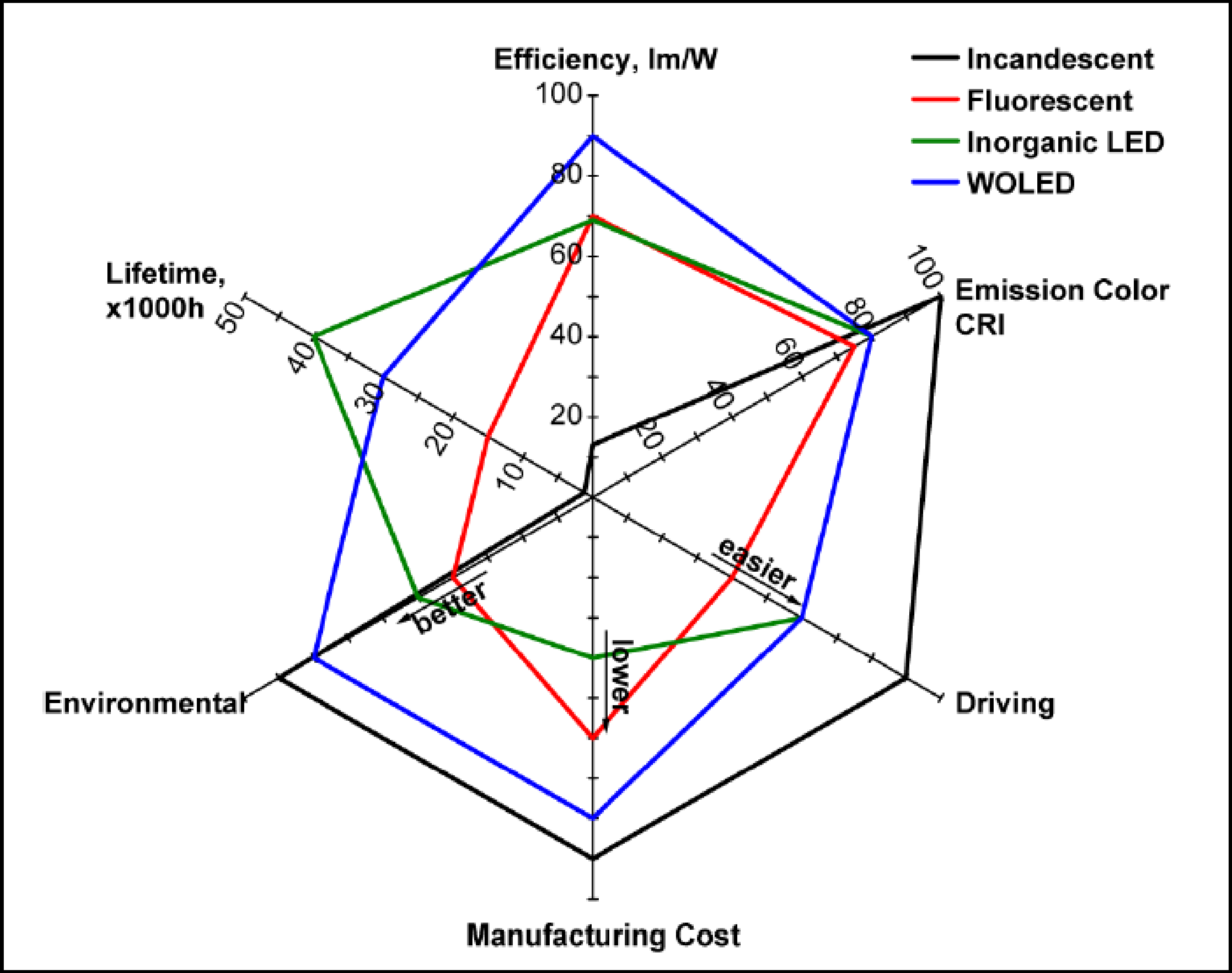
B.C.
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
2500 years ago
15.000 years ago
400.000 years ago
4.5 bn years ago
18th century
1879
$1.50 for light bulb (8 to 16 candles)
$5 for a lamp stand
$0.25 for a socket
$12 for a battery (for 1.5h)
1930-1940
1975-1995
1960s-
1987-



LED lamp (blue)
CFL (green)
Incandescent (purple)
superimposed the **solar spectrum (yellow)**.

Note that the energy used by each lamp is at least the area underneath its curve

http://www.except.nl/en/#.en.articles.92-led-artificial-light-guide



Advanced Materials, 23, 233–248, 2011

What is the problem ???

The cost of solar energy conversion to electricity

and

the electricity percentage need for lighting

20% of produced electricity is consumed in lighting

Viability of solar cells (PVs) and LED &WOLED lighting

In order to be a fully sustainable energy technology, PVs has to qualify in certain indicators of viability such as:

- the CO_2 emissions
- the end-of-life management and recycling
- the energy pay-back time

Quite opposite to the fossil energy sources, the CO_2 emissions associated with photovoltaic energy conversion occur almost entirely

during system manufacturing

instead of system operation

The CO_2 emissions of the present grid connected roof-top systems have been estimated to be

- significantly lower than those of fossil fuel power plants,
- but somewhat higher than those of biomass, wind energy and nuclear energy.

Depending on the PV technology the cell contain small amounts of different hazardous and regulated materials, such as Cd, Pb and Se, which raises concerns about their disposal into municipal landfills. However, the technology for recycling the solar cells already exists and it can be considered also economically feasible.

The energy payback time of the photovoltaic systems depends

- energy content of the entire photovoltaic system,
- local irradiation conditions.

For both of the technologies **cost**

the high efficiency strategy and *the low manufacturing cost strategy*

Module price (\$/Wp) = manufacturing cost (\$/m^2) / module performance (Wp/m^2)

Dye sensitized solar cells

Organic solar cells/WOLEDs

Multiple electron-hole pair cells/QDLEDs

& Tandem approachs

Tandem or

multi-junction cells

Concentrating systems

multiple electron-hole pair

Cells /QDLEDs

The chemistry, physics and material science of organic semiconductors and QDs

Early history of semiconductors*

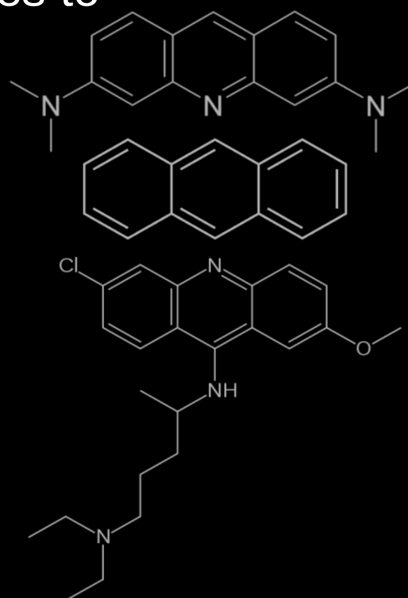
Alessandro Volta introduced the word semiconductor (SC) in 1782

#of SC compounds known in 1950 only 65

- «On semiconductors one should not do any work, that's a mess, who knows whether there are semiconductors at all» wrote Pauli to Rudolf Peierls in 1931

  «Working on semiconductors means scientific suicide» said a friend of Georg Busch in 1940 ……

After 1950s organic semiconductor term starts to be used…
Acridine orange, quinacrine, anthracene,.. .etc are the first molecules to introduced as SC**



Organic Carbon based
has several useful forms
not afraid to hybridize
is a group 4 element
electronegativity is in the middle of the range
bonds readily to other carbons

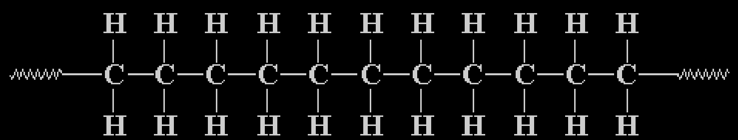
*G. Busch, Eur. J . Phys 10 (1989) 254-264
**A. Bernanose, M. Comte, P. Vouaux, J. Chim. Phys. 1953, 50, 64; M. Pope et al. J. Chem. Phys. 1963, 38, 2042-2043

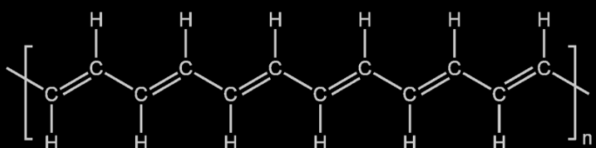
Advantages of organic semiconductors

Light weight
Mechanical flexibility
Chemical modifications possible
processing (e.g. ink-jet printing, spin coating)

Easy and cheap

Comparable conductivities, become even better when doped

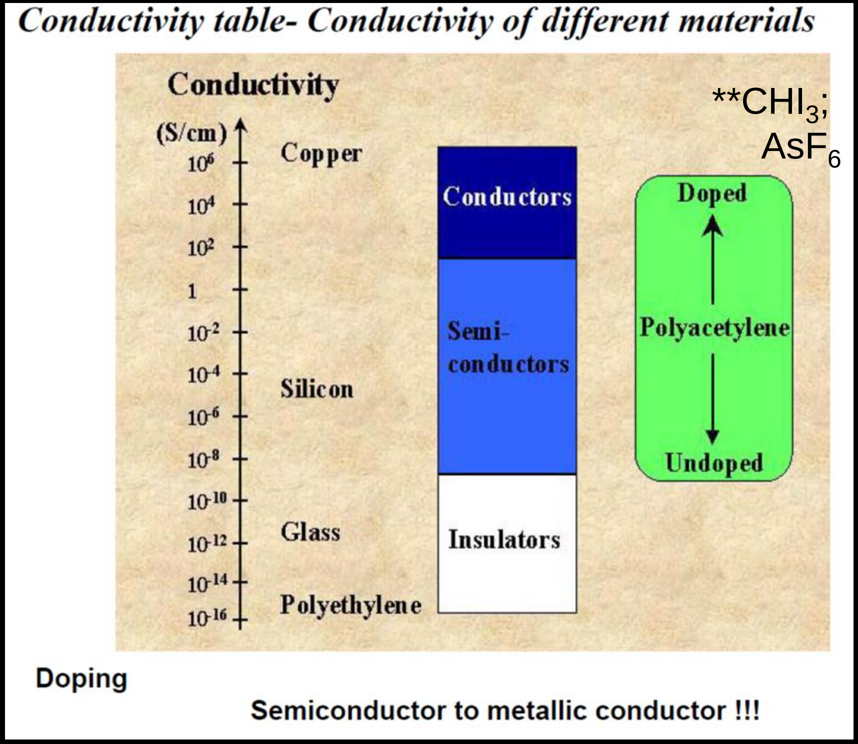




Disadvantages of organic materials

Poor cristallinity
Possible degradation
Low mobility

(*e.g. e^- μ (RT) Ge = 4500 cm^2/Vs
Anthracene = 1.06 cm^2/Vs
h+ μ (RT) Ge = 3500 cm^2/Vs
Anthracene = 1.31 cm^2/Vs)



*http://wwwmayr.in.tum.de/konferenzen/Jass08/courses/4/buth/slides_buth.pdf
**J. Chem. Soc. Chem. Commun., 578, (1977); Phys. Rev. Lett. 39, 1098–1101 (1977)

Organic Semiconductors

Small Molecules
Polymers

Organometallic compounds

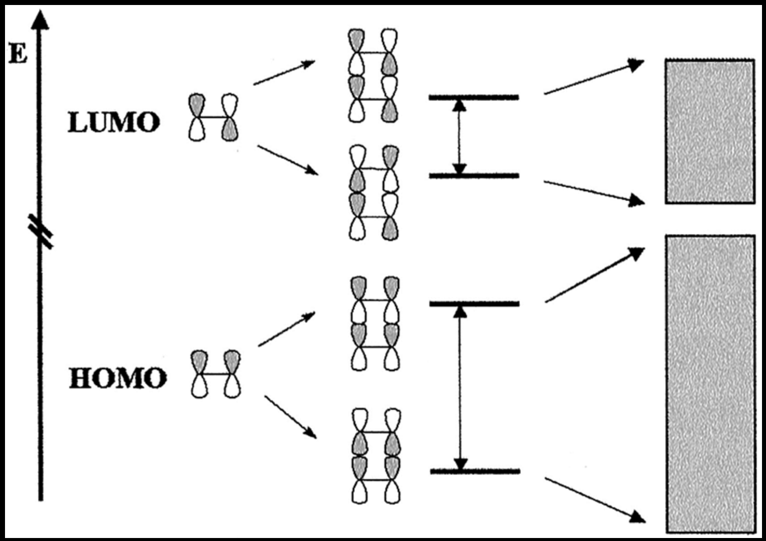
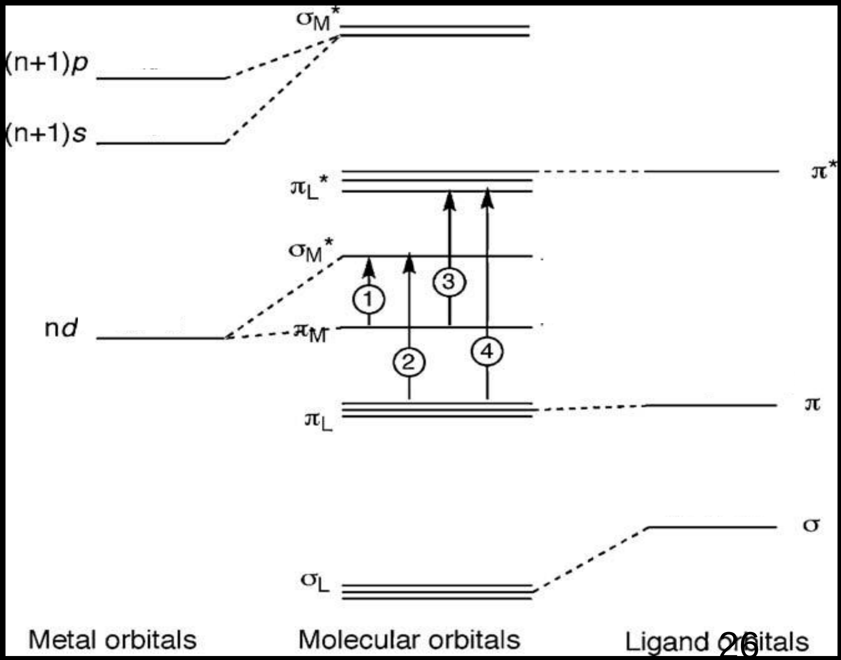


Illustration of the bonding-antibonding interactions between the HOMO/LUMO levels of two ethylene molecules in a cofacial configuration;
&
the formation of the valence and conduction bands when a large number of stacked molecules interact.

1. Metal-centered (MC) excited states
2. Ligand-to-metal charge-transfer (LMCT) excited states
3. Metal-to-ligand charge-transfer (MLCT) states
4. Intraligand (IL) ππ* excited states

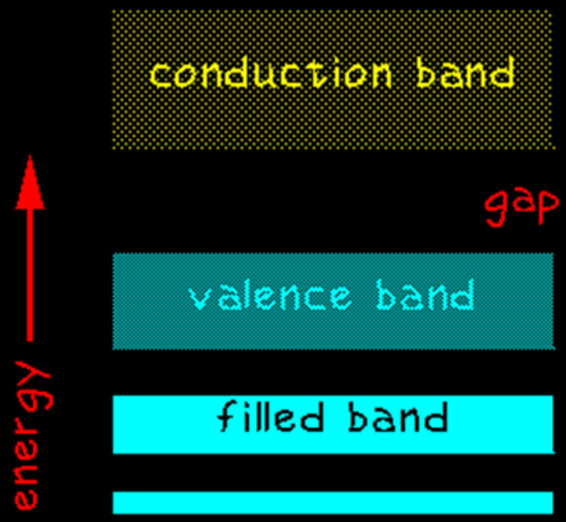


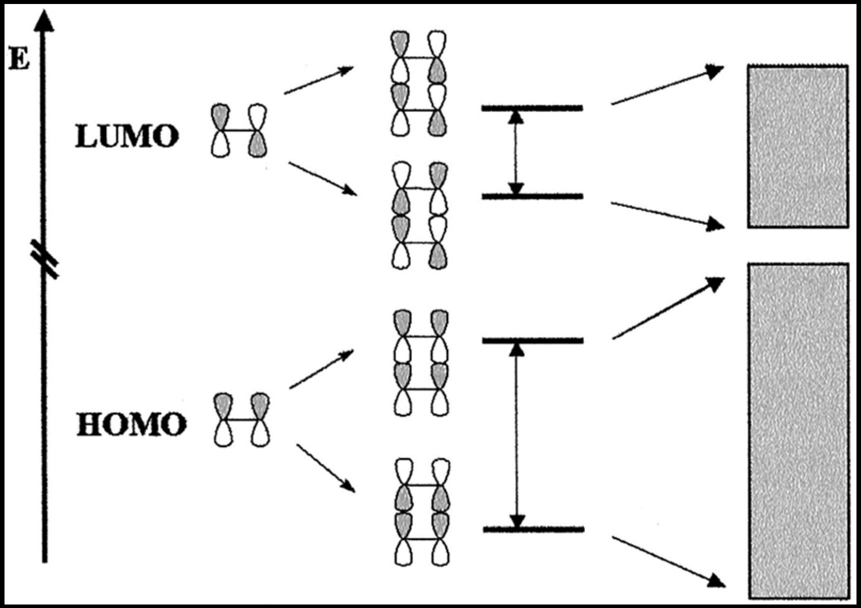
Molecular orbital diagram for a transition metal complex*

*V. Balzani, Photochem. Photobiol. Sci. 2 (2003) 459.;
P. S. Wagenknechta,P. C. Ford, Coordination Chemistry Reviews, 255 (2011) 591;
Pi-T. Chou, Y. Chi, Chem. Eur. J. 13 (2007) 380 .

26

Inorganic semiconductors | **Organic semiconductors**





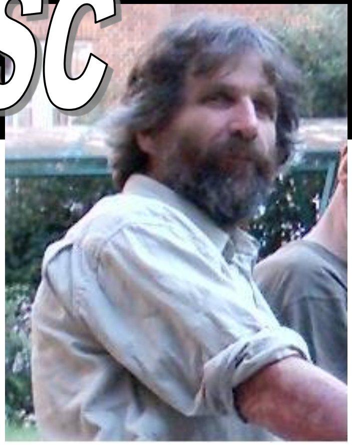
e⁻ withdrawing groups (-NO_2, CF_3, CCl_3, -CN, -SO_3H, -COOH, -COH, -COR, -COOR)

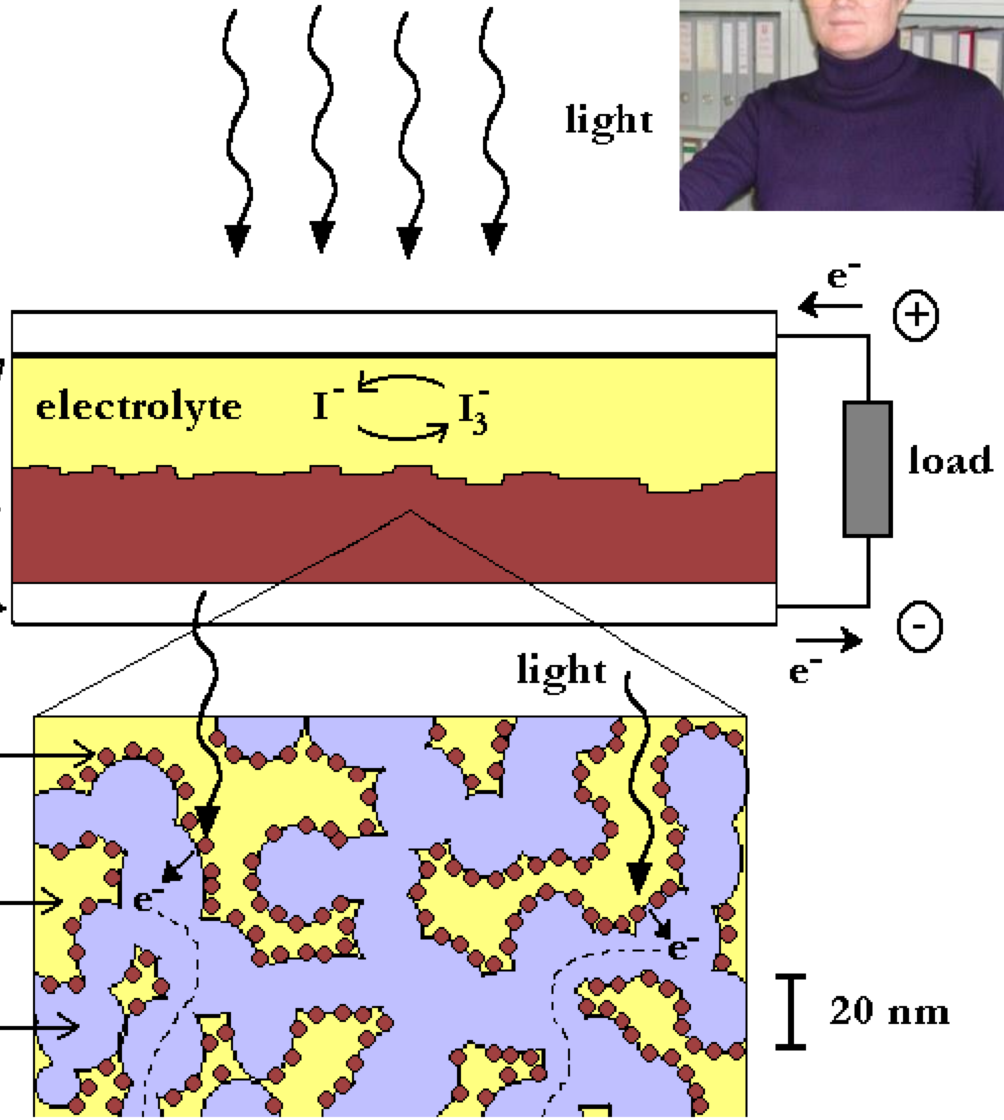
Red. Pot. ↓ **LUMO ↓** // Oxd. Pot. ↑ **HOMO ↓**

e⁻ releasing groups (-NH_2 -NHR -NR_2, -OH, -$NHCOCH_3$ –NHCOR, -OCH_3 –OR, -R)

Red. Pot. ↑ LUMO ↑ // Oxd. Pot. ↓ **HOMO ↑**

DSSC

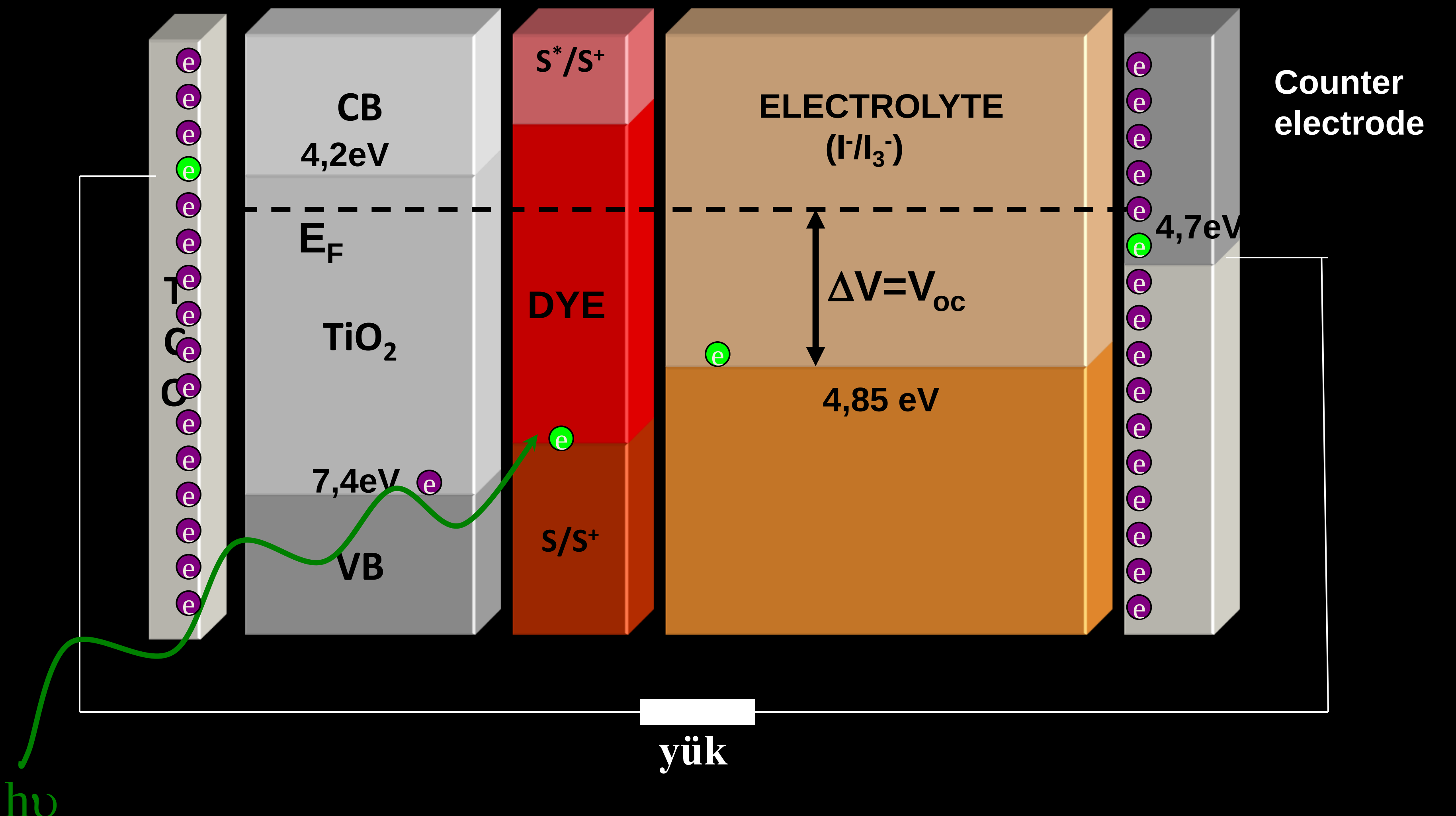




Semiconductor
Anatase TiO_2
Eg=3.2 eV

Alternatives: wide range of semiconductor metal oxides

DSSCs



CB
4,2eV
E_F
TiO2
7,4eV
VB
S*/S+
DYE
S/S+
ELECTROLYTE
(I-/I3-)
ΔV=Voc
4,85 eV
4,7eV
Counter electrode
yük
hυ

Grätzel solar cell

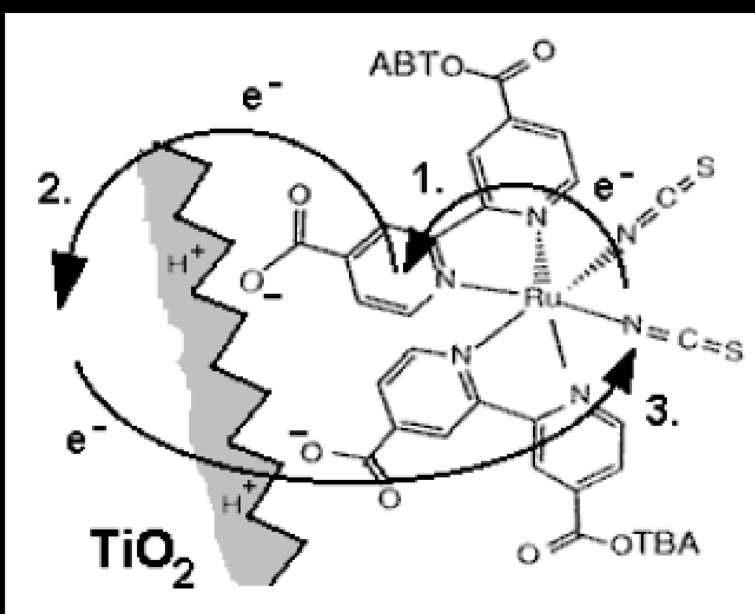
- Compounds for each task
- low- to medium-purity materials sufficient
- low-cost processes
- lower efficiency (> 10 %)

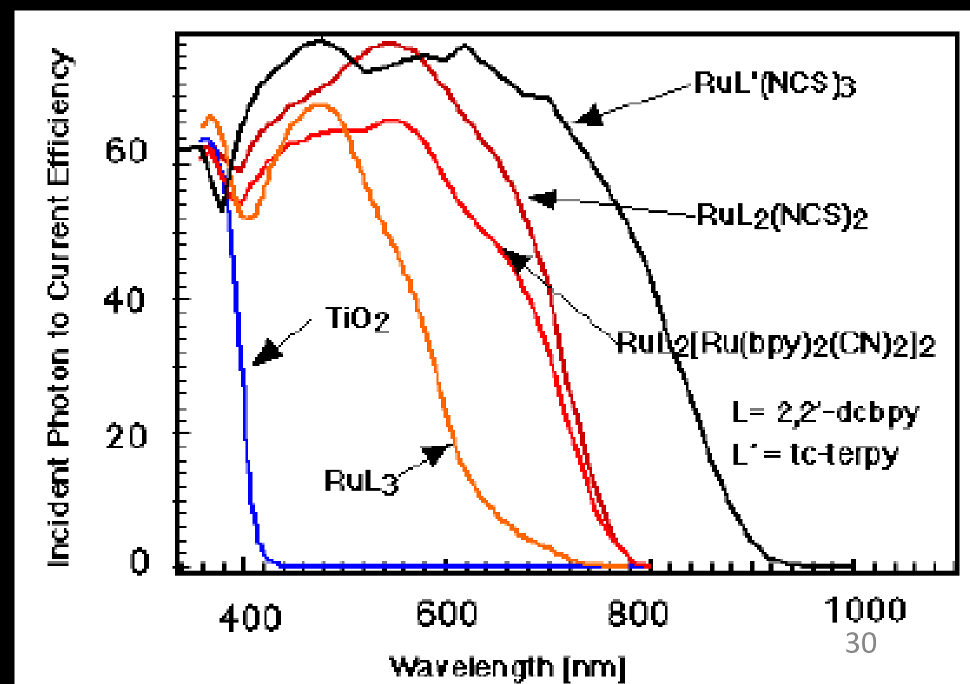
Conventional semiconductor solar cell

- One compound
- high-purity materials needed
- expensive production
- higher efficiency (> 20 %)

Limitations

- long-term stability
- weather influences
- absorption wavelength of the dye
- ~~electrolyte~~





DYES

- Adequate conductivity
- Good oxidative stability (water, oxygen)
- Good radical cation/anion stability
- Good temperature stability

- Compatible energy states with the metal oxide (eg. TiO_2) & electrolyte

Ruthenium dyes

Phthalocyanine dyes

Coumarin dyes

Indoline dyes

Triaril amine dyes

Carbazole dyes

Perylene dyes

Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Inorganica Chimica Acta 361 (2008) 671–676
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis of an amphiphilic ruthenium complex with swallow-tail bipyridyl ligand and its application in nc-DSC

Cigdem Sahin [a,b], Cem Tozlu [a,c], Kasim Ocakoglu [a], Ceylan Zafer [a], Canan Varlikli [a,*], Siddik Icli [a,*]

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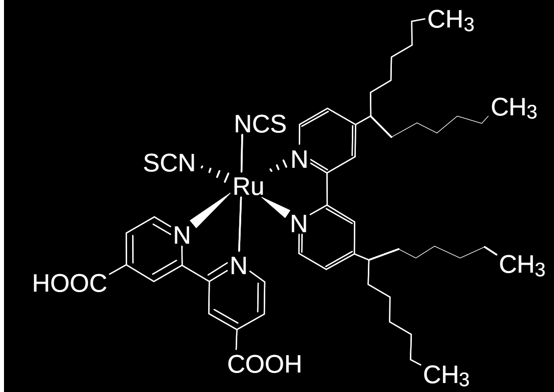
Dedicated to Michael Grätzel



Complex	V_{oc} (mV)	I_{sc} (mA/cm^2)	I_m (mA/cm^2)	V_m (mV)	MPP	FF	η (%)	Electrolyte	Active area (cm^2)
CS9 (inDMF)	630	14,59	12,62	450	5,68	0,62	5,68	BMII	0,292
CS9 (inACN:t-BuOH)	590	14,44	12,55	420	5,27	0,62	5,27	In ACN	
Z-907 (inACN:t-BuOH)	650	18,58	14,10	400	5,64	0,47	5,64	BMII In ACN	0,292

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Contents lists available at SciVerse ScienceDirect

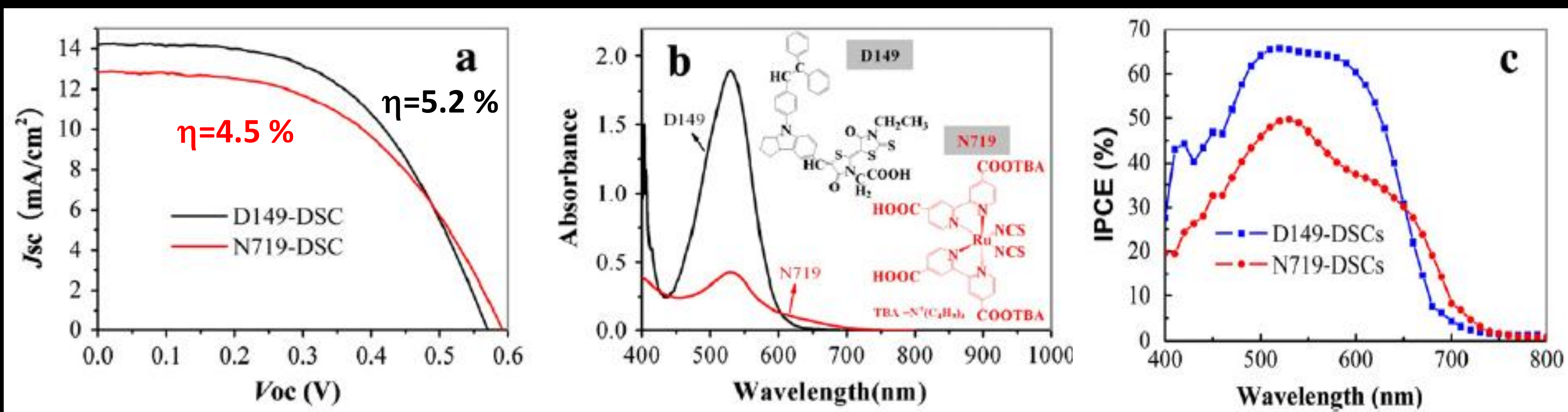
Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

A comparative study on indoline dye- and ruthenium complex-sensitized hierarchically structured ZnO solar cells

Yuannv Ren [a], Yan-Zhen Zheng [a,b], Jiaxing Zhao [a], Jian-Feng Chen [b], Weilie Zhou [c], Xia Tao [a,*]

[a] State Key Laboratory of Organic–inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
[b] Research Center of the Ministry of Education for High Gravity Engineering & Technology, Beijing University of Chemical Technology, Beijing 100029, China
[c] Advanced Materials Research Institute University of New Orleans New Orleans, LA 70148, USA



improved performance is attributed to ; enhanced light harvesting and reduced electron transfer resistance.

Solar Energy Materials & Solar Cells ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

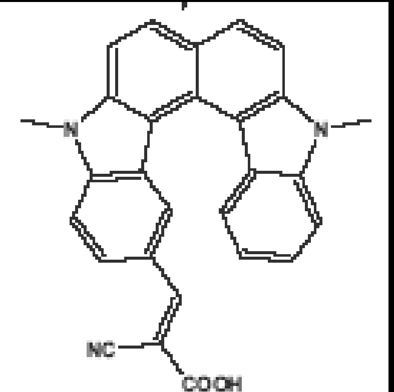
Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

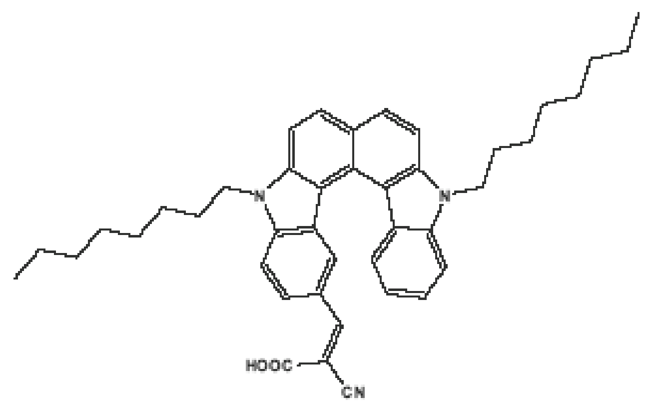
Carbazole-based organic dye sensitizers for efficient molecular photovoltaics

Ceylan Zafer[a,*], Burak Gultekin[a], Cihan Ozsoy[a], Cem Tozlu[a,b], Banu Aydin[a], Siddik Icli[a]

[a] Solar Energy Institute, Ege University, TR-35100 Izmir, Turkey
[b] Department of Physics, Art and Science Faculty, Mugla University, 48000-Mugla, Turkey



BG501



BG502

DSSC performance parameters of dyes[a].

Dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	M. Power (mW/cm^2)	J_{mpp} (mA/cm^2)	V_{mpp} (mV)	Efficiency (%)
BG-501	7.46	560	0.60	2.49	6.56	380	2.49
BG-502	8.40	660	0.57	3.18	7.23	440	3.18
Z907	15.29	600	0.46	4.20	11.66	360	4.20

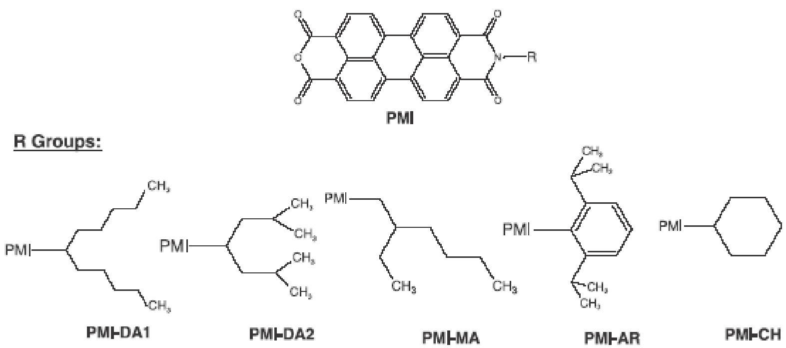
Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Solar Energy Materials & Solar Cells 91 (2007) 427–431
Solar Energy Materials and Solar Cells
www.elsevier.com/locate/solmat

New perylene derivative dyes for dye-sensitized solar cells

Ceylan Zafer[a], Mahmut Kus[a,b], Gulsah Turkmen[a], Haluk Dincalp[c], Serafettin Demic[a], Baha Kuban[d], Yildirim Teoman[d], Siddik Icli[a,*]

[a]Solar Energy Institute, Ege University, TR-35040 Izmir, Turkey
[b]Department of Chemistry, Faculty of Art and Science, Mugla University, TR-48000 Mugla, Turkey
[c]Department of Chemistry, Faculty of Art and Science, Celal Bayar University, TR-45030 Manisa, Turkey
[d]Türkiye Şişe ve Cam Fabrikaları A.Ş. (ŞİŞECAM), TR-80620 Istanbul, Turkey

Available online 13 November 2006



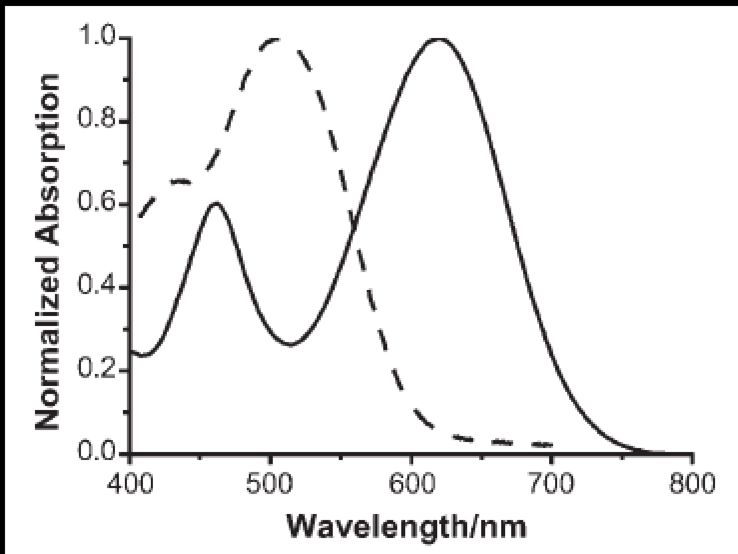
I–V mesurement results of DSSs sensitized with PMI-DA1, PMI-DA2, PMI-MA, PMI-AR, PMI-CH, and standard dye *Z*–907 under illumination with 100 mW/cm^2 light intensity by AM 1.5 solar simulator

	PMI-DA1	PMI-DA2	PMI-MA	PMI-AR	PMI-CH	*Z*-907
V_{oc} (V)	0.300	0.300	0.26	0.251	0.273	0.550
I_{sc} (mA/cm^2)	9.79	8.40	6.73	4.1	0.24	18.02
V_{mpp} (V)	0.200	0.190	0.15	0.169	0.190	0.310
I_{mpp} (mA/cm^2)	8.09	6.12	4.37	3.6	1.9	13.64
MPP (mW)	1.61	1.16	0.65	0.60	0.367	4.22
FF	0.55	0.46	0.37	0.58	0.6	0.42
η (%)	1.61	1.16	0.65	0.60	0.37	4.22

An Improved Perylene Sensitizer for Solar Cell Applications

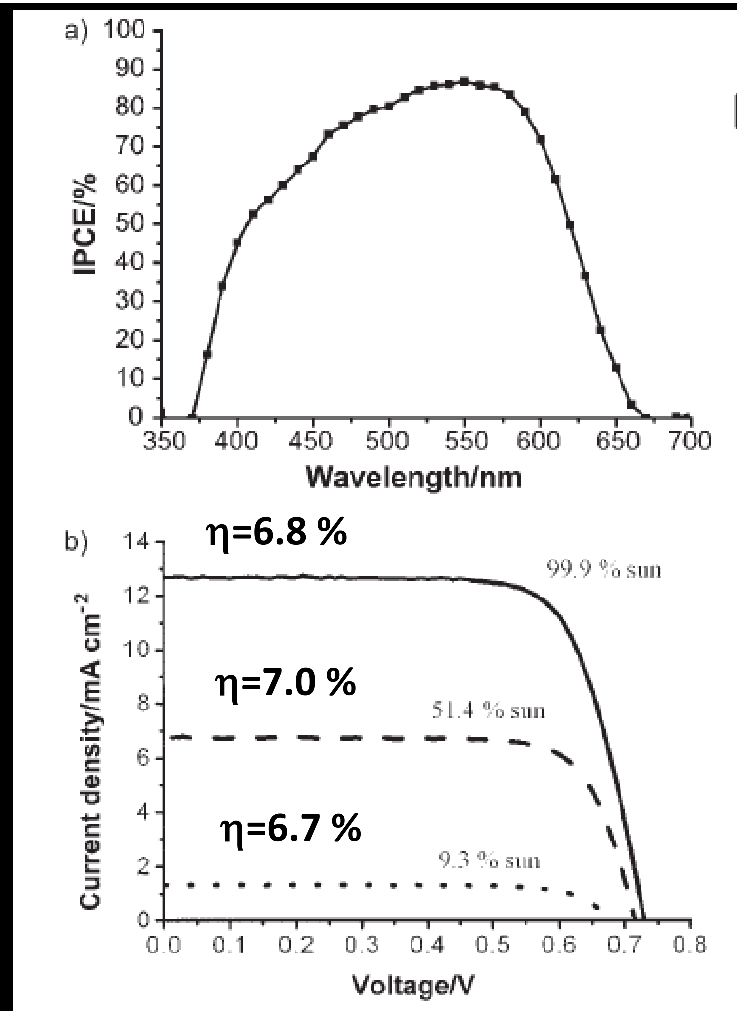
Chen Li,[a] Jun-Ho Yum,[b] Soo-Jin Moon,[b] Andreas Herrmann,[c] Felix Eickemeyer,[d] Neil G. Pschirer,[d] Peter Erk,[d] Jan Schöneboom,[d] Klaus Müllen,[a] Michael Grätzel,[b] and Mohammad K. Nazeeruddin*[b]

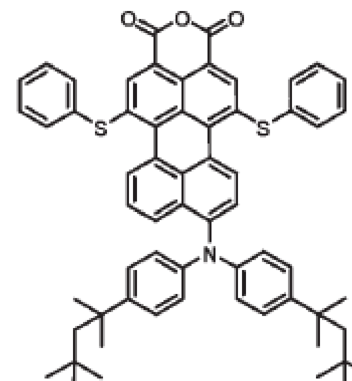
ChemSusChem 2008, 1, 615 – 618



Normalized UV/Vis absorption spectra of 5 in dichloromethane (solid line) and absorbed on a nonocrystalline 6-µm transparent TiO2 film (dashed line).

SSDSSC performance was only 1.78%





5

a) IPCE spectrum and b) J–V curve of 5-sensitized solar cells based on a volatile electrolyte (active area 0.2 cm2). The redox electrolyte was composed of 0.6m 1-butyl-3-methylimidazolium iodide, 0.05m iodine, 0.1m LiI and 0.5m tert-butylpyridine in 15:85 (v/v) valeronitrile/acetonitrile.

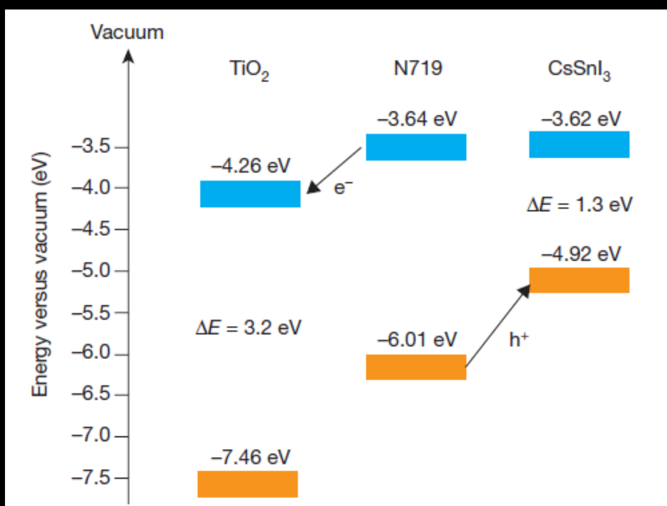
LETTER

486 | NATURE | VOL 485 | 24 MAY 2012

doi:10.1038/nature11067

All-solid-state dye-sensitized solar cells with high efficiency

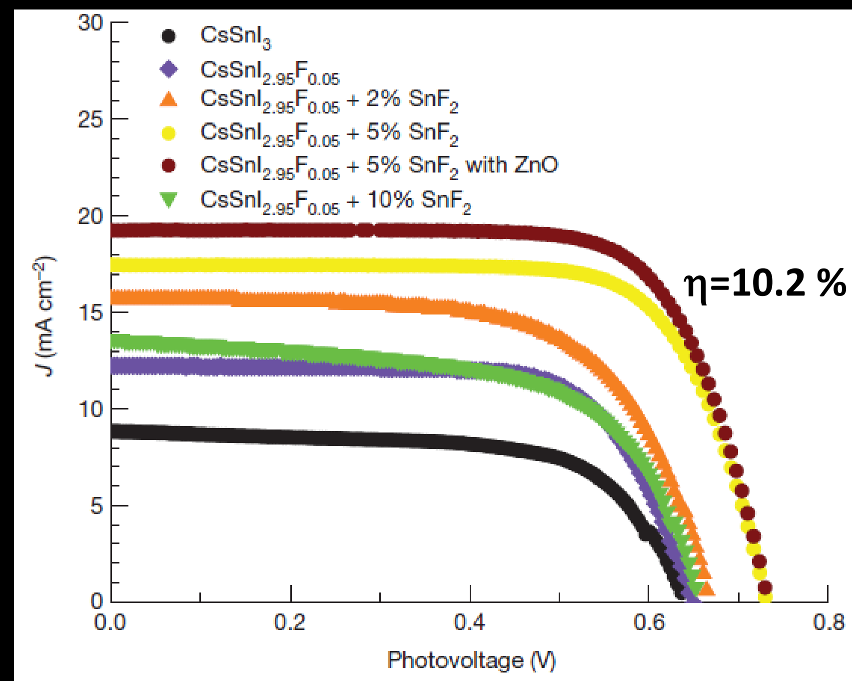
In Chung[1], Byunghong Lee[2], Jiaqing He[1], Robert P. H. Chang[2] & Mercouri G. Kanatzidis[1]



The key characteristics of CsSnI3:

(1) it is solution-processable, and thus permeates throughout the entire TiO2 structure, allowing facile charge separation and hole removal, and

(2) it exhibits very large hole mobilities.



three-dimensional ZnO photonic crystal layers
ZnO photonic crystal had a different hole diameter
-values of 375nm and 410nm were used.

EU_SEI
25 Wp/m^2 η=3.0% -2007
η=5.0% -2009

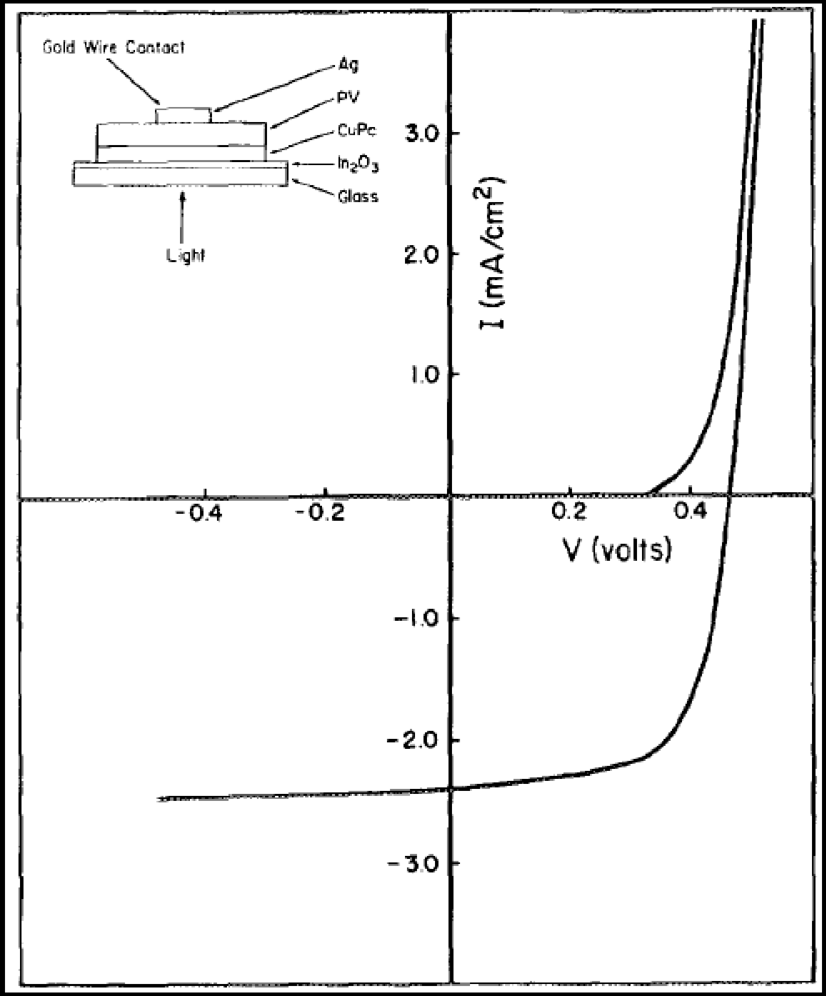
Sony
η 8.4% using a 150mW module (this result was confirmed by an official agency in April 2009)

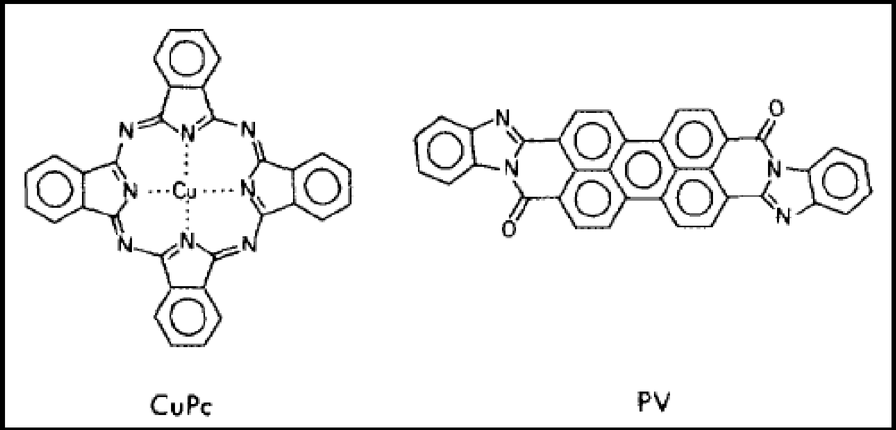
G24i
Isc ≅ 0.2-1.0 mA
Voc ≅ 1.1 V

OSC

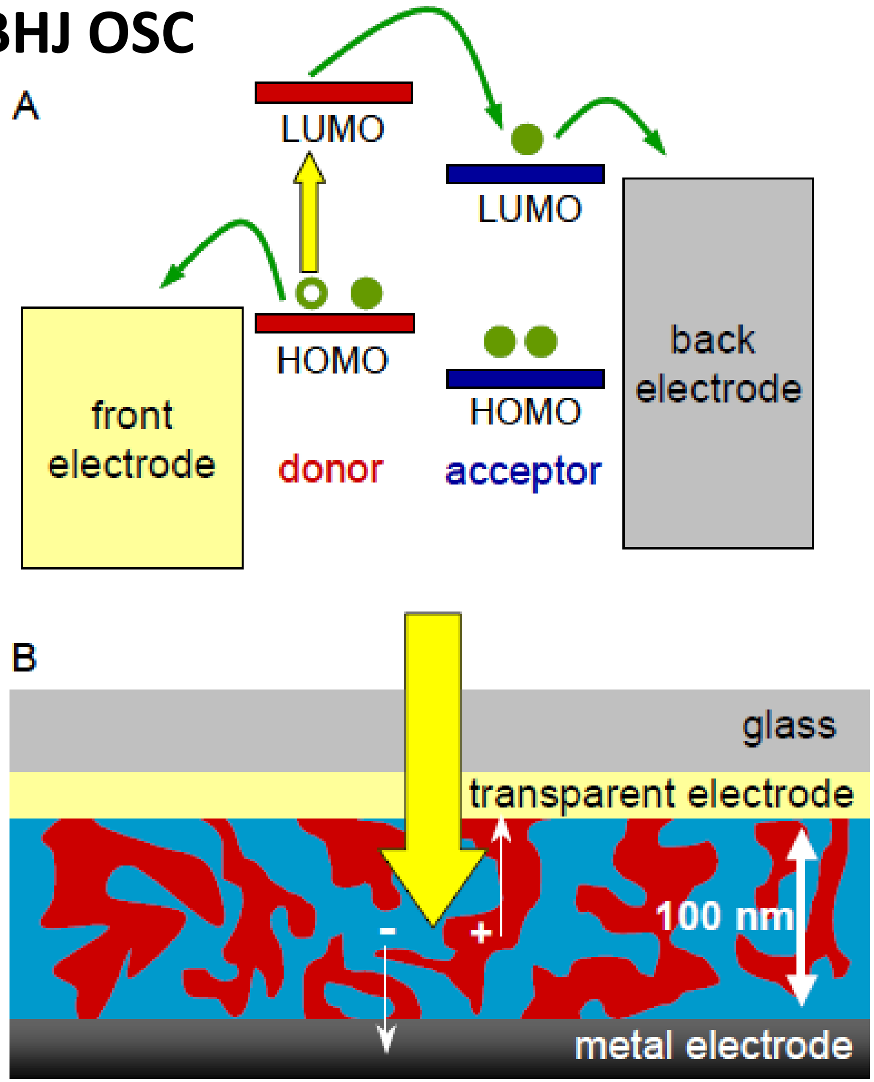
First start with the Tang-Cell

C. W. Tang, Appl.Phys. Lett. 1986, 48, 183

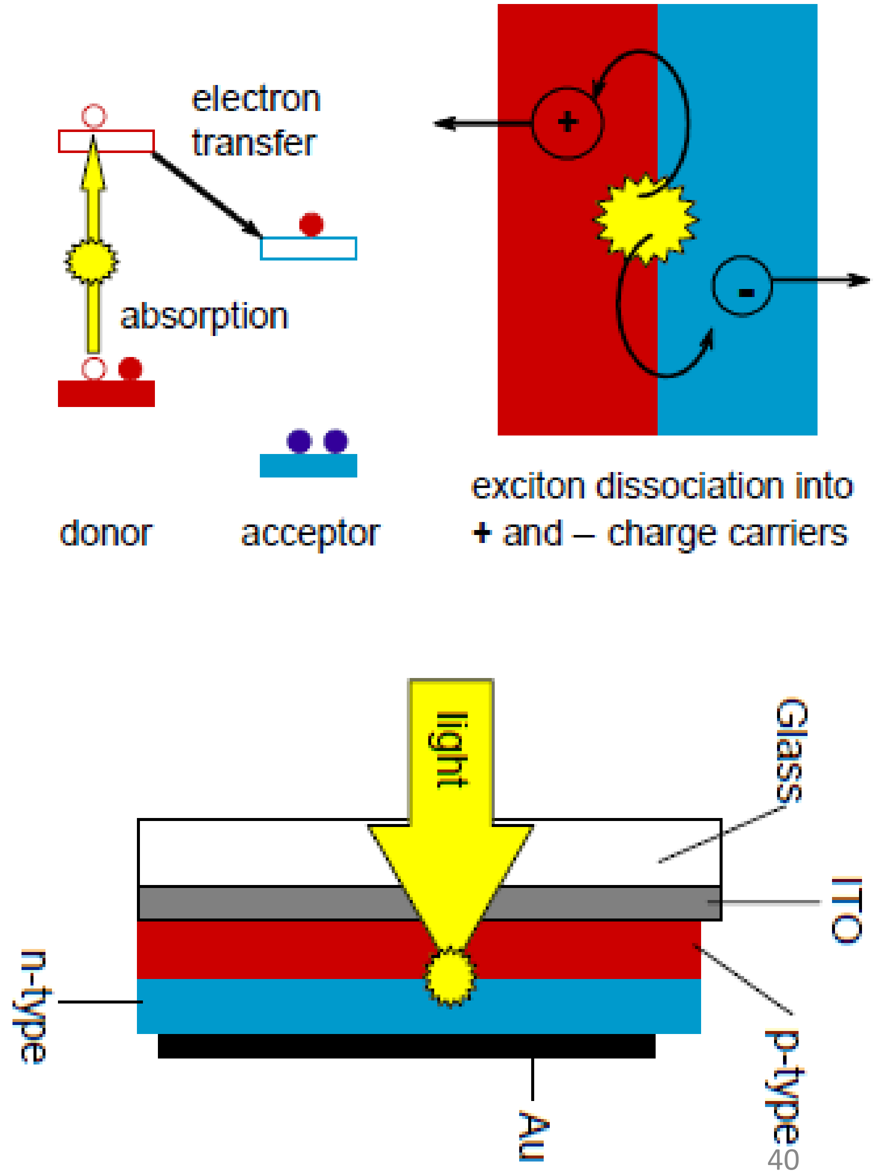




BHJ OSC

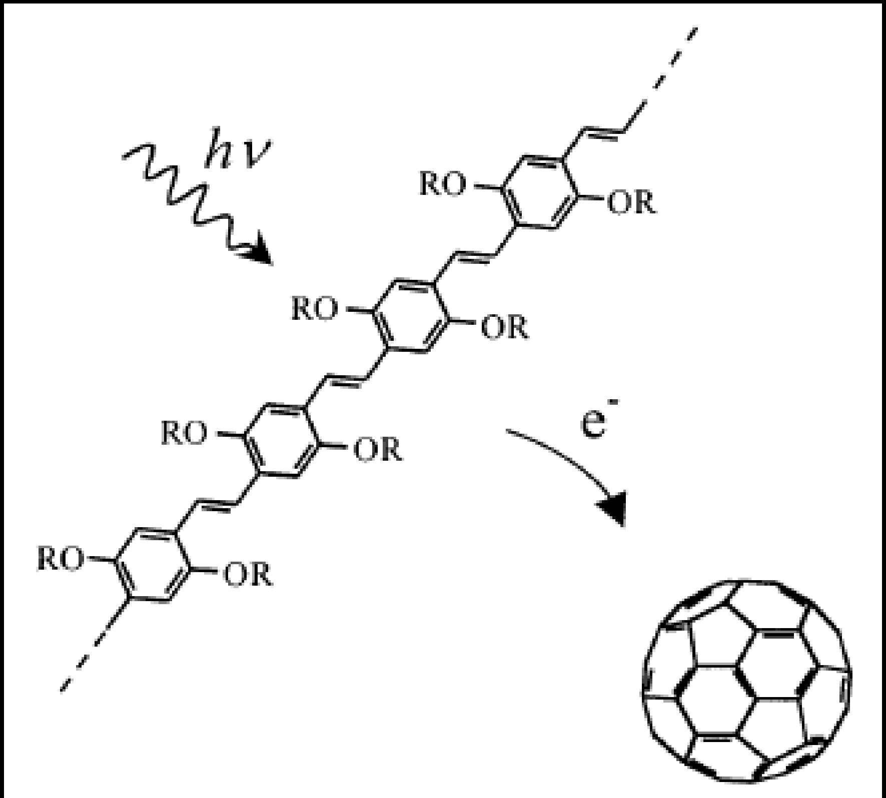


Double layer OSC



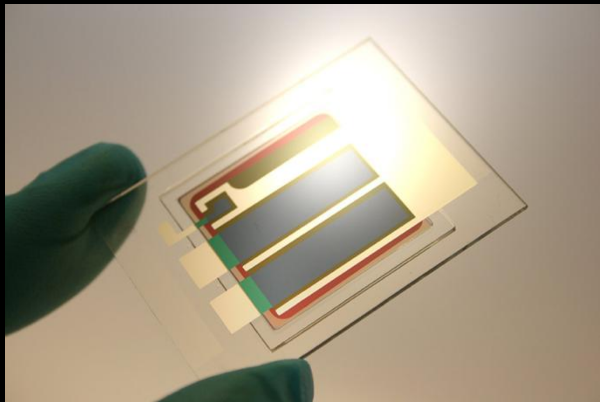
http://user.chem.tue.nl/janssen/SolarCells/Polymer%20solar%20cells.pdf

Alan J. Heeger
1936-
2000 Nobel prize winner



N. S. Sariciftci *et al., Science* **258**, 1474 (1992)

N. Serdar Sariciftci

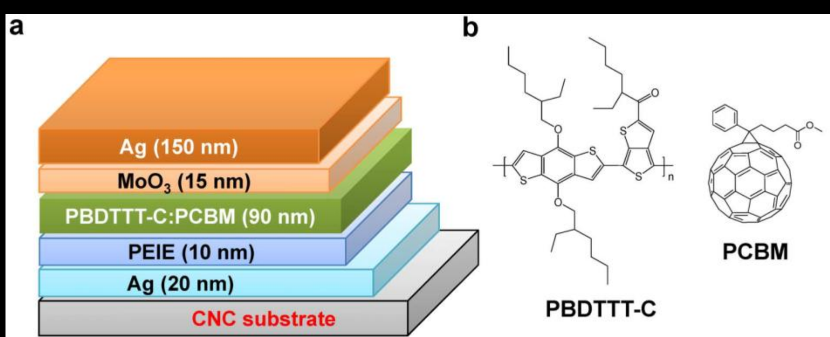


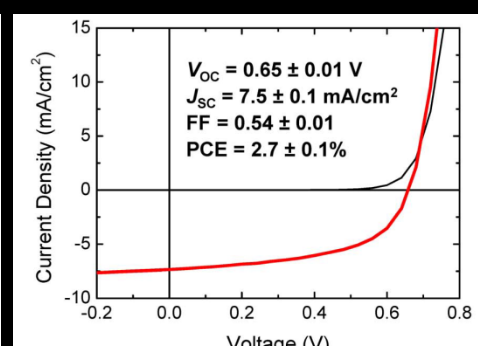
Heliatek world record cells with 12.0% efficiency on an active area of 1.1 cm². © Heliatek GmbH

For achieving this

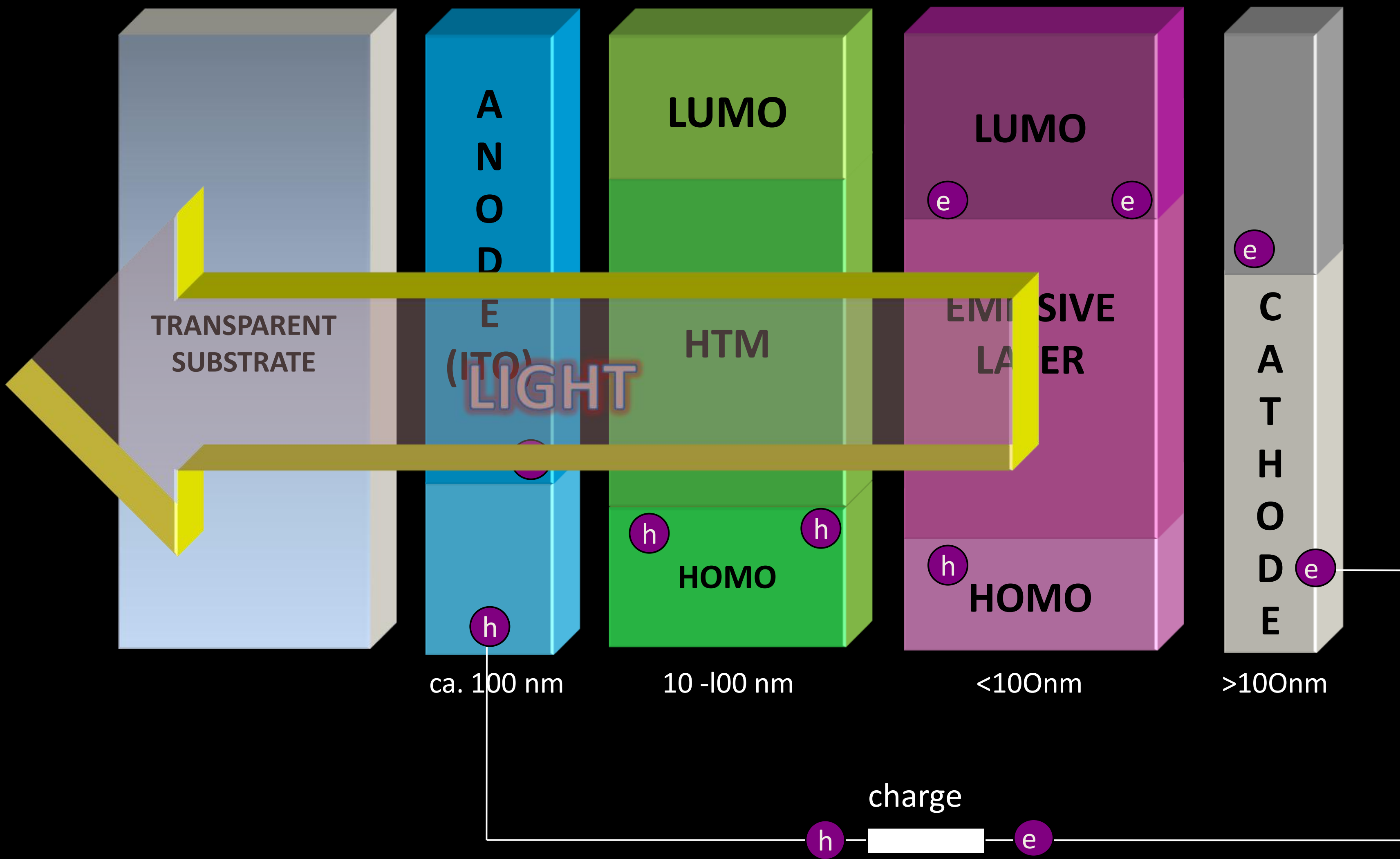
Various	donor-acceptor couples	(P3HT:PCBM is the most popular)
	organic solvents	(chlorobenzene gave better results)
	plasmonic additives	(Ag@SiO2 presented good results)

Recyclable organic solar cells on cellulose nanocrystal substrates
Scientific Reports 3, Article number: 1536, March 2013



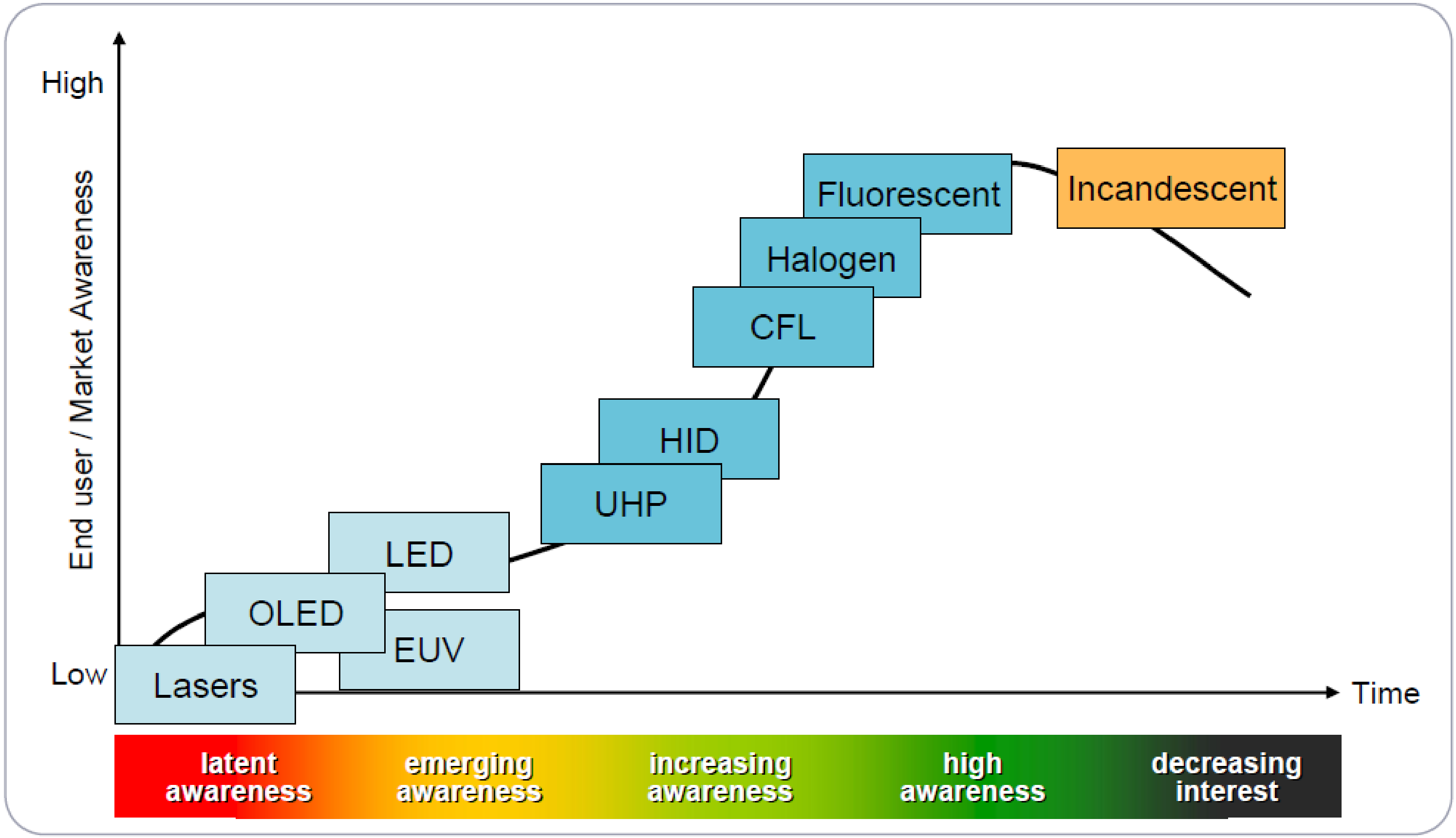


OLED


TRANSPARENT SUBSTRATE
ANODE
(ITO)
LIGHT
LUMO
HTM
HOMO
LUMO
EMI SIVE
LA ER
HOMO
CATHODE
e
h
ca. 100 nm
10 -l00 nm
<10Onm
>10Onm
charge

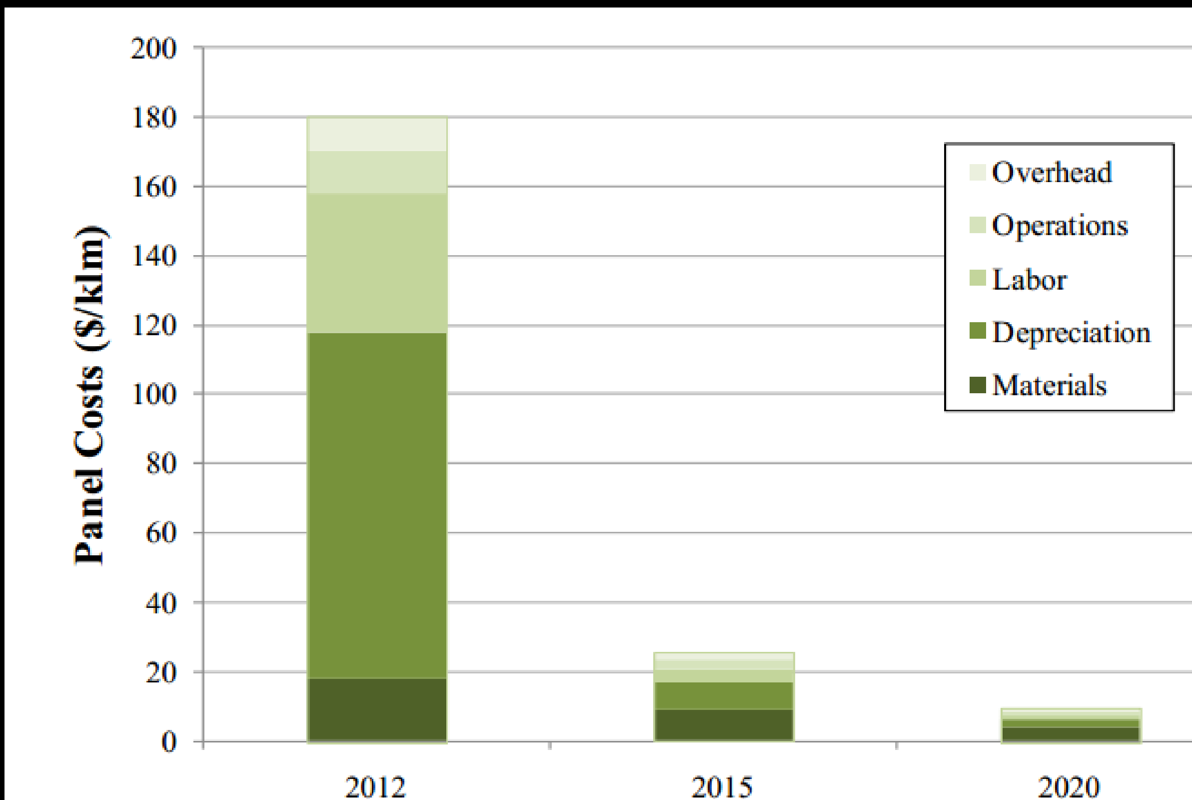
Lighting Technology Roadmap

Product-technology innovation will continue to drive growth in Lighting



Kaynak: Gero Heusler, Philips Lighting, November 8th, 2006

- TK Hatwar et al, Kodak, “Advanced Process Technology for OLED Manufacturing”, IDMC **2009**, paper S05-03
- Michael Eritt et al, e Fraunhofer Institute for Photonic MicroSystems, “Up-Scaling of OLED Manufacturing for Lighting Applications”, SID Digest **2010**, 699-702, paper 46.4
- John Patrin, Veeco, “Development of Linear Evaporation Sources for OLED Display and Lighting Manufacturing”, Intertech-Pira OLED Summit, September **2010**



For the cost reductions:

- Substrate,
- electrode, active organik layer, encapsulation material
- Coating process

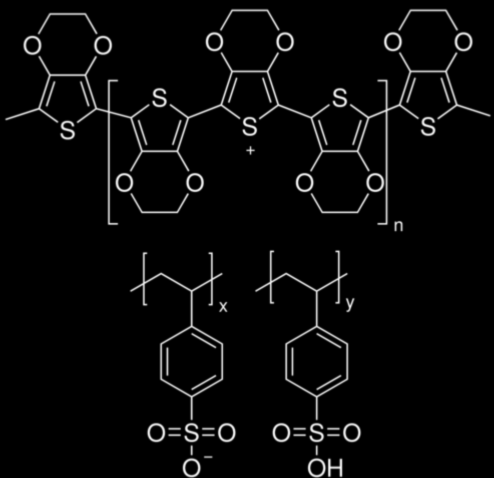
≅%90

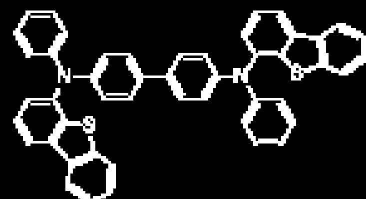
- High brightness
- Large area production

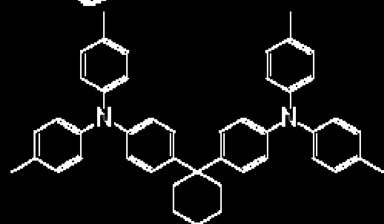
Active area ≅ 15x15 cm^2 70 lm/W 10.000 h

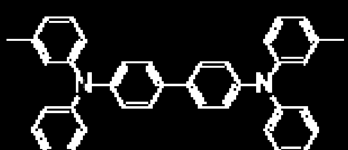
Ref: US. DOE ; office of en. eff. &ren. en. «LED and OLED production lines» report, July 2012

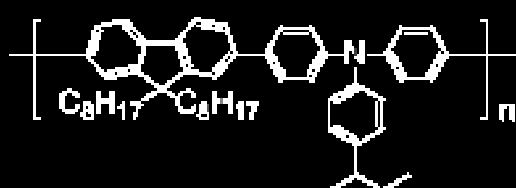
HTM/EBL

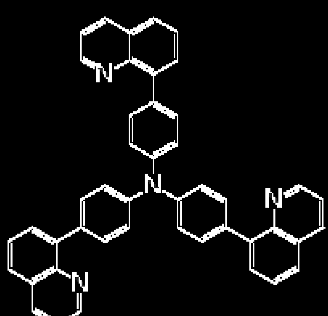








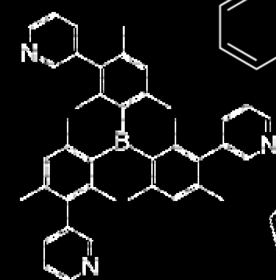


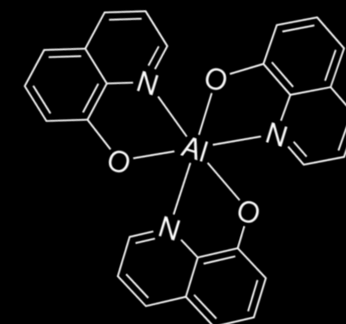


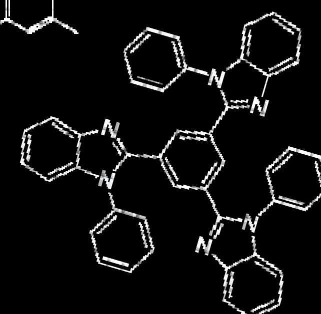
ETL/HBL

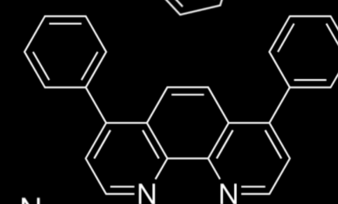
e^- deficient →poor h^+ acceptor molecules

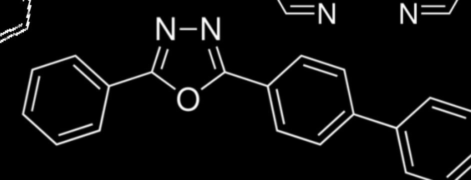
e^- deficient groups ↑ → charge transport↑
Polymer → phase separation ↓
introduction of e^- withdrawing groups (e.g. CN) →
HOMO ↓ LUMO↓

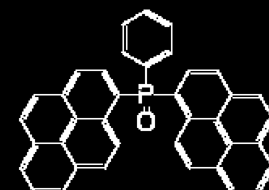


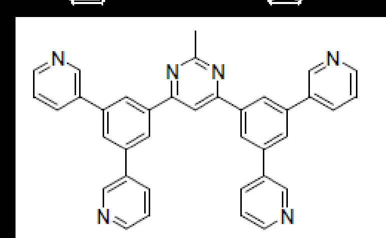


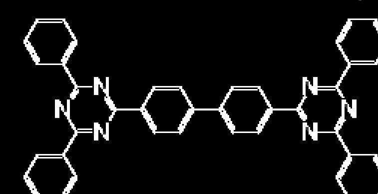










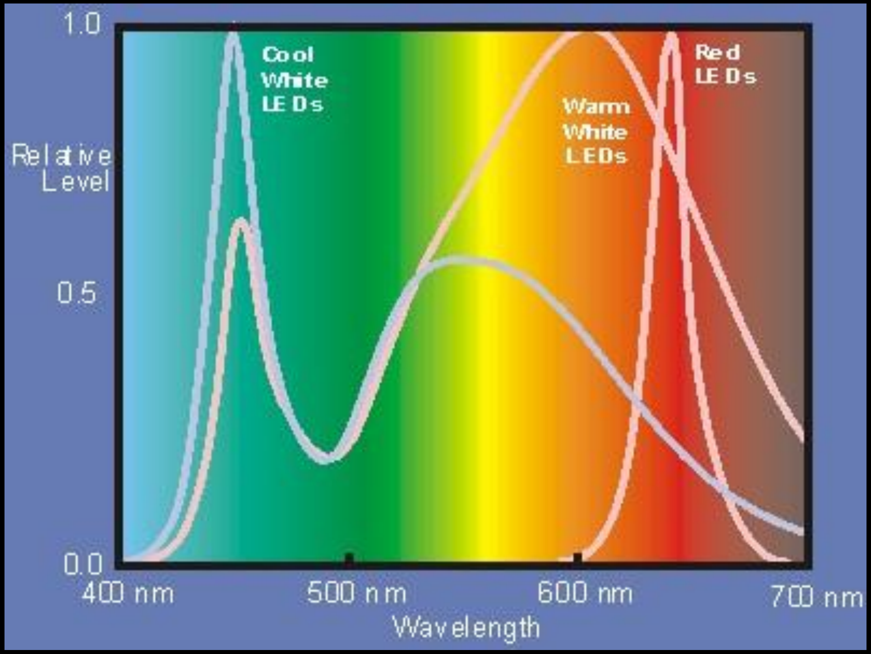


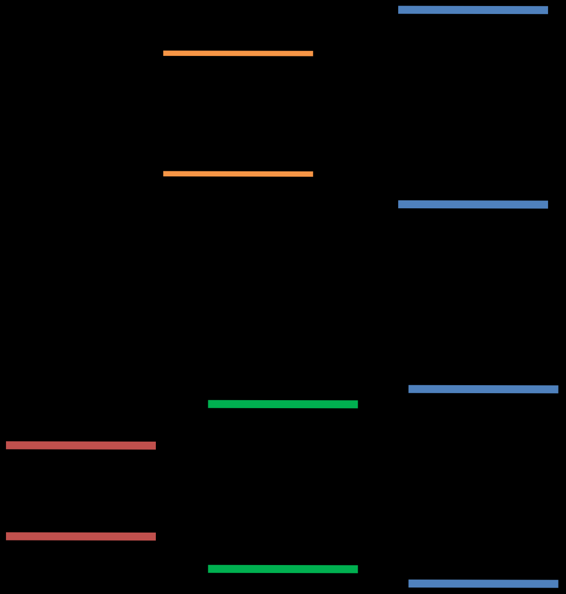
General approches in white light

a) Use of blue and orange red phosphoresent materials as separate layers*

b) Coating of R G B layer by layer**

c) Blue, yellow, orange or R G B emitter in a single layer host***





*Applied Physics Letters 64, 815-817 (1994).

**Applied Physics Letters 91, 263503 (2007).

***Advanced Materials 20, 696-702 (2008); Advanced Materials 16, 624-628 (2004).

General approches in white light

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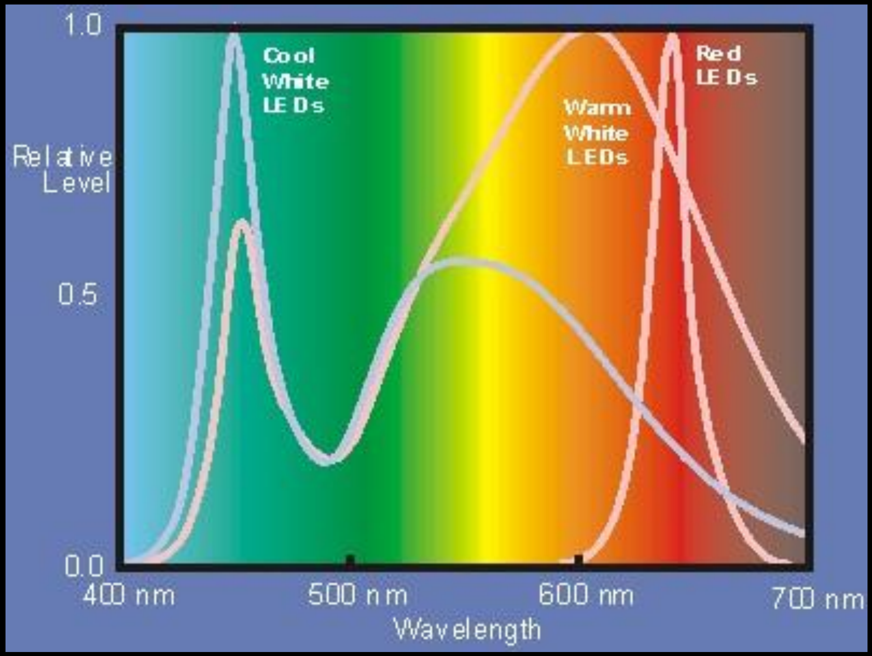
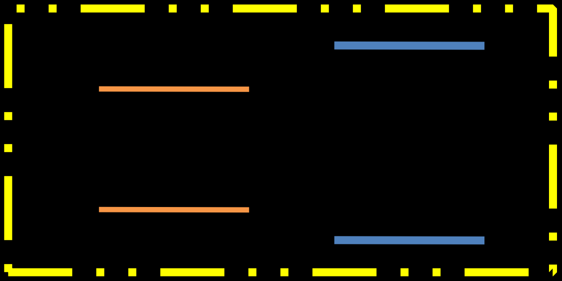
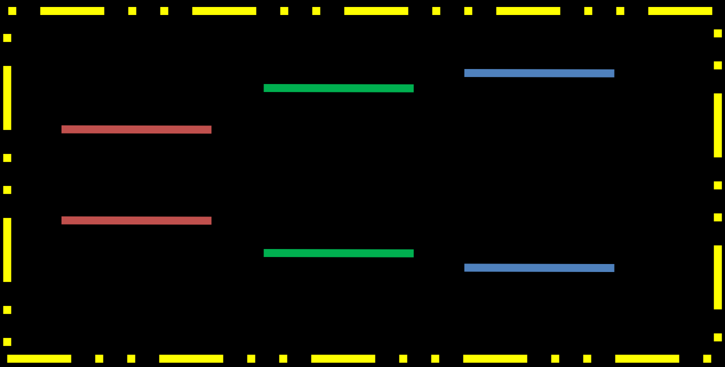




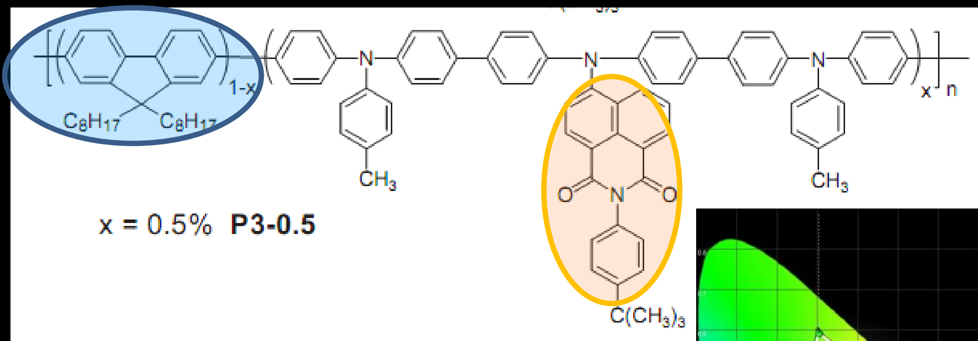


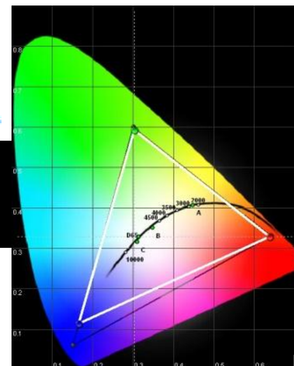
*Applied Physics Letters 64, 815-817 (1994).
**Applied Physics Letters 91, 263503 (2007).
***Advanced Materials 20, 696-702 (2008); Advanced Materials 16, 624-628 (2004).

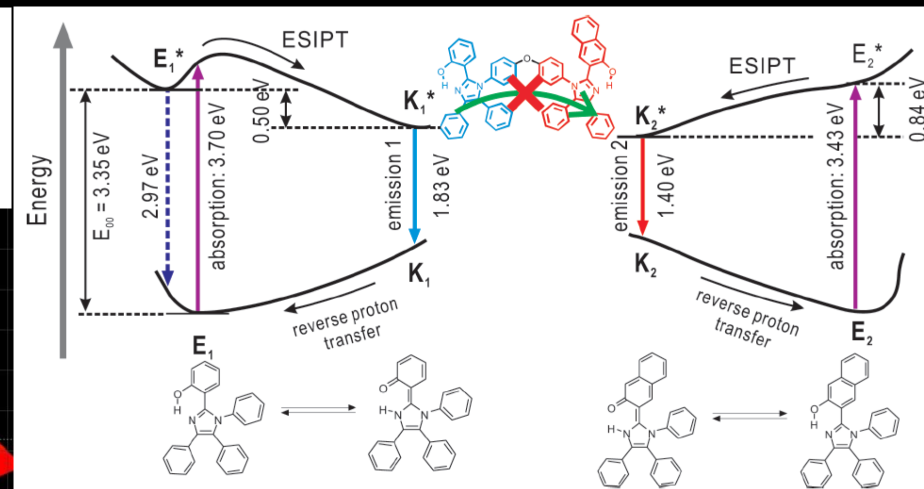
White light from single molecule…

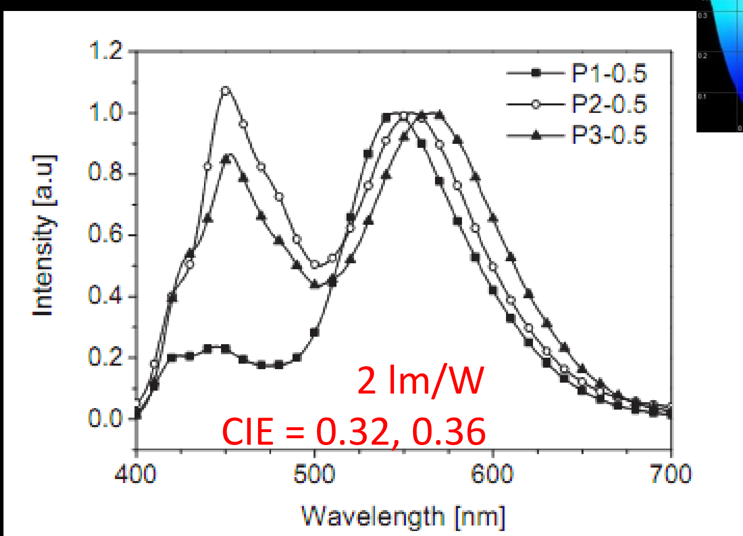
Red and green emiting chromophores in blue emitting polymer chain*

Excited state keto- enol- tautomers in a small molecule**



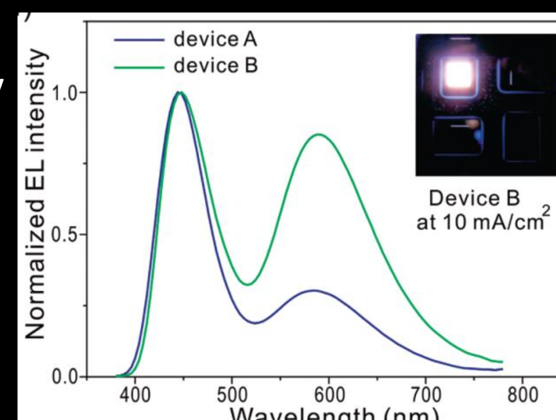






ITO/2-TNATA(60 nm)/NPD (20 nm)/EML(W1, 40 nm)/BPhen(20 nm)/LiF(1 nm)/Al(100 nm) device A
ITO/NPD(40 nm)/EML(W1, 30 nm)/BPhen(50 nm)/LiF(1 nm)/Al(100 nm), device B

0.98 cd/A at 6.7 V
(0.34, 0.29)
1092 cd/m2 max



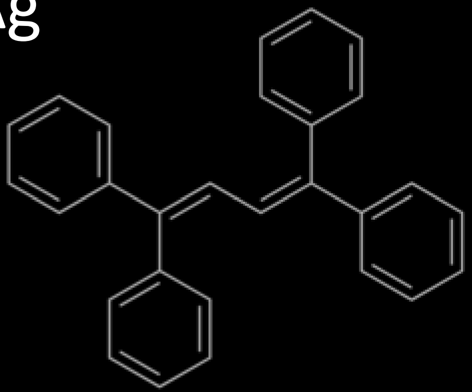
* Advanced Functional Materials 16, 101–106, 2006
**J. AM. CHEM. SOC.. 131, 14043–14049, 2009

First report:

Kido, J. Hongawa, K. ; Okuyama, K. ; Nagai, K. ,
White light-emitting organic electroluminescent devices using the poly(N-vinylcarbazole) emitter layer doped with three fluorescent dyes,
Applied Physics Letters 64, 815-817 (1994).

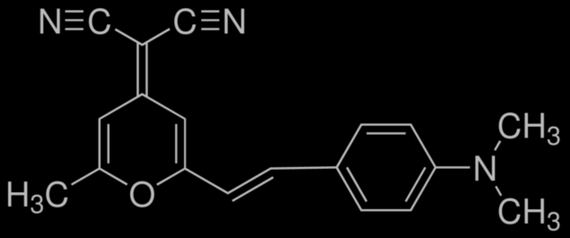
ITO/ doped PVK/ TAZ/ Alq / Mg:Ag

blue-emitting 1,1,4,4-tetraphenyl-1,3-butadiene,



green-emitting coumarin 6, and

orange-emitting DCM 1



luminance of 3400 cd/m^2 drive voltage of 14 V

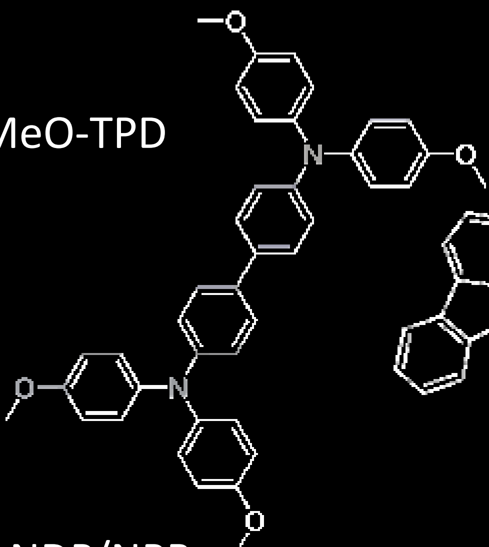
Sebastian Reineke, Frank Lindner, Gregor Schwartz, Nico Seidler, Karsten Walzer, Björn Lüssem & Karl Leo

White organic light-emitting diodes with fluorescent tube efficiency

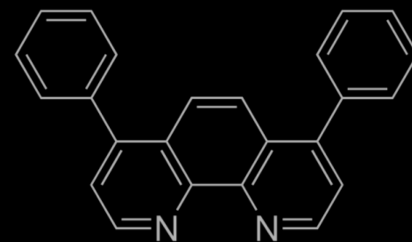
Nature 459, 234–238 (2009)

Glass (n=1.8)/ITO (90 nm)/MeO-TPD:NDP-2 (45 nm)/NPB (10 nm) /TCTA:Ir(MDQ)2(acac) (6 nm)/ TCTA (2 nm)/TPBi:FIrpic (4 nm)/TPBi (2 nm)/TPBi:Ir(ppy)3/TPBi (10 nm)/Bphen:Cs (20-250nm)/ Ag (100 nm)

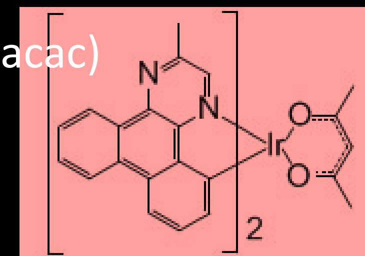
MeO-TPD



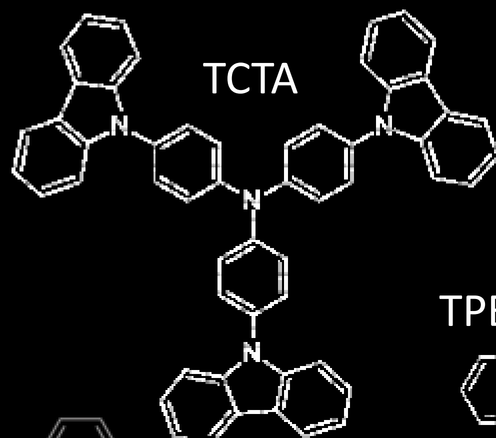
Bphen



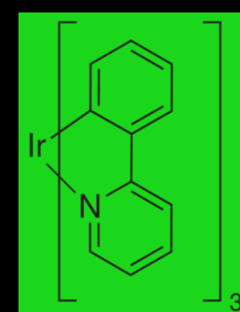
Ir(MDQ)2(acac)



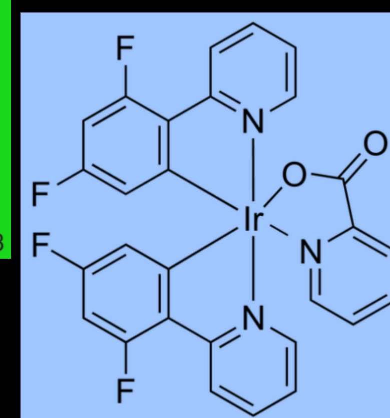
TCTA



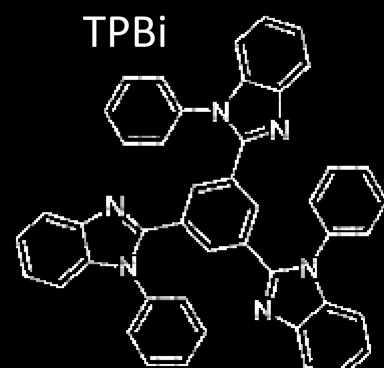
Ir(ppy)3



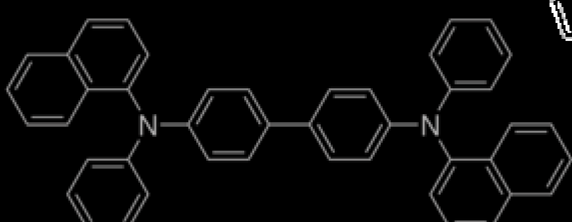
FIrpic



TPBi



NDP/NPB

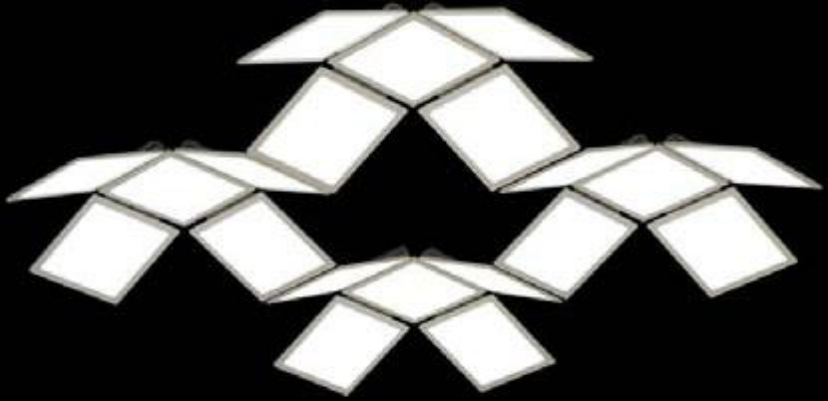


90 lm/W at 1.000 cd/m²

Market

45 OLED panel LG Chem.
CRI > 85
53 lm/W da 3060 lm ≈57 W
15,000 saat (3,000 cd/m^2)

7 panel WAC Lighting Sol™
25 lm/W da 140 lm ≈6,4 W

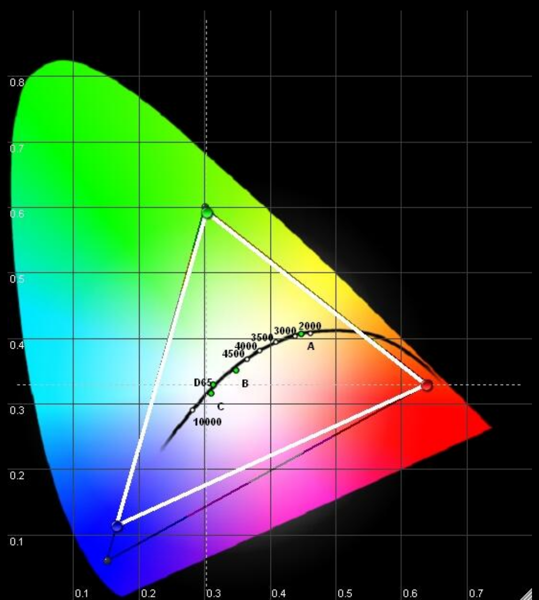


5 panel Acuity Brands,
48 lm/W da 314 lm ≈5,5 W

Firms working on WOLEDs & their efficiency reports (Ref:The OLED Handbook, RonMertens)

Firm	Dimensions (mm)	Power Effc. (lm/W)
PhilipsLumiblade	32 x 32	20
PhilipsLumiblade Plus	70 x 70	45
OSRAM Orbeos	79 x 79	25
Lumiotec Ver 1	145 x 145	11
Lumiotec Ver 2	35 x 75	11
Verbatimvelve	140 x 140	28
Kaneka	-	20
LG Chem	-	45-60

Possible coating process: PVD



Single layer, wet processed WOLED literature

Ref	Year	Power Effc. (lm/W)
Org. Elec., 2013, 14, 2172–2176	2013	42,5
Org. Elec., 2012 13, 2235–2242	2012	30,0
Org. Elec., 2010, 11, 1344–1350	2010	15.6
Adv. Mater. 2009, 21, 361-365	2009	23,4
Adv. Mater. 2009, 21, 4181-4184	2009	20,3
Adv. Mater. 2008, 20, 696-702	2008	7,6
Adv. Mater. 2008, 20, 696-702	2008	9,5
Appl. Phys. Lett. 2006, 88, 141101	2006	4,2
Appl. Phys. Lett. 2005, 87, 193502	2005	5,5

Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

COMMUNICATION

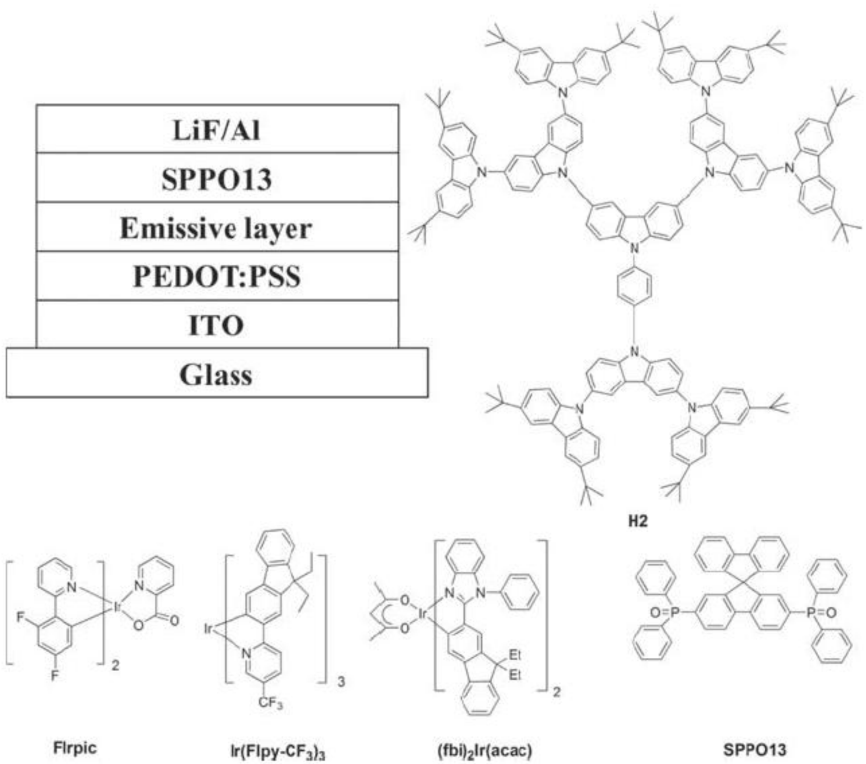
High-Efficiency Single Emissive Layer White Organic Light-Emitting Diodes Based on Solution-Processed Dendritic Host and New Orange-Emitting Iridium Complex

Baohua Zhang, Guiping Tan, Ching-Shan Lam, Bing Yao, Cheuk-Lam Ho, Lihui Liu, Zhiyuan Xie, Wai-Yeung Wong,* Junqiao Ding, and Lixiang Wang**

COMMUNICATION

ADVANCED MATERIALS
www.advmat.de

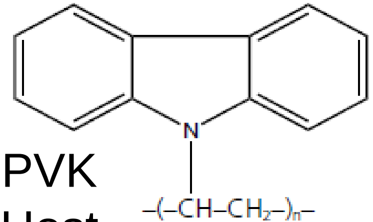
Adv. Mater. 2012, 24, 1873–1877



Scheme 1. The device configuration of the solution-processed WOLEDs and the chemical structures of the materials used.

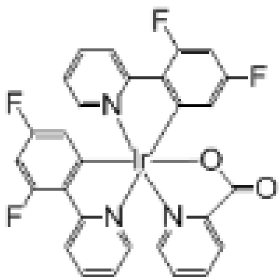
RECORD eff...

70.6 cd/A
26.0 %
47.6 lm/W

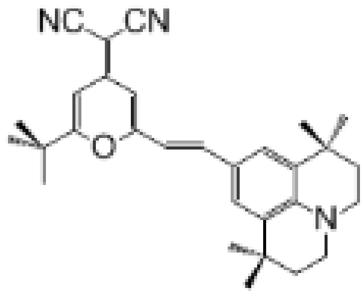


PVK
Host

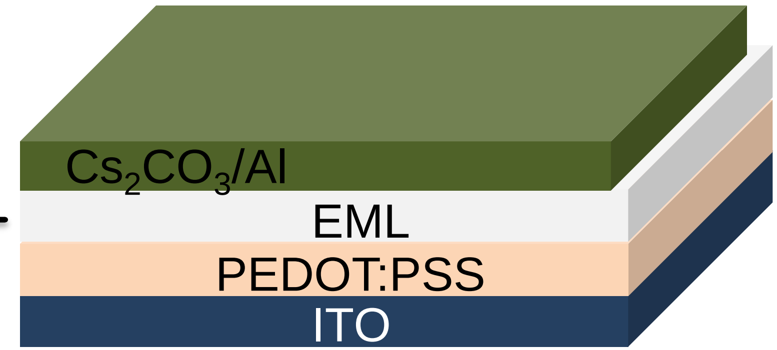
OXD-7
Host

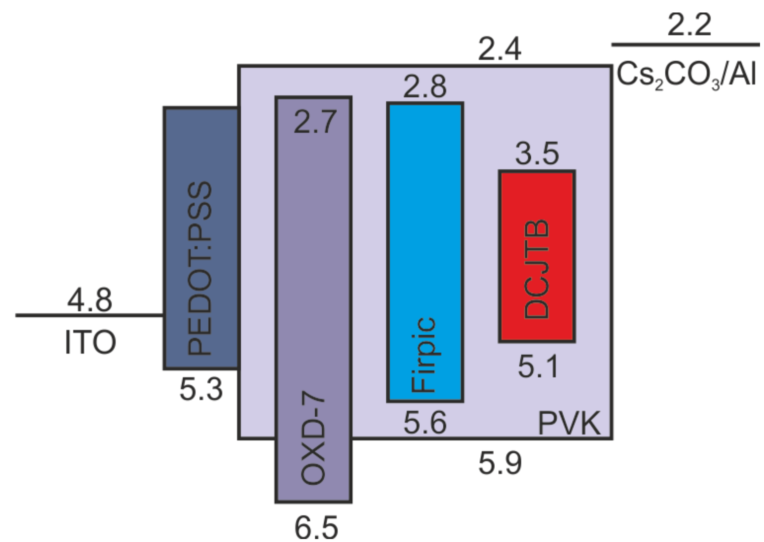


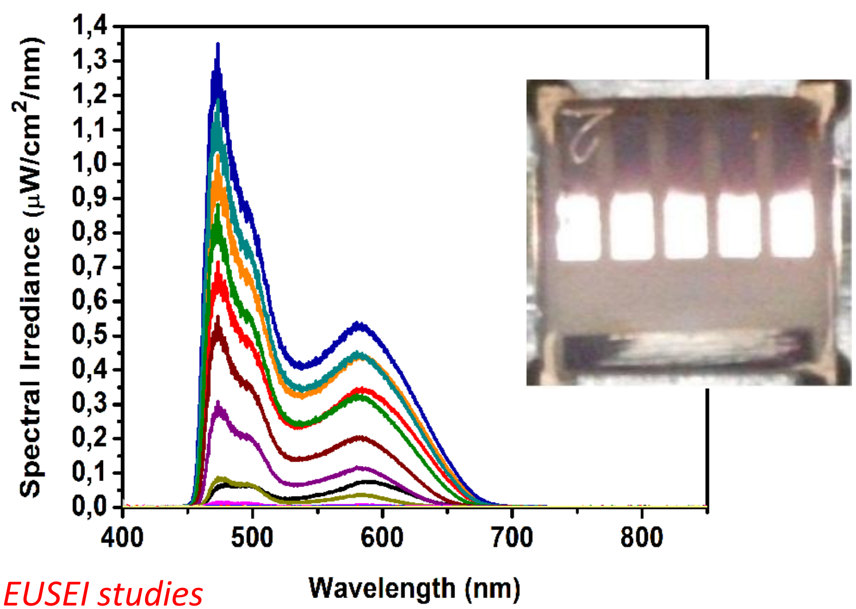
FIrpic
(B)



DCJTB
Orange Red







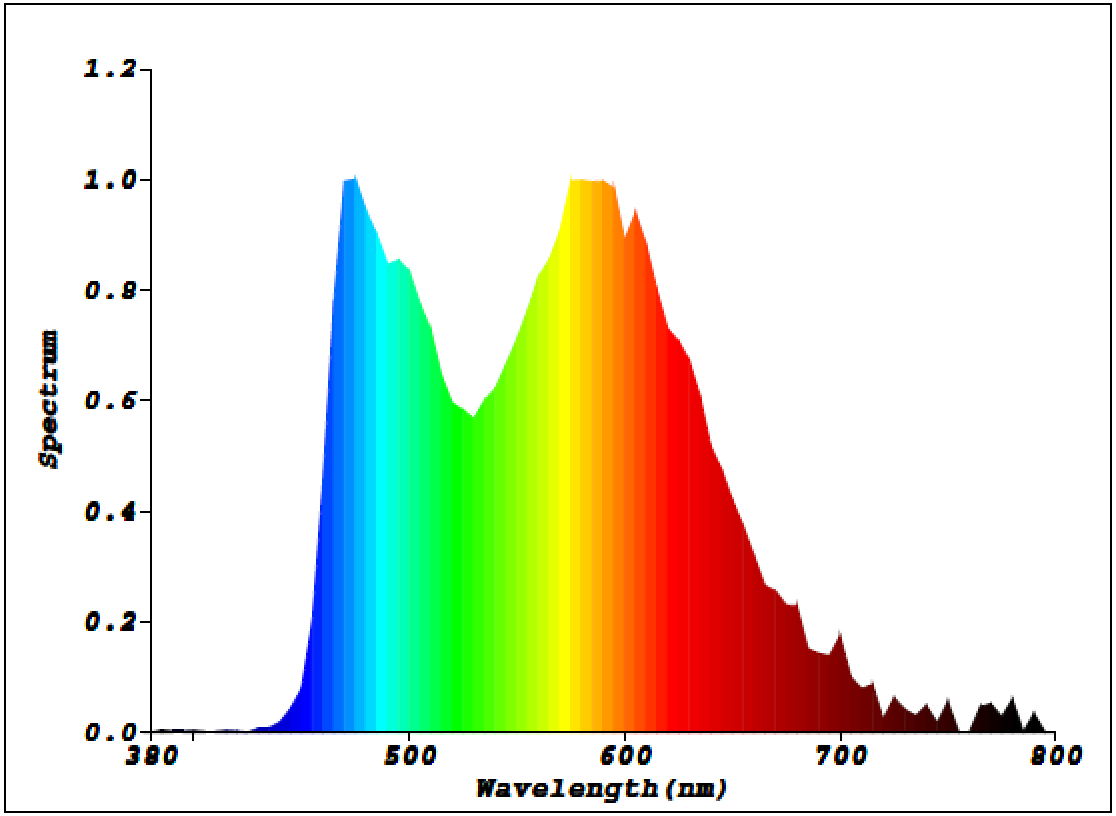
$V_{turn-on}$ =6.3 V

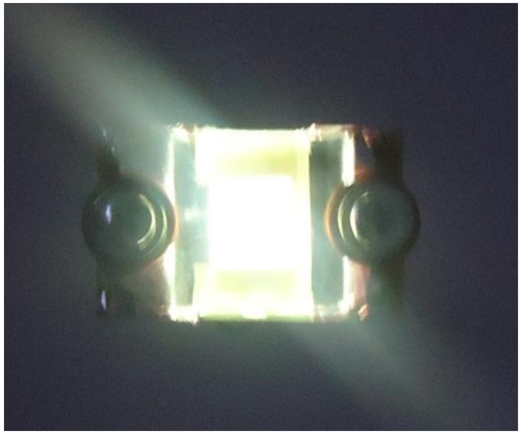
5.8 lm/W

21500 cd/m^2

17.6 cd/A

EUSEI studies





Active area 12x12 mm^2

Chromaticity Coordinate: x=0.3864 y=0.4190

Render Index: Ra=73.9

Efficacy: 21.81 lm/W

@20 mA

EUSEI studies

cost of the noble metals such as Os, Pt and Ir
Ru is the relatively low cost alternative.

Ruthenium Complexes

- Reversible redox process
- Chemically, photochemically and thermally stable
- Phosphorescent emitter
- Good solubility

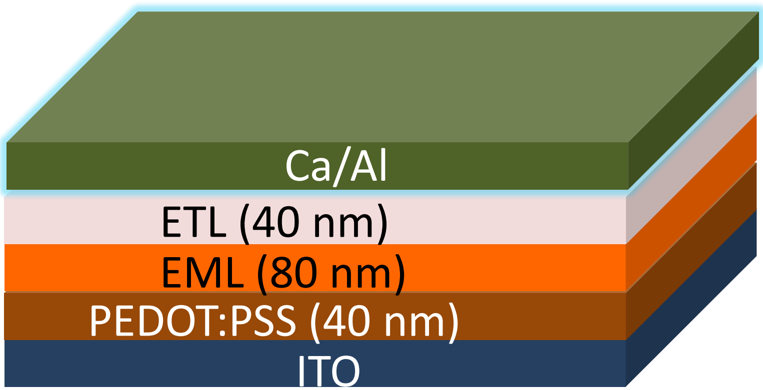
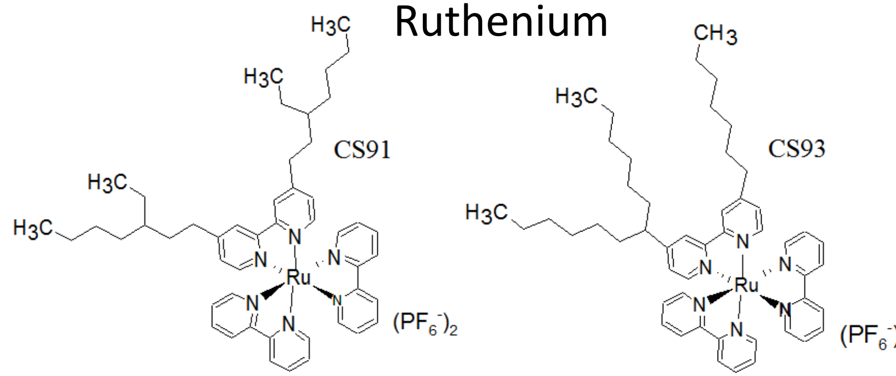
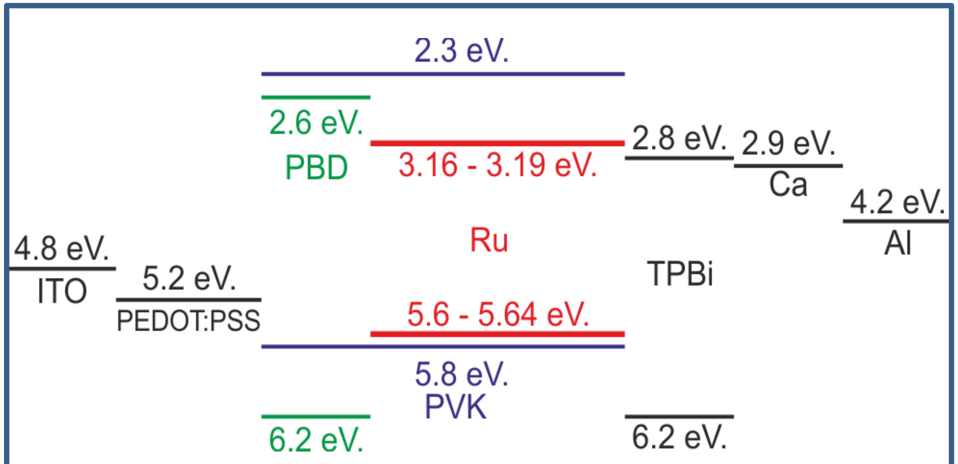
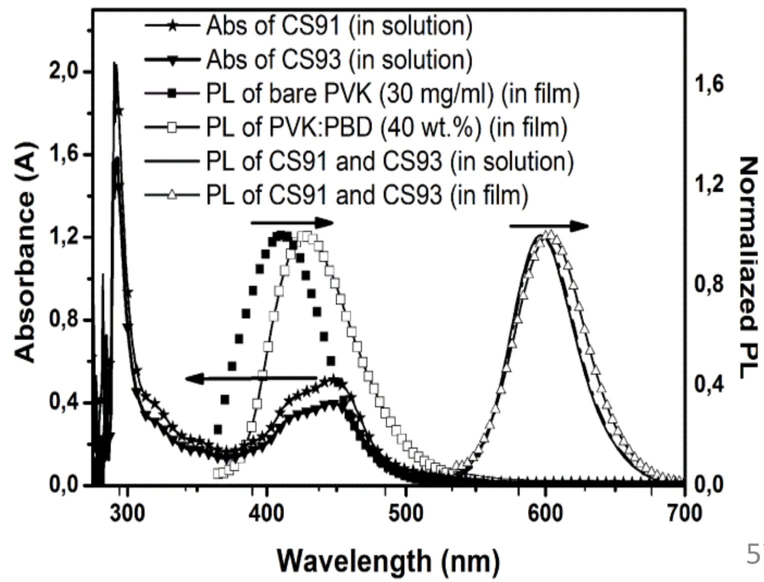


Figure: Device Structure

Ruthenium







EUSEI studies *Dyes and Pigments 95 (2012) 23-32*

Performance characteristics for ITO/PEDOT:PSS/PVK:PBD(40 wt.%):x%CSy /TPBi/Ca/Al devices.

	Luminance [cd m^{-2}]		Luminous efficiency [cd A^{-1}] [a]		Power efficiency [lm W^{-1}] [b]		Quantum efficiency [%][b]		Turn-on voltage [V]		λ_{max} (CIE) [nm]	
X conc. [wt.%]	CS91	CS93	CS91	CS93	CS91	CS93	CS91	CS93	CS91	CS93	CS91	CS93
0.25	1157	395	1.4	1.8	0.3	0.4	0.1	0.12	9.7	9.5	427, 603 (0.53, 0.35)	427, 600 (0.44, 0.31)
0.50	1507	1215	2.8	3.6	0.5	0.8	0.17	0.21	9.2	9.0	427, 603 (0.56, 0.37)	427, 600 (0.55, 0.37)
1.0	1529	3824	2.7	7.0	0.4	1.7	0.13	0.39	11.0	8.5	427, 603 (0.59, 0.38)	427, 600 (0.57, 0.39)
2.0	789	3536	1.2	5.8	0.2	1.3	0.07	0.34	11.2	8.7	607 (0.6, 0.38)	600 (0.59, 0.39)
3.0	344	3426	0.3	3.2	0.07	0.7	0.03	0.2	11.5	9.8	612 (0.61, 0.37)	600 (0.59, 0.39)

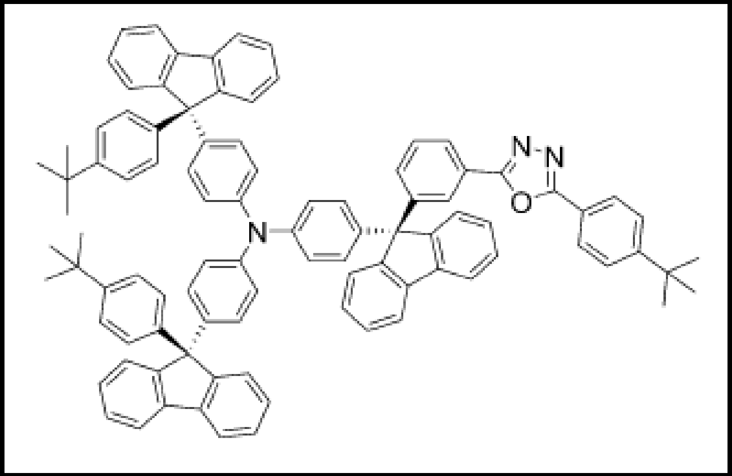
[a]: values at 10 mA cm^{-2}

[b]: values at the driving voltage of 15V.

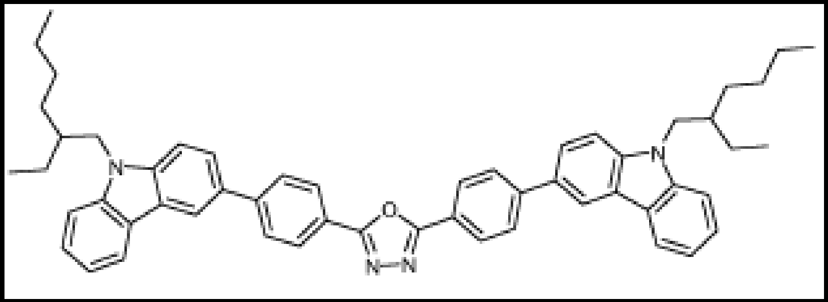
The higher EQE observed for CS93 doped devices are due to decreased aggregation and self-quenching of the CS93 with branched alkyl substituents from the first exocyclic carbon of bpy ligand.

EUSEI studies *Dyes and Pigments 95 (2012) 23-32*

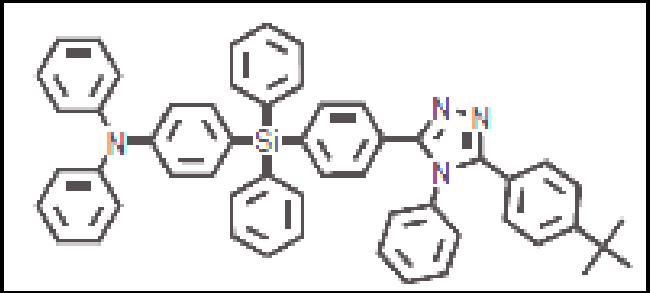
BIPOLAR HOSTS



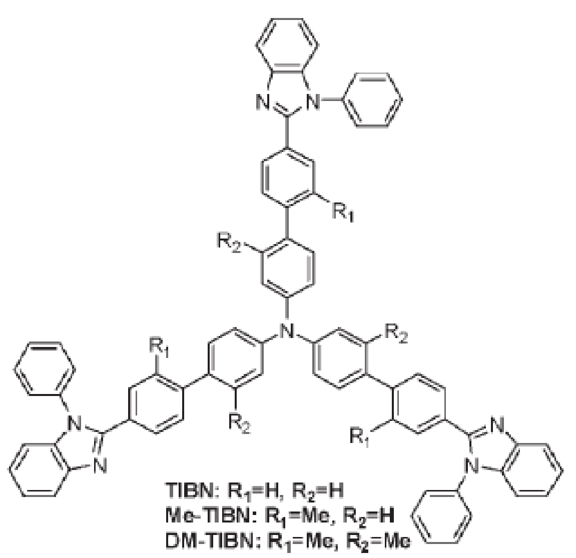
J. Mater. Chem., 2008, 18, 3461–3466



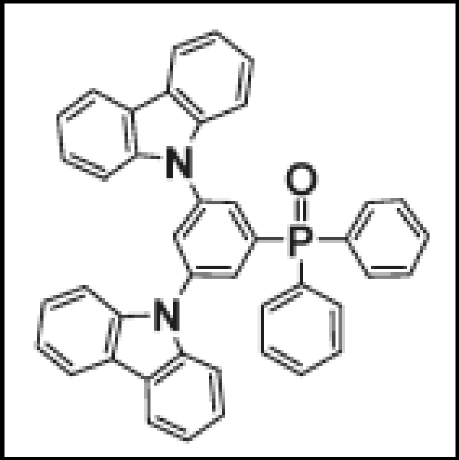
J. Mater. Chem., 2008, 18, 4091–4096



Adv. Mater. 2011, 23, 4956–4959

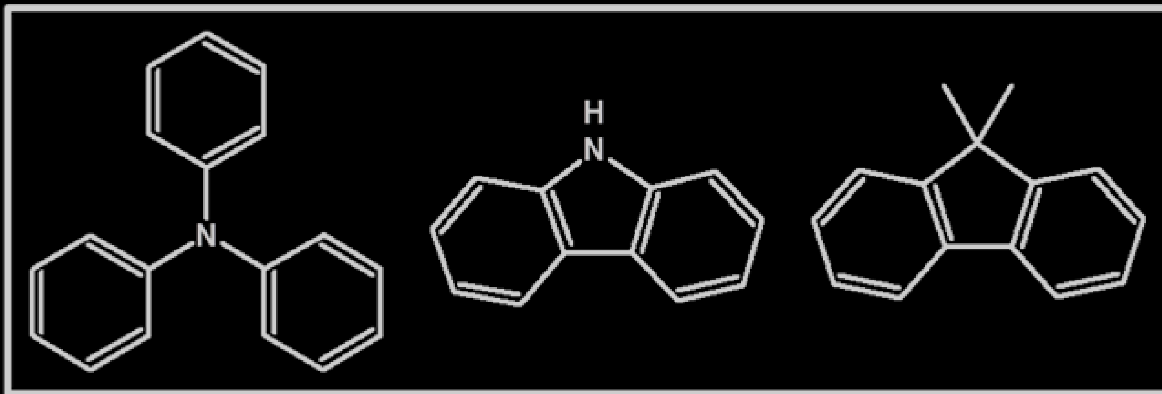


Adv. Funct. Mater. 2008, 18, 584–590



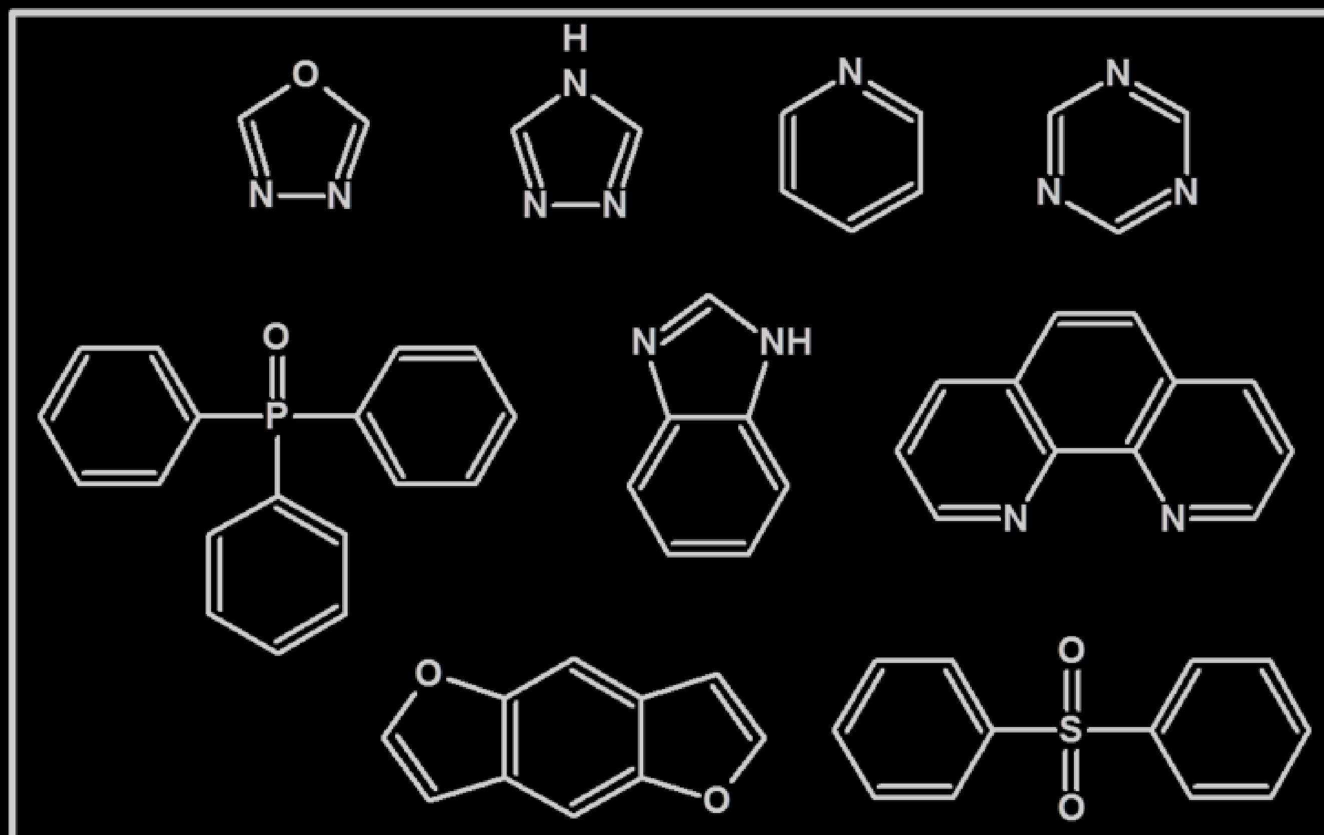
Org. Lett., Vol. 13, No. 12, 2011, 3146-3149

Donor-Acceptor groups for bipolar hosts

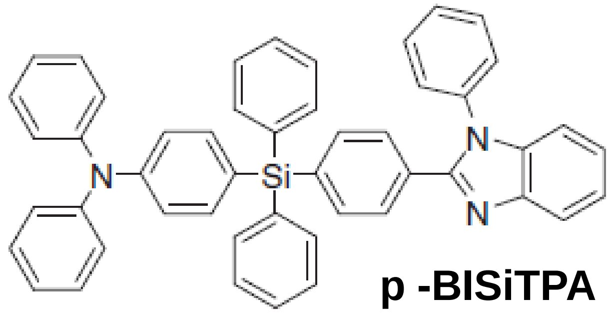


Electron donating groups

Electron withdrawing groups



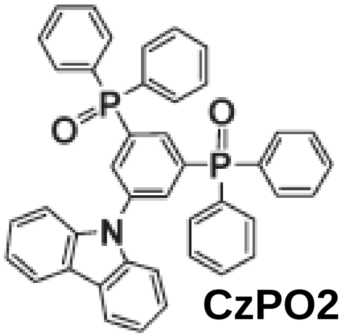
High efficiencies by using bipolar hosts



p -BISiTPA

EQE: 16.1% for blue, 22.7% for green, 20.5% for orange, and 19.1% for white electrophosphorescence. (vacuum deposition)

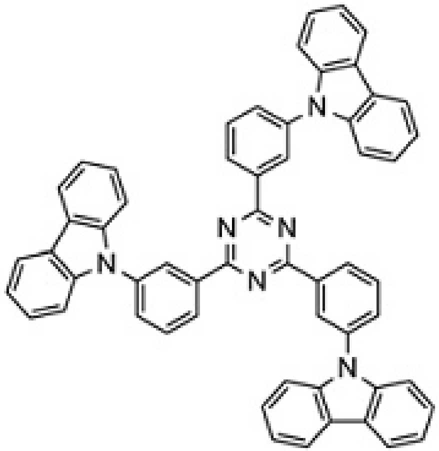
Adv. Funct. Mater., 2011, 21, 1168–1178



CzPO2

EQE 12,0% was obtained for the WOLED by using two phosphorescent emitter, FIrpic (blue) and [(fbi)2Ir(acac)] (orange), which is one of the highest efficiency for solution-processed phosphorescent WOLEDs. (solution process)

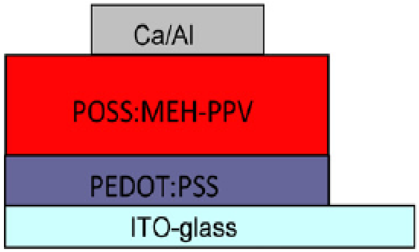
Org. Lett., 2011, 13, 3146-3149.



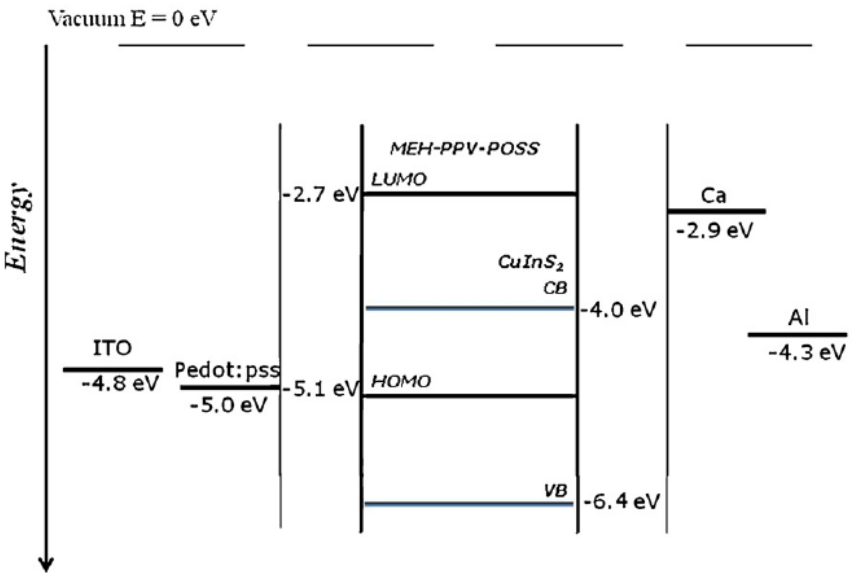
TCPZ

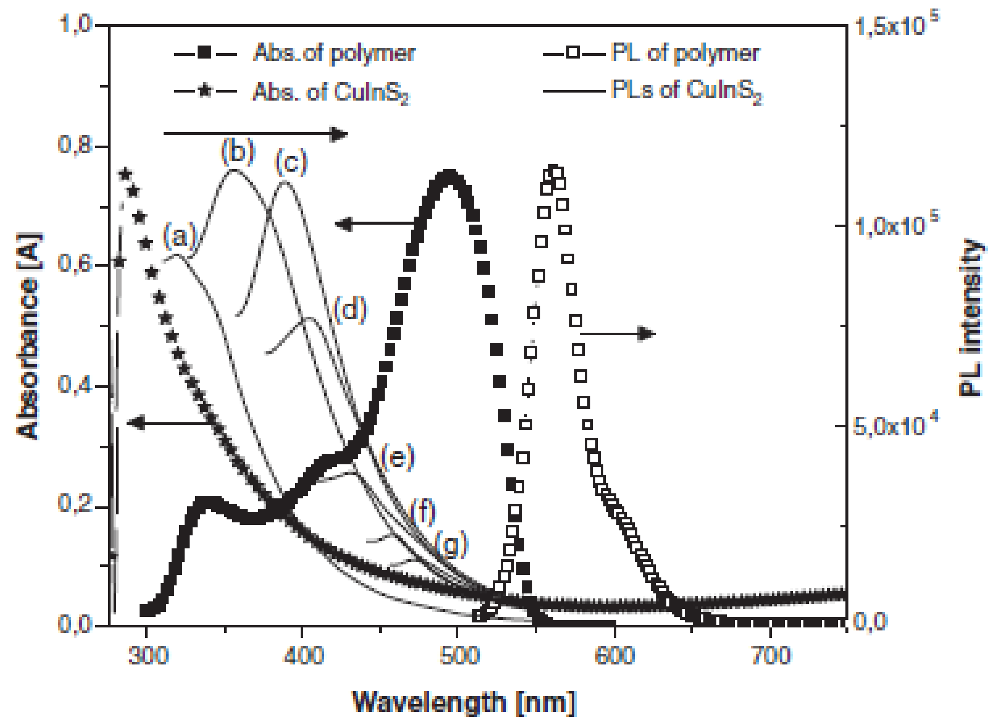
Maximum efficiency; 31.2 lm/W and 13.7% EQE was obtained for the WOLED by using two phosphorescent emitter Ir(piq)3 (red) and FIrpic (blue).
(vacuum deposition)

Organic Electronics, 2012, 13, 1937–1947.



MEH-PPV → Emission layer, μ_{h+} 10^{-6} $cm^2/V\ s$ > μ_{e-} 10^{-8} $cm^2/V\ s$
Calsiyum → Electron transfer barrier ↓
$CuInS_2$ → Trap for the holes
Pedot: PSS → hole transfer barrier ↓

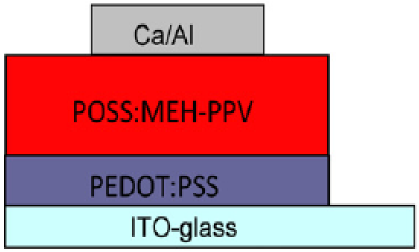




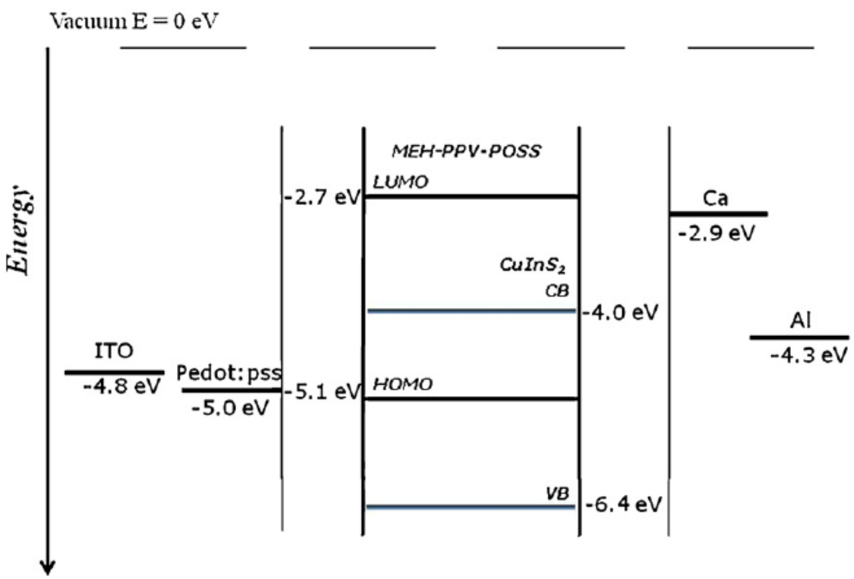
Absorption (star line) and photoluminescence (solid lines) spectra of CuInS2 quantum dots at different exc: (a) 300 nm, (b) 310 nm, (c) 340 nm, (d) 360 nm, (e) 380 nm, (f) 400 nm, (g) 410 nm, and MEH-PPV-POSS polymer (solvent: PhCl).

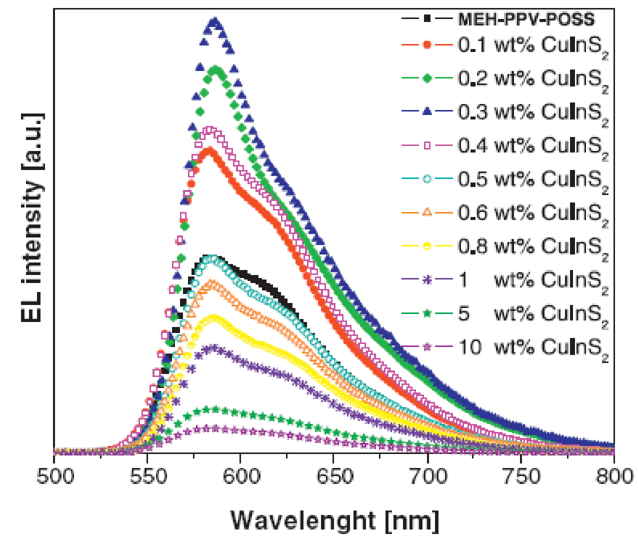
EUSEI studies

Synthetic Metals 161 (2011) 196–202



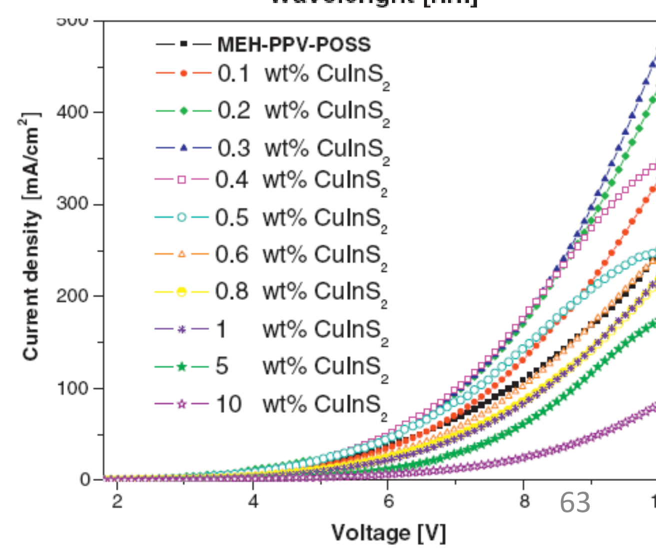
MEH-PPV → Emission layer, μ_{h+} 10^{-6} $cm^2/V\,s$ > μ_{e-} 10^{-8} $cm^2/V\,s$
Calsiyum → Electron transfer barrier ↓
$CuInS_2$ → Trap for the holes
Pedot: PSS → hole transfer barrier ↓





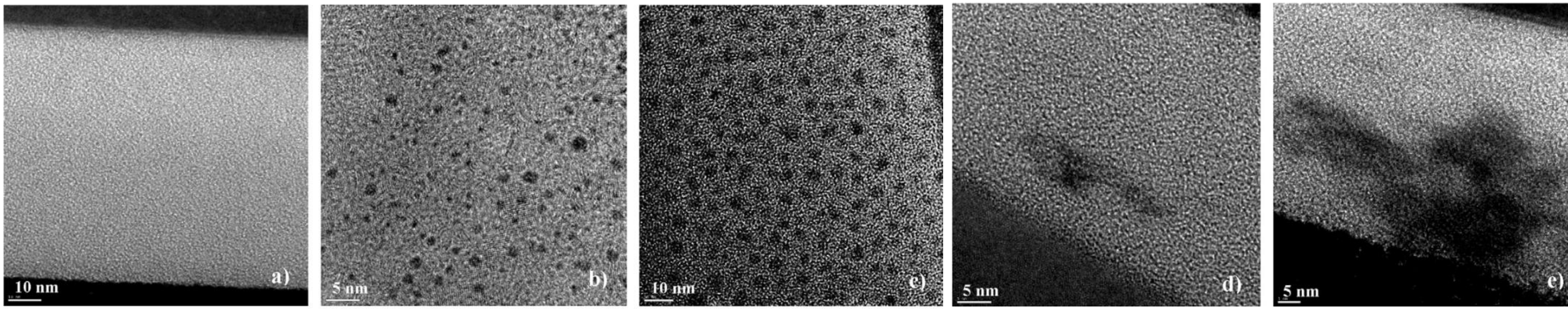
EL from MEH-PPV-POSS

%0 →%0.3 wt $CuInS_2$ → EL↑, current density ↑
→Luminance 2.5 fold↑,
1083 cd/m^2 → 2701 cd/m^2
→eff. ↑, 0.63 cd/A → 0.89 cd/A



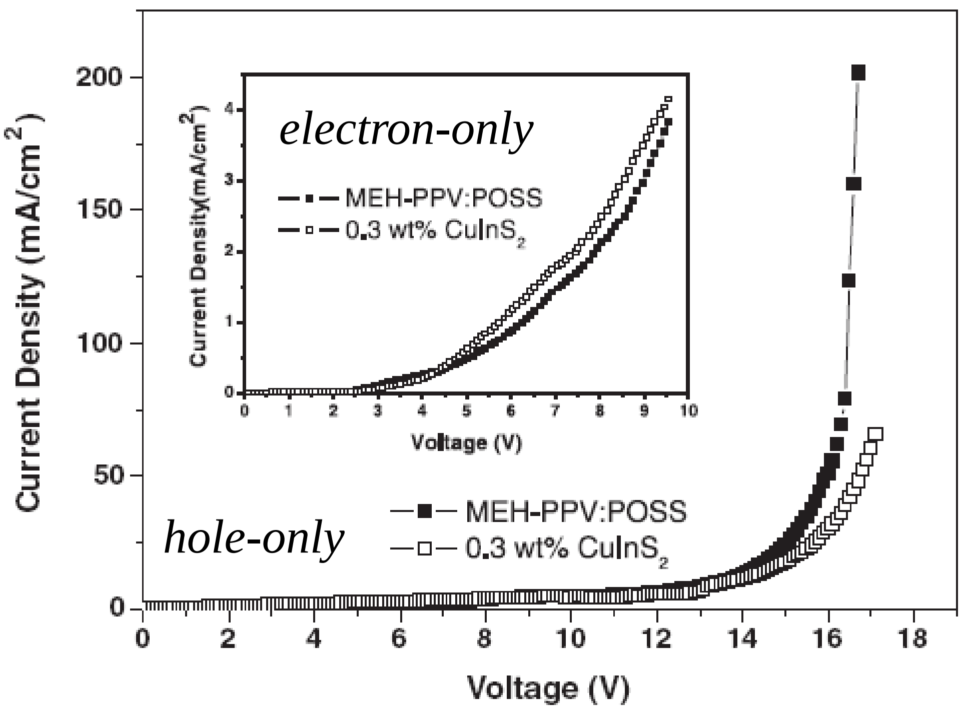
EUSEI studies

Synthetic Metals 161 (2011) 196–202



Transmission electron microscopy images of MEH-PPV-POSS:$CuInS_2$ composites (a) 0, (b) 0.1, (c) 0.3, (d) 1, and (e) 10 wt% $CuInS_2$

Hole-only & electron only *J*-V characteristic



hole-only [ITO/MEH-PPV-POSS ± $CuInS_2$(0.3wt%)/Au]

electron-only [Al/MEH-PPV-POSS ± $CuInS_2$ (0.3 wt%)/Ca/Al]

Hole only device + %0.3 wt $CuInS_2$

➔ *J* ↓↓

Electron only device + %0.3 wt $CuInS_2$

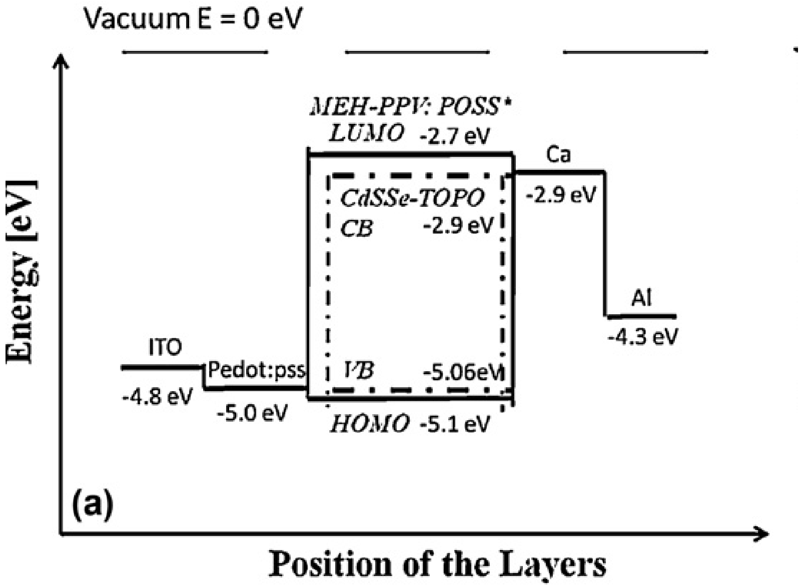
➔ *J* ↑

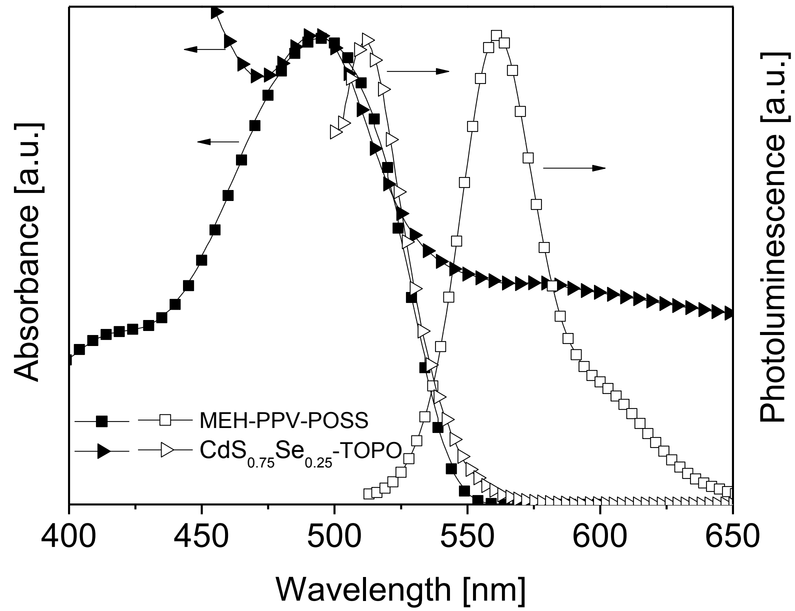
➔ "trap for holes"

EUSEI studies

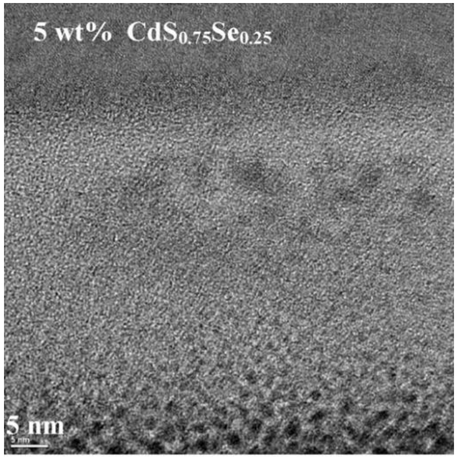
Synthetic Metals 161 (2011) 196–202

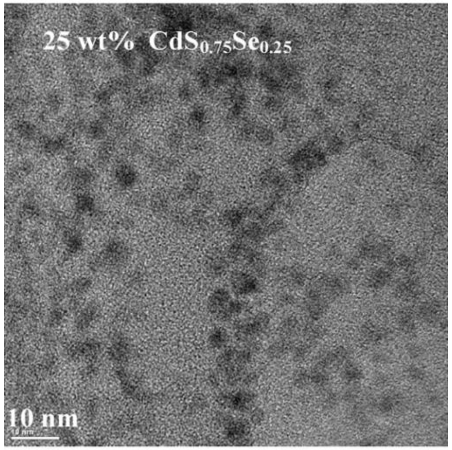
MEH-PPV-POSS : $CdS_{0.75}Se_{0.25}$

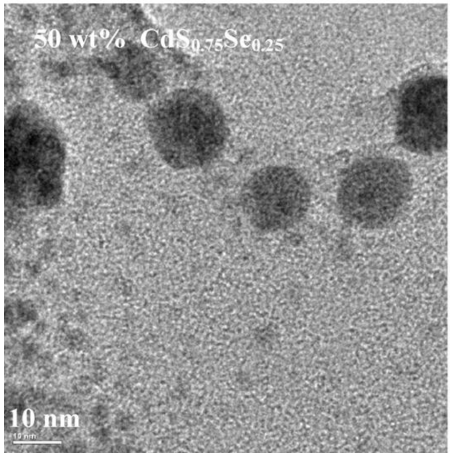




- $CdS_{0.75}Se_{0.25}$ QD doping → 1, 5, 25, 50 wt%
- VB v& CB enerji levels → cyclic voltammetry

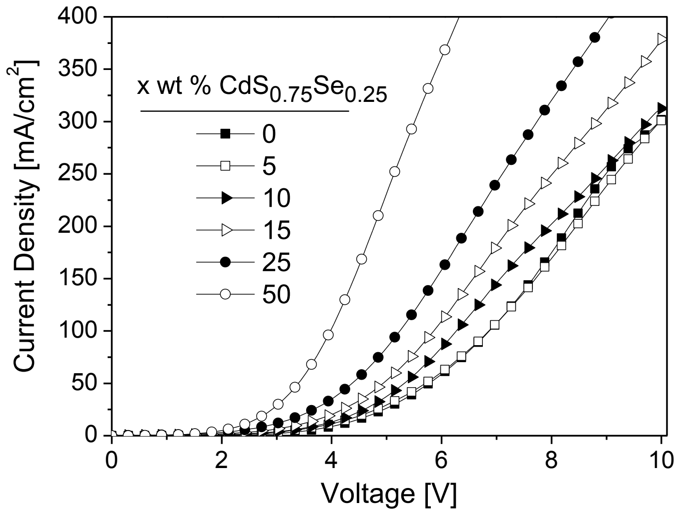


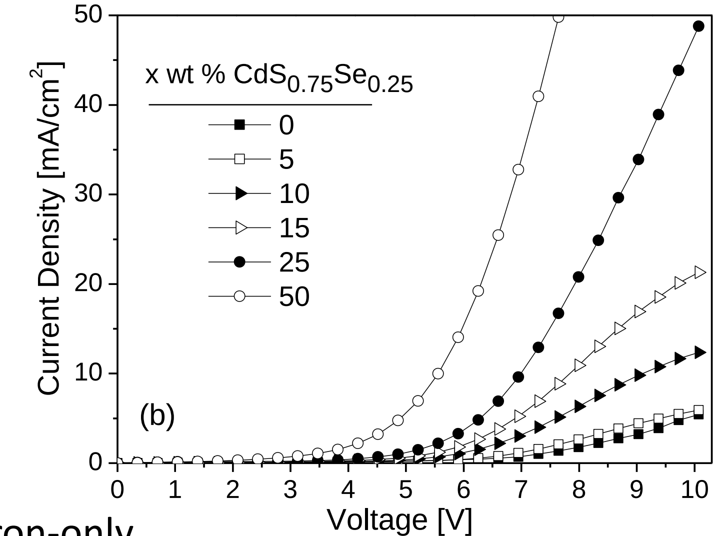




EUSEI studies

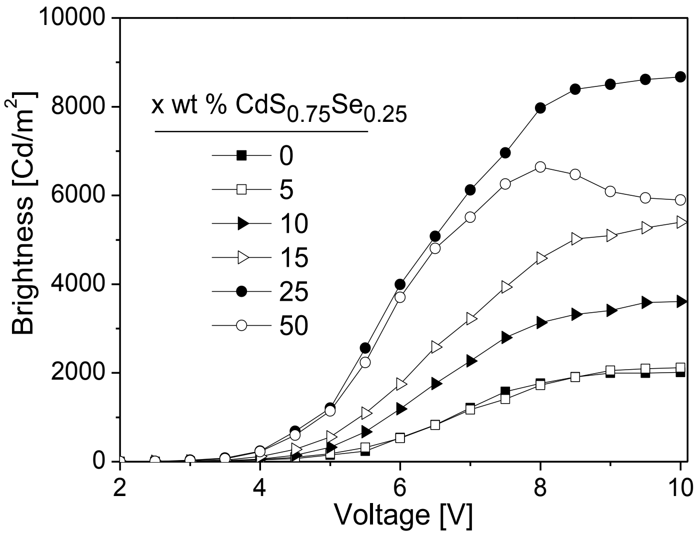
Materials Science and Engineering B 177 (2012) 921– 928

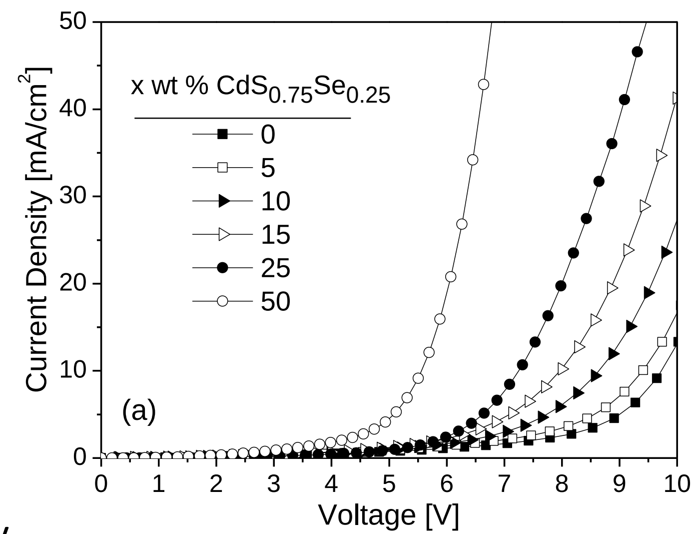




electron-only

[Al (65 nm)/MEH-PPV-POSS: x wt % $CdS_{0.75}Se_{0.25}$/ Ca (40 nm)/Al (100 nm)]





hole-only

[ITO/MEH-PPV-POSS: x wt % $CdS_{0.75}Se_{0.25}$/Au (50 nm)]

[$CdS_{0.75}Se_{0.25}$]↑ → J ↑

% 25 wt% doping → Brightness 4.3 fold↑

% 50 wt% doping → J ↑↑, brightness↓↓

EUSEI studies

Materials Science and Engineering B 177 (2012) 921– 928

Many of the most pressing scientific problems that are currently faced today are due to

the limitations of the materials

that are currently available and, as a result,

breakthroughs in this field are likely to have a significant impact on the future of human technology*.

Material Chemistry and Applied Physics have much to contribute to nanotechnology evolution

*From Wikipedia, the free encyclopedia, Materials science

Sıddık İÇLİ

Ceylan Zafer

Elias Stathatos

Çiğdem Şahin

Gamze Saygılı

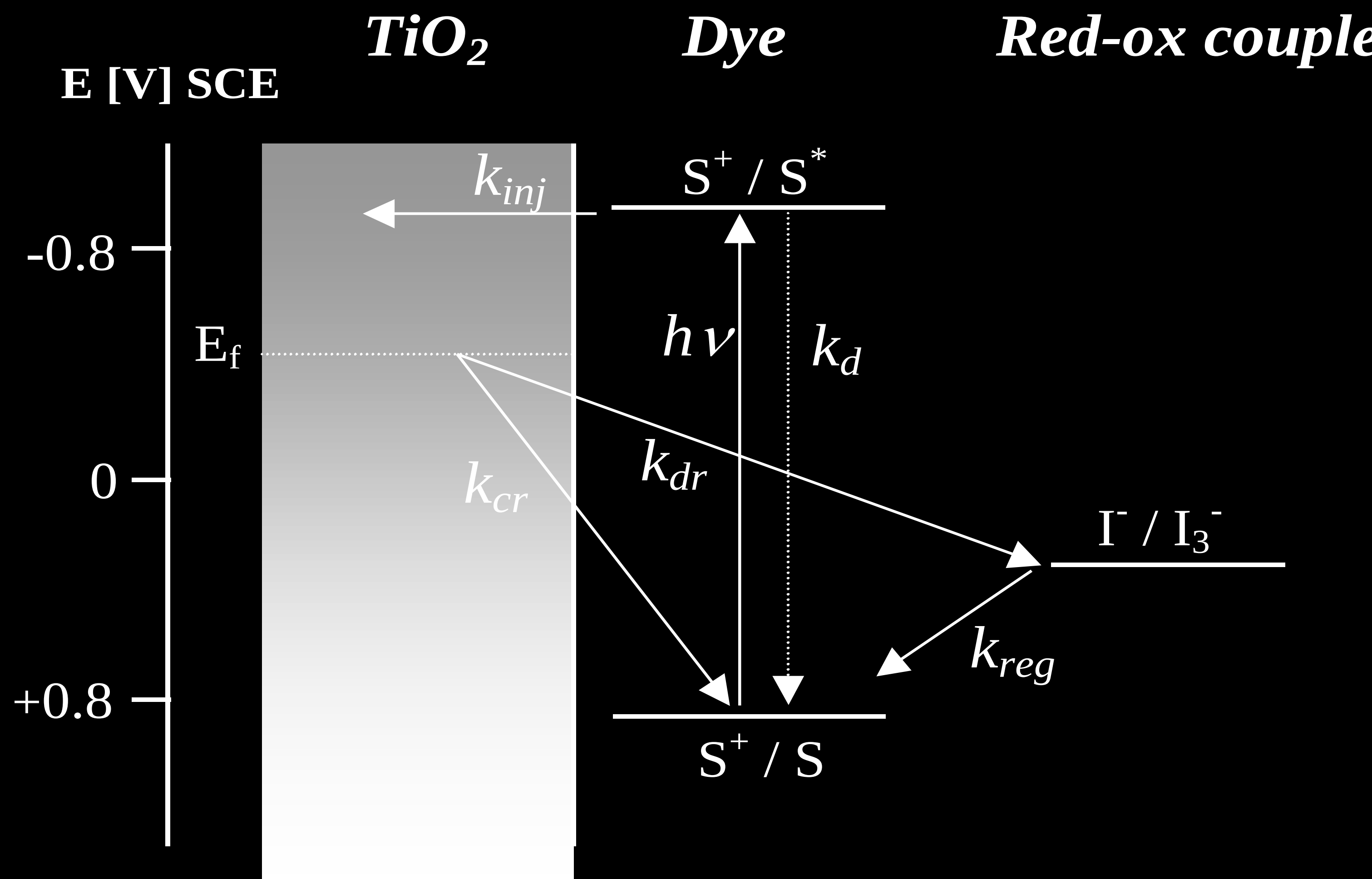
Project funds of

TÜBİTAK	DPT
EÜGEE	EU

Thanks For Your Attention

"Be a scientist, save the world."

-Richard Errett Smalley



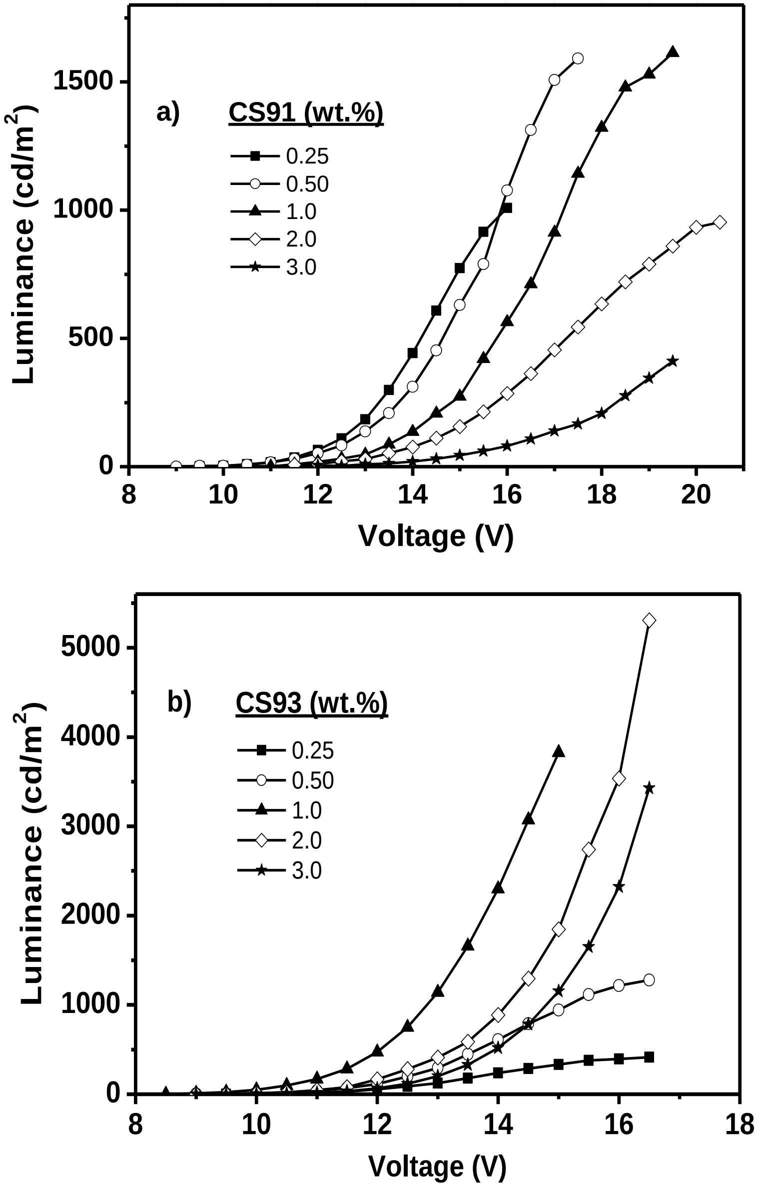
k_{inj} injection of electrons into TiO_2 by dye excited states,

k_d sum of radiationless and non-radiationless decay of dye excited states,

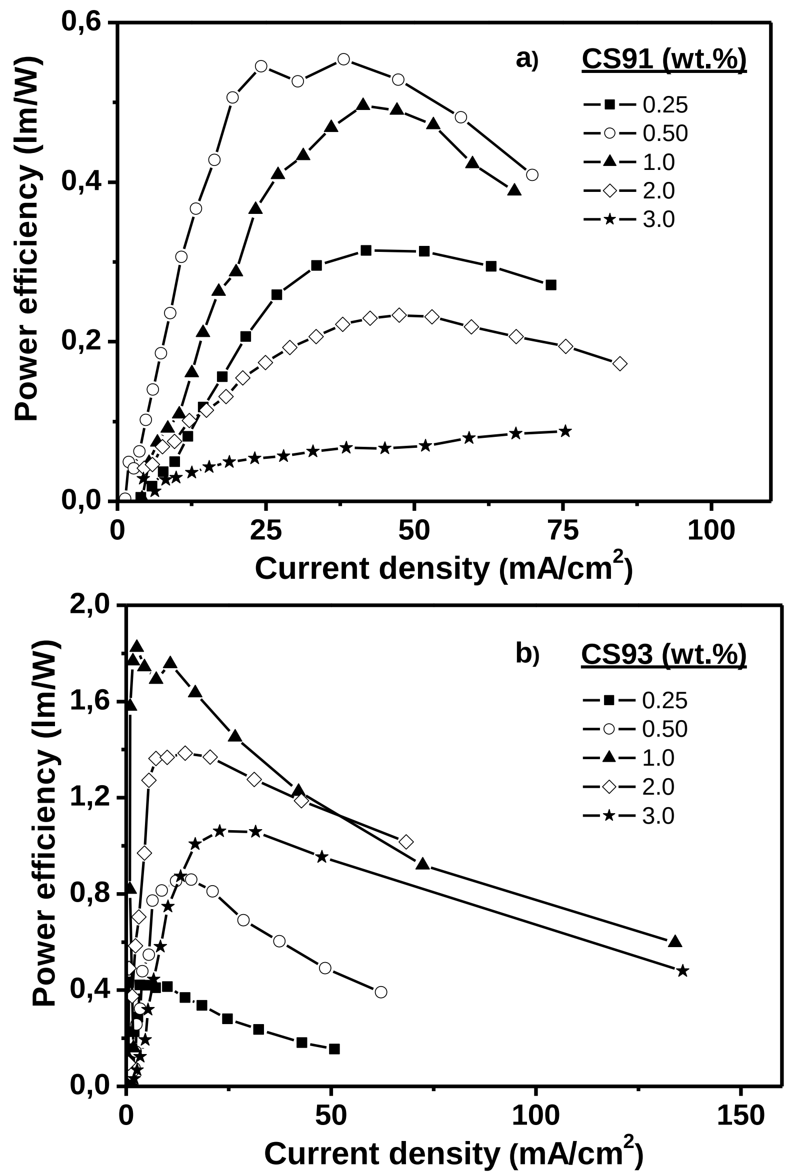
k_{cr} charge recombination of injected electrons in TiO_2 with dye cations,

k_{dr} recombination or "dark reaction" between injected electrons in TiO_2 with the oxidized form of the redox couple

k_{reg} dye regeneration reaction by the redox couple.



Luminance - voltage curves of CS91 (a) and CS93 (b) based devices.



Power efficiency-current density curves of CS91 (a) and CS93 (b) based devices.

EUSEI studies *Dyes and Pigments 95 (2012) 23-32*

1000 cd/m² deki performans değerleri

Device	Voltage [V]	Current density [mA/cm²]	Current efficiency [Cd/A]	EQE [%]	Power efficiency [lm/w]	$\lambda_{EL\ max}$ [nm] at 6V	FWHM [nm]
Pureppv	6.7	96	1.00	0.24	0.43	588	87
%1 TPBi	6.7	70	1.31	0.32	0.64	588	87
%5 TPBi	6.7	64	1.48	0.33	0.69	587	85
%25 TPBi	6.7	61	1.61	0.36	0.76	588	82
%50 TPBi	6.6	56	1.87	0.40	0.87	588	80
10 nm TPBi	6.6	68	1.47	0.32	0.69	588	87
30 nm TPBi	6.4	47	2.00	0.51	0.92	588	87
50 nm TPBi	7.2	57	1.81	0.40	0.75	587	87
70 nm TPBi	8.6	100	1.04	0.22	0.36	588	87
10 nm Bphen	5.6	58	1.81	0.43	1.04	588	87
25 nm Bphen	5.1	46	2.28	0.52	1.28	588	87
40 nm Bphen	4.6	40	2.50	0.64	1.42	588	87
55 nm Bphen	4.7	48	2.04	0.45	1.02	587	87
Ppvcis	6.2	48	1.95	0.40	0.45	588	73
Ppvcis+%50 TPBi	7.0	36	2.36	0.49	1.33	588	68
Ppvcis+ 30 nm TPBi	6.5	23	3.58	0.70	1.78	588	73
Ppvcis+ 40 nm Bphen	4.4	32	3.60	0.97	2.34	588	73

EUSEI studies

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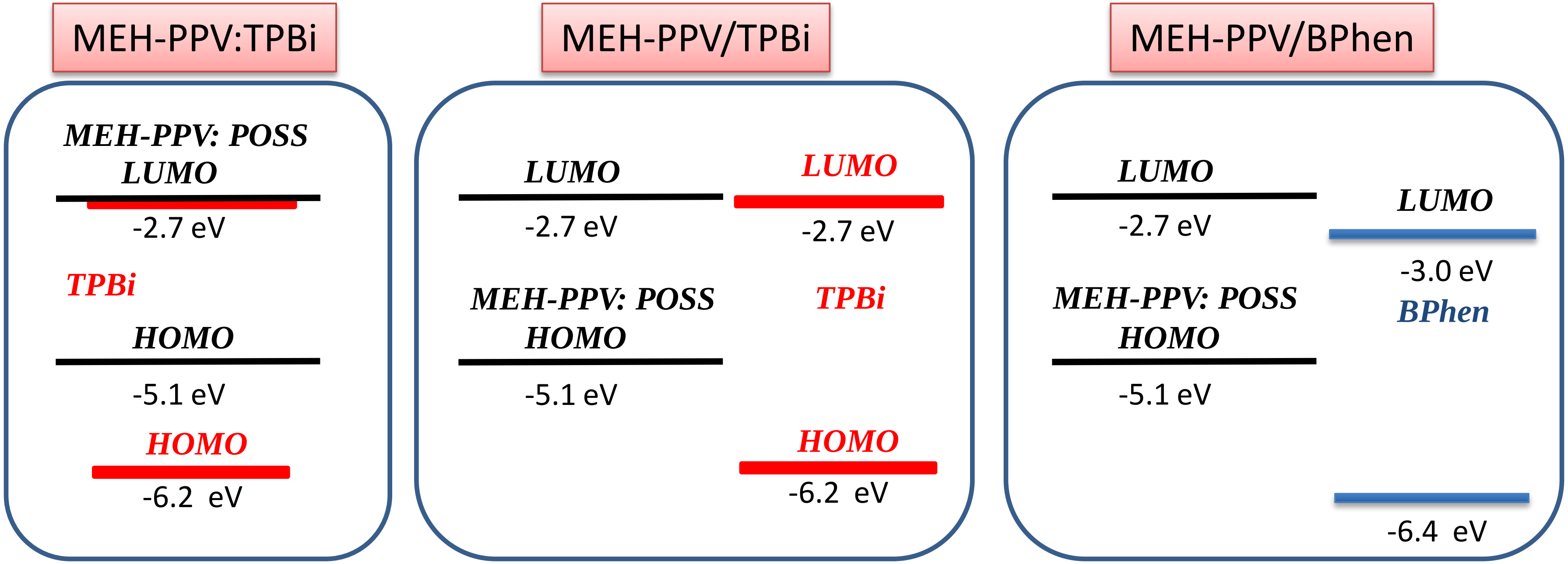

TPBi e^- mobility ~ 10^{-5} cm^2/Vs BPhen e^- mobility ~ 10^{--4} cm^2/Vs

Device	Voltage [V]	Current density [mA/cm^2]	Current efficiency [Cd/A]	EQE [%]	Power efficiency [lm/w]	$\lambda_{EL\ max}$ [nm] at 6V	FWHM [nm]
Pureppv	6.7	96	1.00	0.24	0.43	588	87
PPV:CIS	6.2	48	1.95	0.40	0.45	588	73
PPV:CIS+%50 TPBi	7.0	36	2.36	0.49	1.33	588	68
PPV:CIS+30nm TPBi	6.5	23	3.58	0.70	1.78	588	73
PPV:CIS+40nmBphen	4.4	32	3.60	0.97	2.34	588	73

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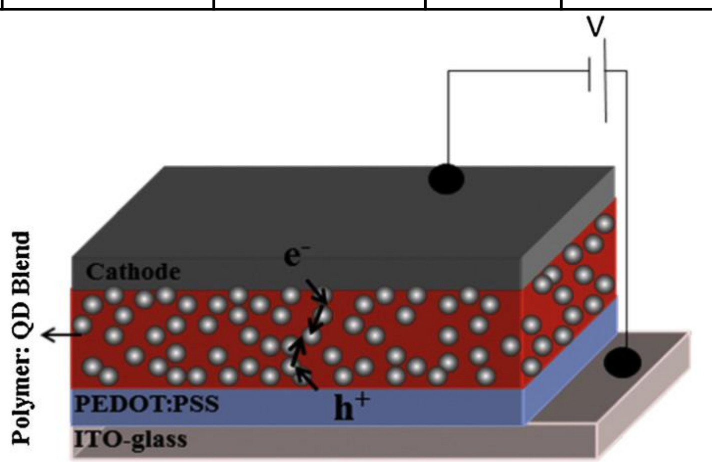
1000 cd/m² deki performans değerleri

Dopant amount [x wt %]	Voltage [V]	Current density [mA/cm²]	Current efficiency [Cd/A]	EQE [%]	Power efficiency [lm/w]	$\lambda_{EL\ max}$ [nm] at 6V	FWHM [nm]
0	6.7	96	1.00	0.23	0.43	588	87
5.0	6.7	92	1.06	0.23	0.49	588	87
10.0	6.0	85	1.21	0.27	0.63	588	84
15.0	5.4	72	1.28	0.28	0.75	588	82
25.0	4.7	67	1.42	0.43	0.92	588	81
50.0	4.9	204	0.47	0.11	0.30	588	75



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ISAM FLEXIBLE SPORTING GOODS
Here's our two-person solar-powered tent.

If A equals success, then the formula is:

A = X + Y + Z,
X is work.
Y is play.
Z is keep your mouth shut

-- Albert Einstein

"Be a scientist, save the world."

-Richard Errett Smalley