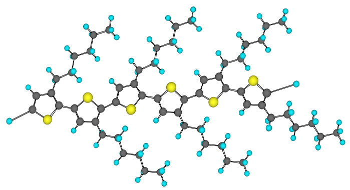
Organic photovoltaic cells

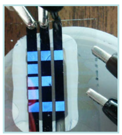
polymeric solar cells

silvia.luzzati@ismac.cnr.it

Ismac optoelectronic & photonic group

- Design & synthesis of conjugated polymers;
- Macromolecular & structural characterisation;
- Optical & vibrational & photophysical characterisation;
- Film and nanofibre preparation;
- Morphological studies;
- Device assembly & test





Permanent staff

* Alberto Bolognesi
* Marinella Catellani
* Silvia Destri
* Maria Cecilia Pasini
* Chiara Botta
* Silvia Luzzati
* Umberto Giovanella
* W.Porzio
* G. Scavia
* M. Canetti

PhD/Post-Doc/Grants

*Francesco Galeotti
*Francesco
* Erika Kozma
* Paolo Betti
* Gabriele Grieco
* Elisa Salmoiraghi
* Jean Philippe Bombenger
* Dariusz Kotowski
* Varum Vohra

Material development

Characterization & devices

Structure & morphology

Organic Solar Cells in ISMAC

from materials

STAFF

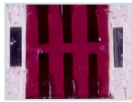
Marinella Catellani
Erika Kozma
Gabriele Grieco
Natalia Lupsac

Silvia Luzzati
Darek Kotowski
Andrea Arcari
Ruggero Cugola
Stefano Millefiorini

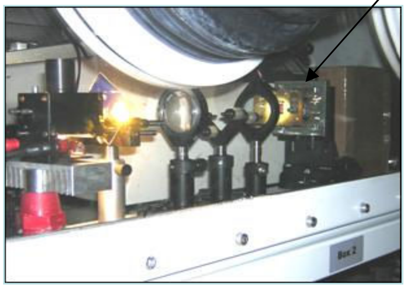
PROJECTS

- Pr. Fin. CNR MISTA II-FREMO (1997- 2000)
- RTN EUROMAP (2000-04)
- Fondazione CARIPLO (2004-10)
- MIUR-FIRB SYNERGY (2005-2008)
- RTN SOLARNTYPE (2006-2010)
- CA ORGAPVNET (2006-2009)

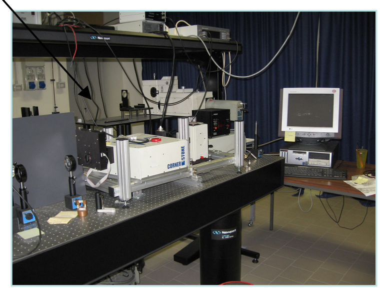
to devices



Solar cell preparation



I-V charaterisation (white light)



EQE

ISMAC

NIS Colloquium - Torino 23 Giugno 2008

outline

Why polymeric solar cells

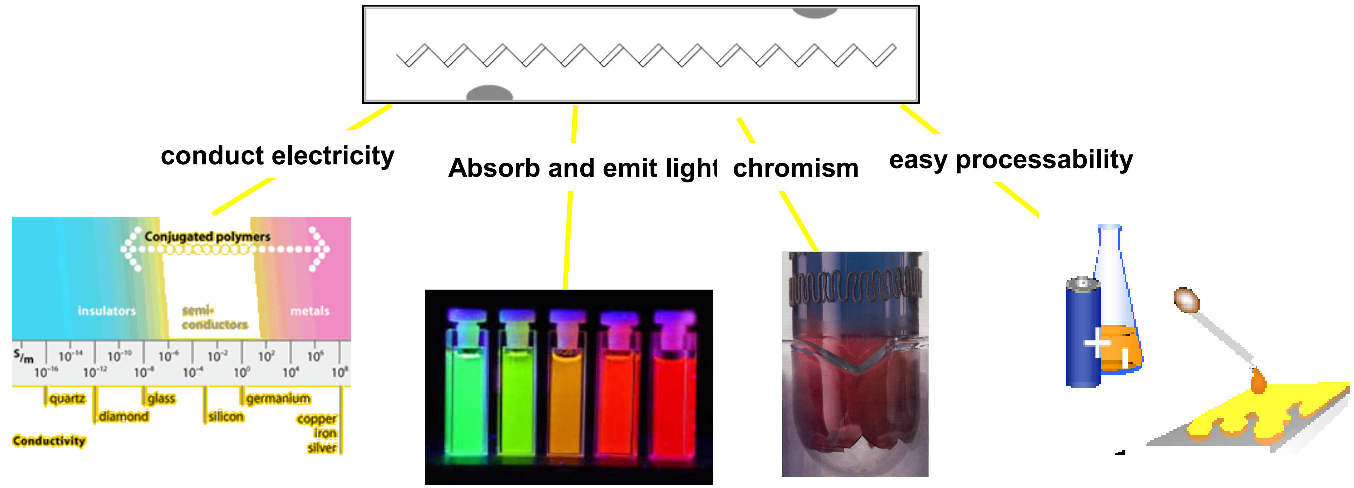
Working principles

The state-of-the-art

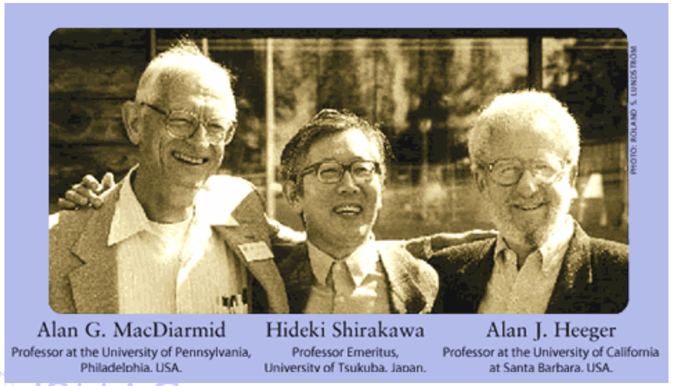
New photoactive materials: the key for progress

Conclusions and perspectives

Conjugated polymers: semiconductors & plastics



2000 Nobel Prize in Chemistry

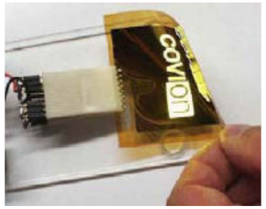


for **the discovery and development of conductive polymers.**

Plastics electronics
- low performances
- moderate miniaturisation
- Low energy
- **Low cost** (photolithigrapy, ink-jet printing, roll-to-roll)

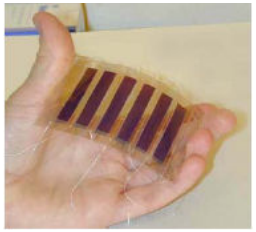
Plastic electronics

1990



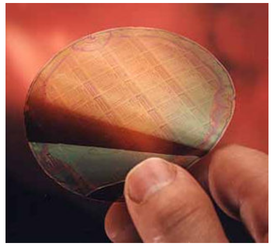
Oled-displays

1995



Solar cells

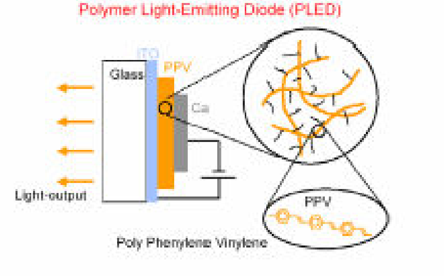
1993



transistors

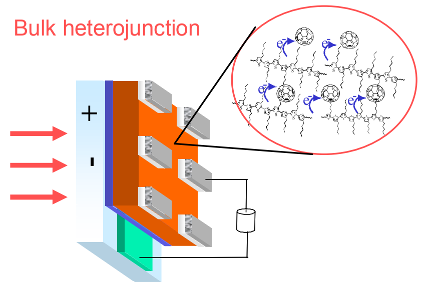
device architecture

Polymer Light-Emitting Diode (PLED)



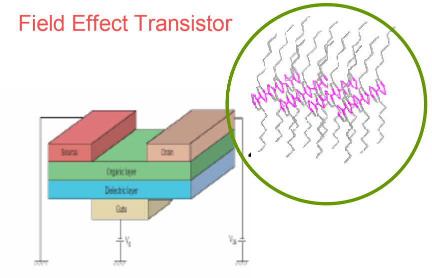
light ← current

Bulk heterojunction



light → current

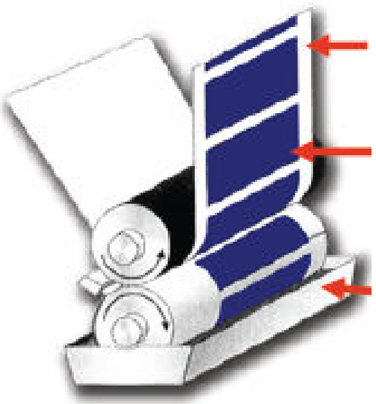
Field Effect Transistor

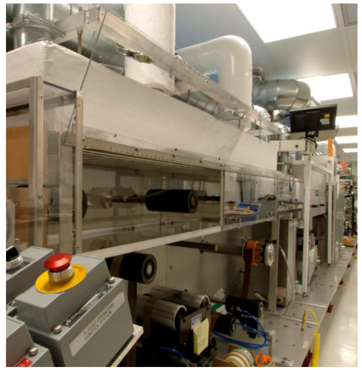


conduction p …, n

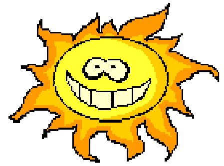
Semiconducting and metallic polymers

"Inks" with electronic functionality





Polymeric solar cells: the advantages



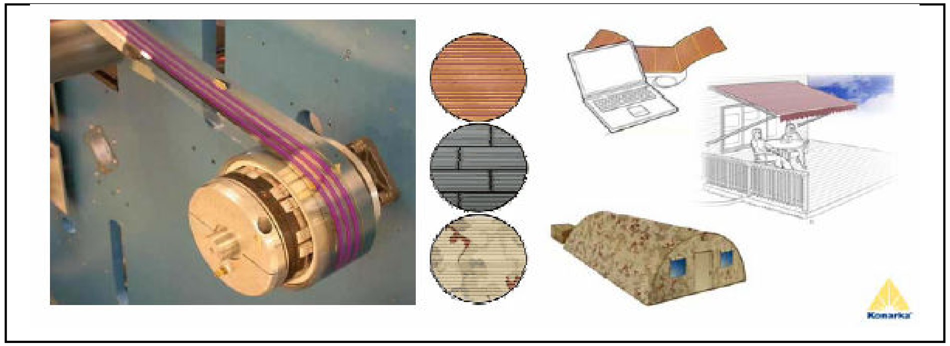
- Light weight
- Flexibility
- Semi-transparency/colour
- Plastics technology up-scaling (roll to roll or ink-jet printing)
- Low energy consumption
- Low environmental impact
- Low investments
- Materials easily available

→ low cost technology and unconventional applications

Polymeric solar cells: possible applications

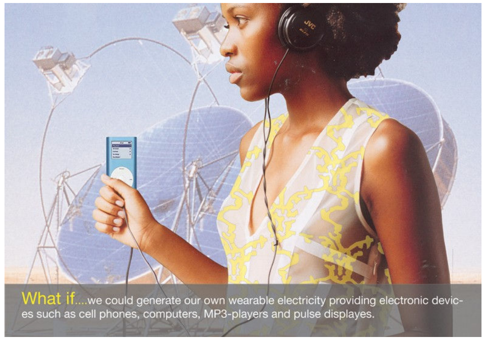
•State of the art. eff. ~ 5%

www.konarka.com



✓**consumables**

• remote applications

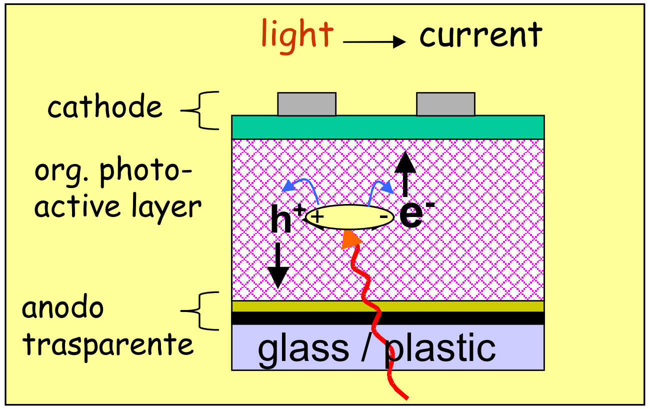


F.C. Krebs et als. Sol. Energy Mater.,Sol. Cell. 90, 1058 (2006)

www.hertz-langberg.com

How they work

device structure

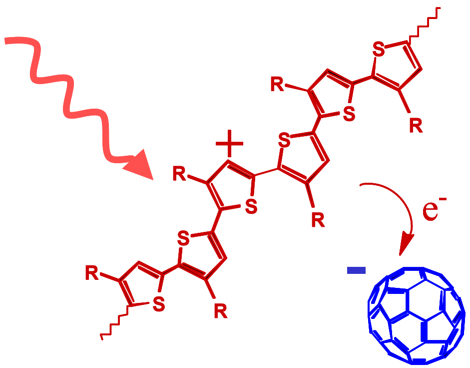


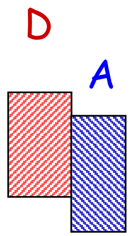
Photovoltaic effect

1. Photon absorption
2. Charge photogeneration
3. transport to the electrodes

Charge photogeneration in organic materials is rather poor

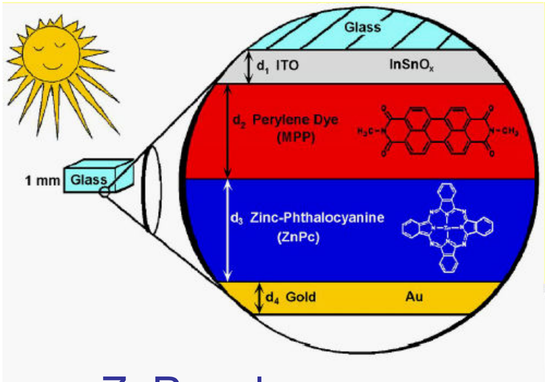
Photoinduced charge transfer





Energy levels

The first organic solar cell



ZnPc : donor

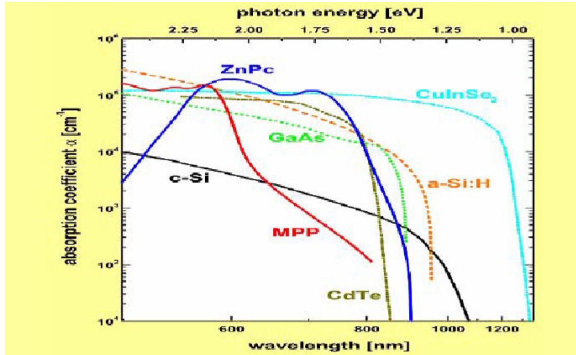
MPP : acceptor

$\eta = 0.47$

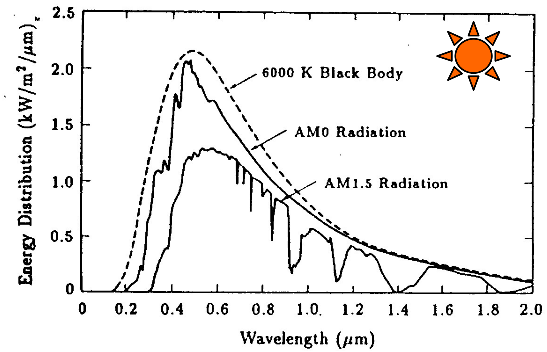
AM 1.5 890 W/m^2

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

absorbance

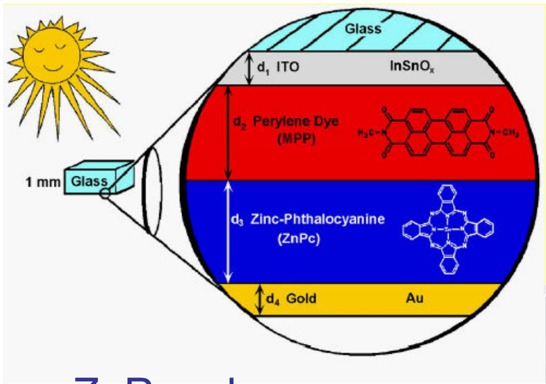


- Absorbance
- Mismatch to solar spectrum



Molecular organic solar cells: D/A bilayers

The first organic solar cell



ZnPc : donor

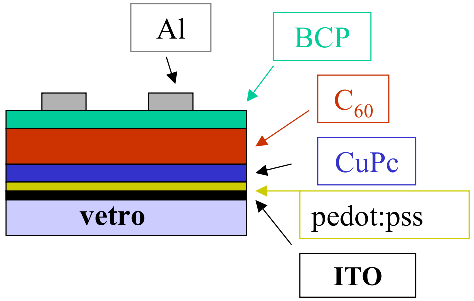
MPP : acceptor

$\eta = 0.47$

AM 1.5 890 W/m^2

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

The evolution



CuPc : donor

C_{60} : acceptor

BCP: e-trans. (bathocuproine)

$\eta = 3.6$ %

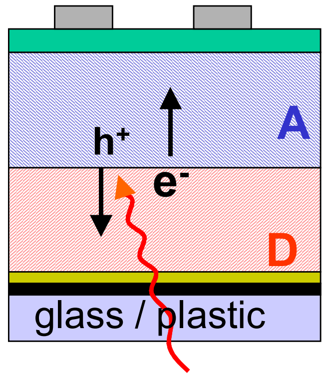
AM 1.5

P. Peumans Appl. Phys. Lett., 79 (2001), 1268

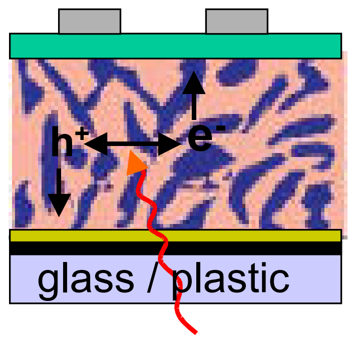
Bulk heterojunctions work better !!

OPV architecture

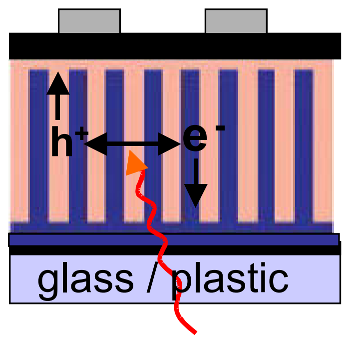
Donor/Acceptor heterojunction



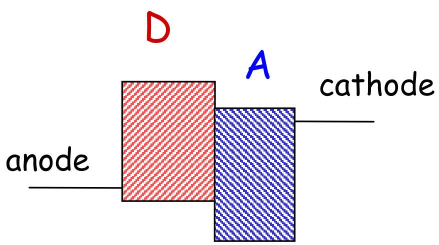
Bi-layer



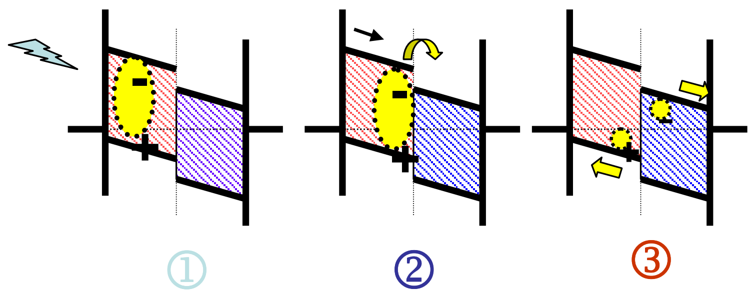
bulk



"ordered" bulk



Energy levels

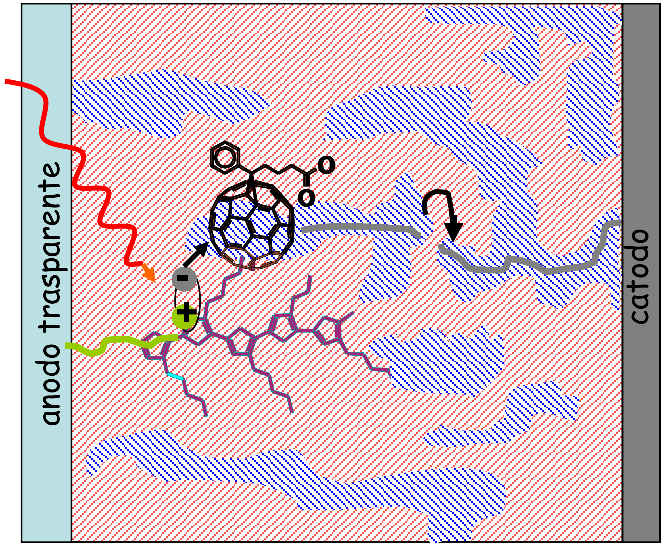


Short circuit

C. J. Brabec, Adv. Funct. Mater. (2001) 11,15

bulk heterojunction solar cells

bulk heterojunction



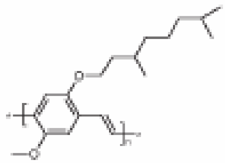
photoactive material

- D:A composite layer
- Photoinduced D:A charge transfer and separation
- Nano-scale phase segregation
- D/A bi-continuous network
- p, n mobility

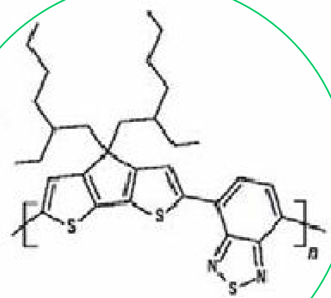
The design of the photoactive material has a central role for efficiency improvements

Materials for bulk heterojunction

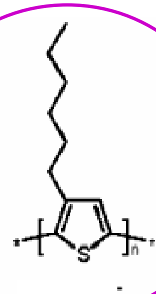
Conjugated donor polymers



MDMO-PPV



PCPDTBT



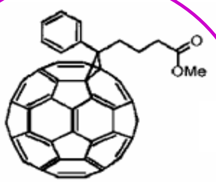
P3HT

acceptors

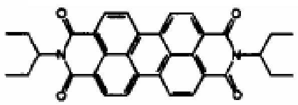
Nature materials vol6, 497 (2007)

eff. 5 %

eff. 5.5%

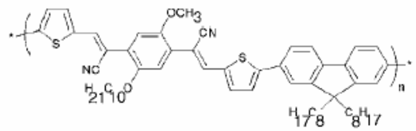


PCBM



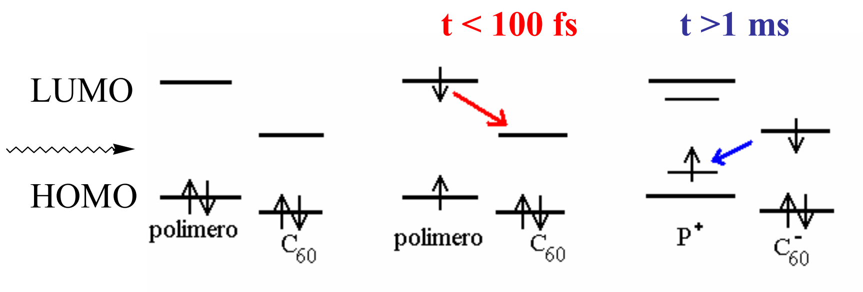
perileni

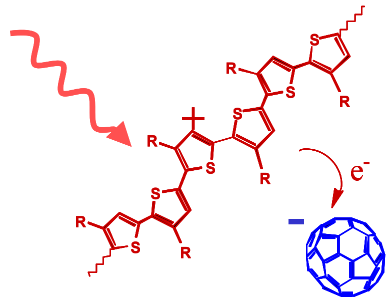
C_{71}-PCBM



PF1CVTP

Trasferimento di carica fotoindotto polimero/fullerene





Polimero: donatore Fullerene: accettore

Trasferimento di carica ultraveloce tra il polimero coniugato fotoeccitato ed il fullerene, stati carichi metastabili con tempi di vita lunghi

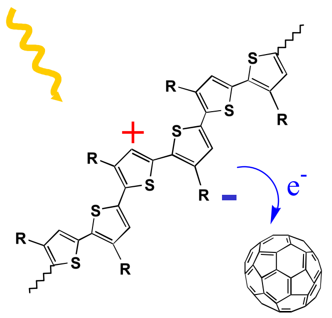
→ la fotogenerazione di carica ha una efficienza di ~100%

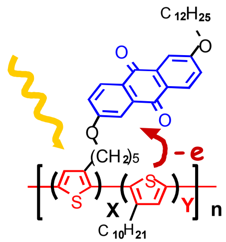
N.S. Sariciftci et als. ***Science*** *(1992), 258, 1474 S. Morita als.* ***Solid State Comm.*** *(1992)* ***82,****249*

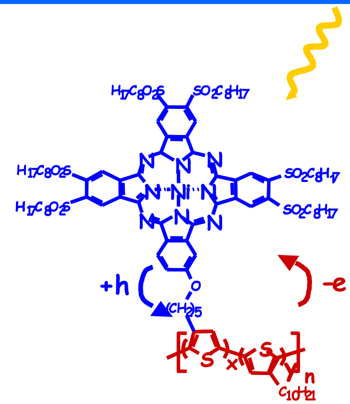
C.J. Brabec et als. ***Chem. Phys. Letts*** *(2001)* ***340 ,*** *232*

ISMAC

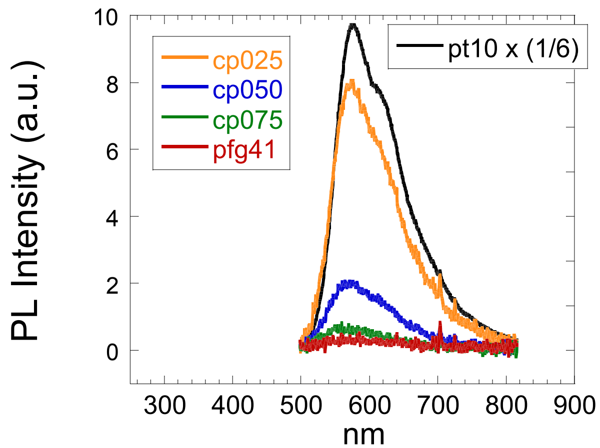
Spectroscopical evidences of photoinduced charge transfer



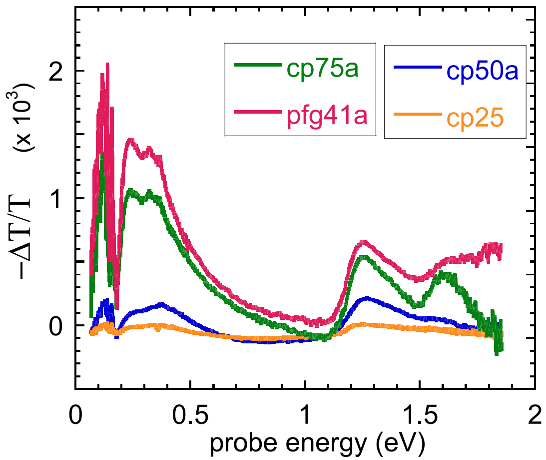




Photoluminescence quenching



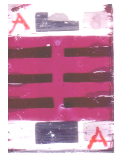
FTIR photoinduced absorption



S. Luzzati et als., JPCB 110, pag. 5351 (2006)

Assemblaggio di una cella solare polimerica

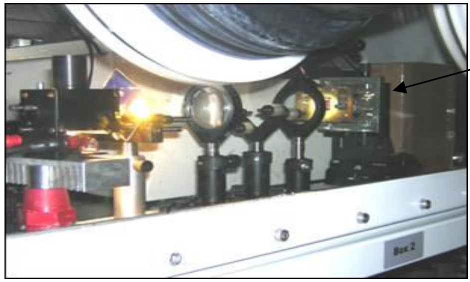
Preparazione dell'ITO etching e pulizia → **Coating con un hole conduction layer PEDOT:PSS** → **Coating con il film attivo**



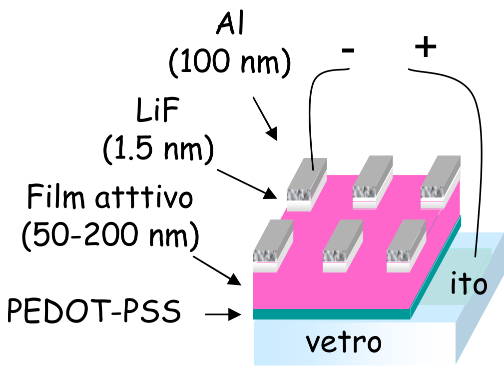
→ **Incapsulamento contro acqua ed ossigeno**

Evaporazione dell'elettrodo →

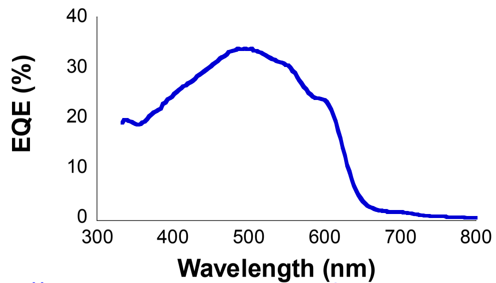
caratt. in ***luce bianca***



dry box

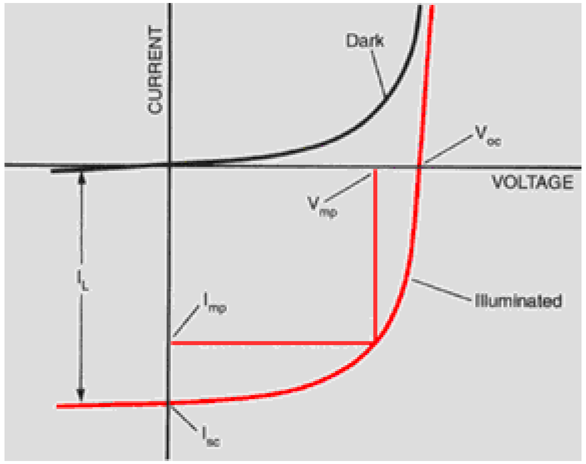


External Quantum Efficiency
(nr. elettroni/nr fotoni inc.)



Photovoltaic parameters

caratteristiche corrente- tensione



V_{oc} : open circuit voltage

I_{sc} : short circuit current

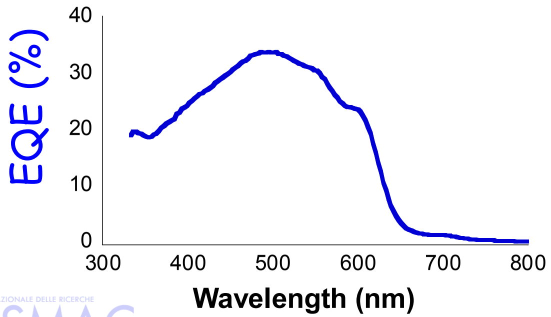
$FF = I_{mp} V_{mp} / I_{sc} V_{oc}$: fill factor

$$\eta = \frac{P_{el.out}}{P_{inc}} = FF \frac{V_{oc} I_{sc}}{P_{inc}}$$ eff. di conversione

standard di illuminazione solare AM 1.5, 100 mW/cm²

External Quantum Efficiency

(nr. elettroni/nr fotoni inc.)



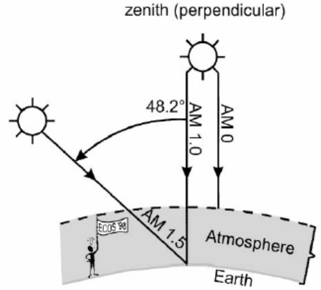
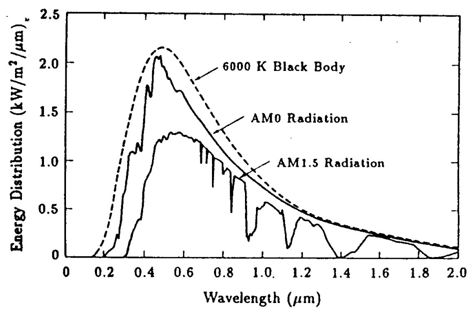


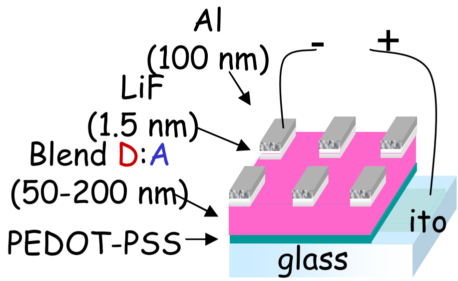
Fig. 4. Schematic explanation of the different AM sun light sp



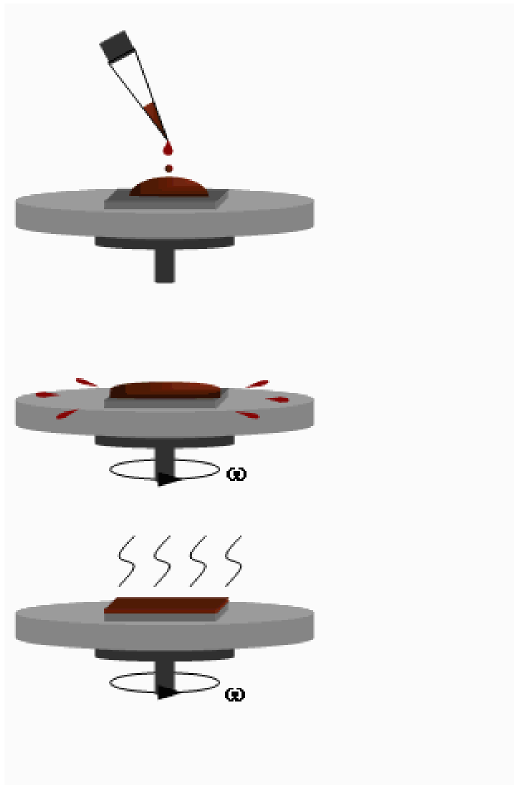
ISMAC

D/A active layer deposition

Bulk heterojunction solar cell



spin coating deposition

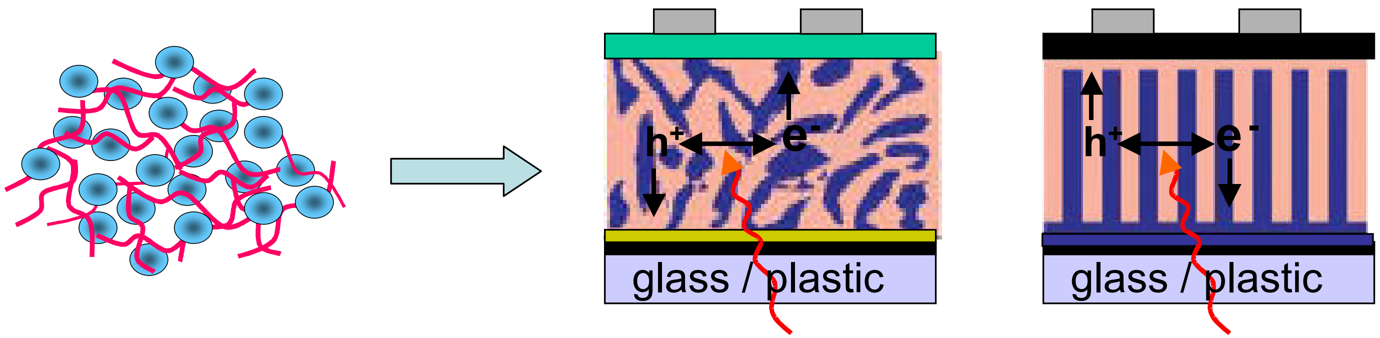


morphology optimisation

- solvent
- thermal annealing
- composition, concentration
- Pol. mol. weight,polydispersity, regioregularity °
- spin coating parameters(ω, …)

morphology requirements

Donor/Acceptor bulk heterojunctions



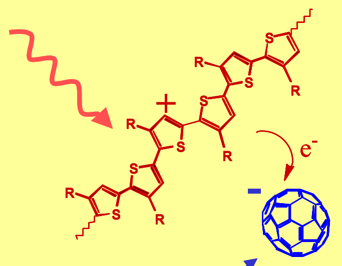
bulk *Ordered bulk*

Nano-scale phase segregation

D/A bi-continuous network

Possibly some vertical gradient

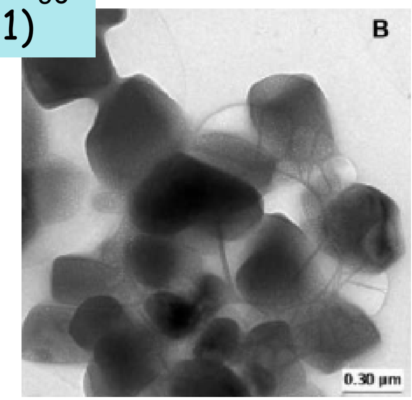
Solubility issues

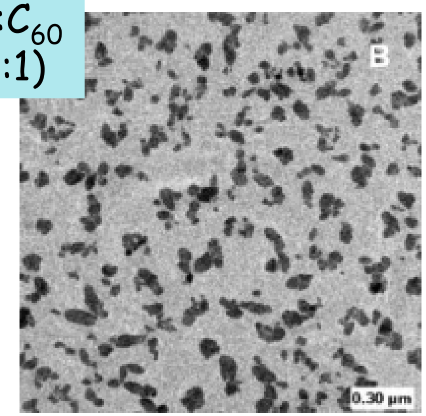


poor solubility

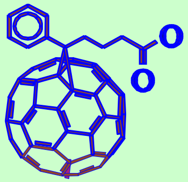
POT:C_{60}
(1:1)

TEM



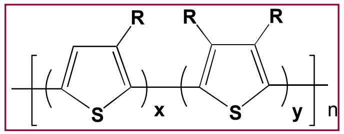


POT:**cop**:C_{60}
(0.8:0.2:1)



Better solubility

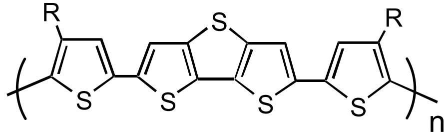
Photoactive plasticiser



Camaioni et als, Thin Solid Films (02) ***403*****,** *489*

P1:PCBM, not enough phase segregation

Millefiorini et als, Thin Solid Films, in press



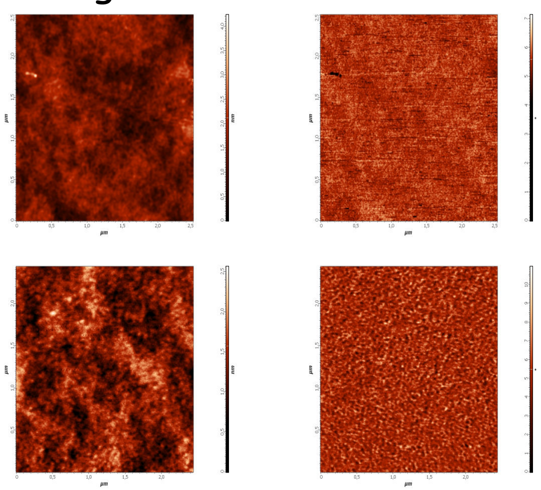
P1

P1:PCBM spin coated from chlorobenzene

P1:PCBM	V_{oc} (V)	Jsc (mA/cm 2)	FF	η
1:1	0.832	2.34	0.33	0. 64%
1:2	0.799	2.81	0.36	0.81%
1:3	0.817	1.74	0.33	0. 47%
1:4	0.796	1.68	0.32	0.35%

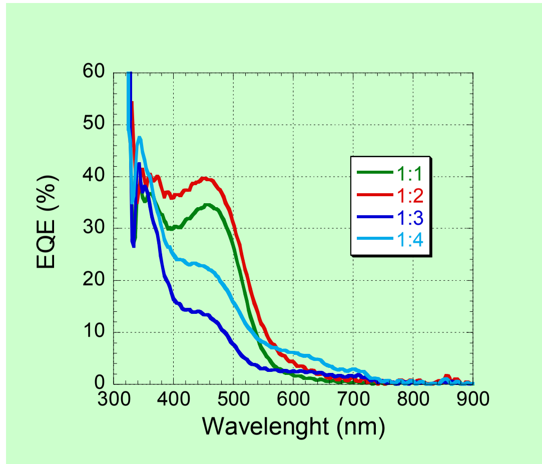
AFM (2,5x2,5 μm)

Height Phase



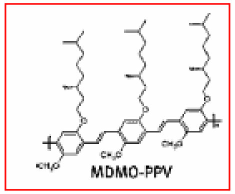
50% PCBM (1:1)

80% PCBM (1:4)

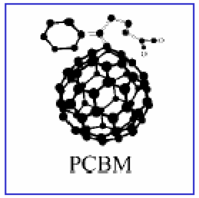


ISMAC

morphology vs solvent

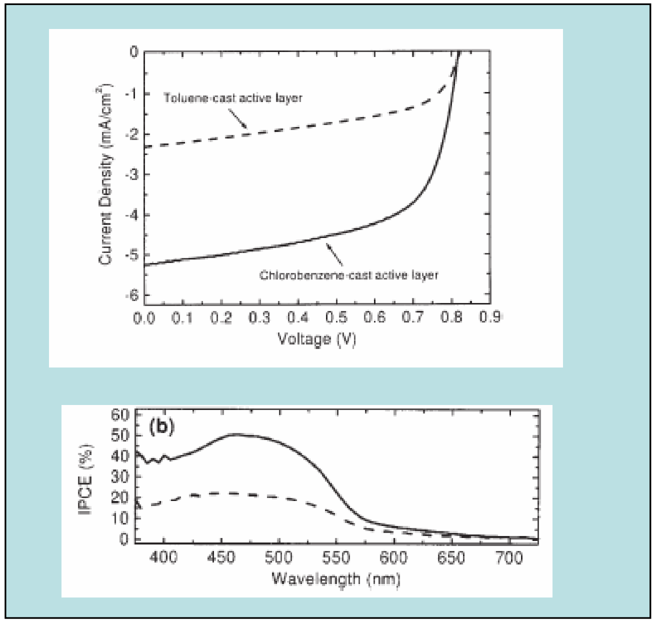


+



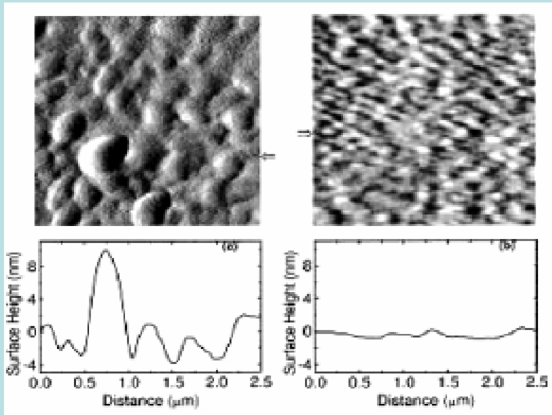
1:4

PV characterisation



AFM

toluene chlorobenzene

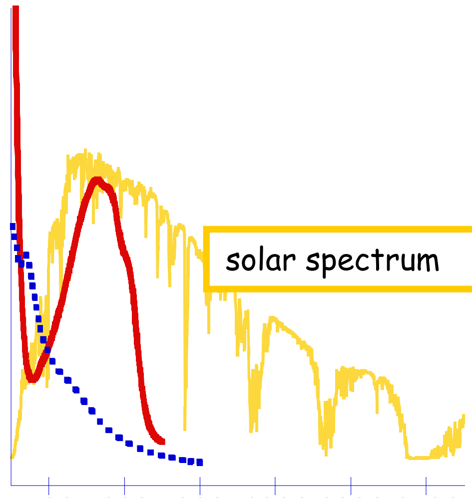


S. E. Shaheen, et al. *Appl Phys. Lett*, **78**, 841 (2001).

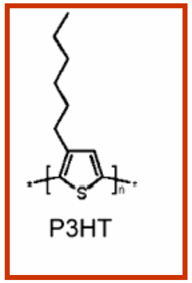
The state of the art

P3HT:PCBM bulk heterojunctions

UV-Vis



el. donor, p semicond. el.acceptor, n semicond.



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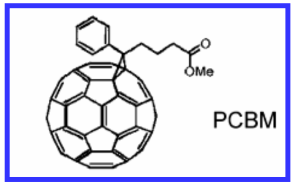


before 2005: $\eta \sim 1\text{-}2$ %

Morphology Optimisation →

*D:A composition , **thermal annealing**, deposition, molecular weight, polymer purity……..*

$\eta \sim$ **5 %**

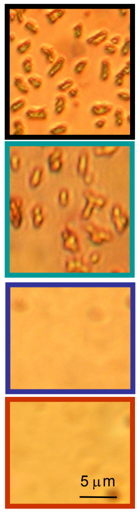
Appl. Phys. Lett. 87, 083506 (2005)
Adv. Funct. Mater. 15 1617 (2005)
Nature Materials 4 864 (2005)

There is room to reach ~ 7.5 %

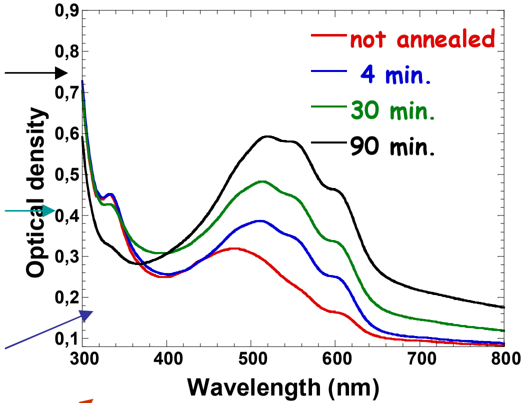
P3HT:PCBM: optimisation by thermal annealing

1:1 w:w, chlorobenzene, 120 °C

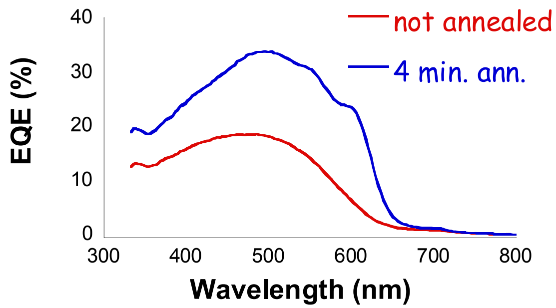
Optical microscopy



UV-Vis vs annealing time



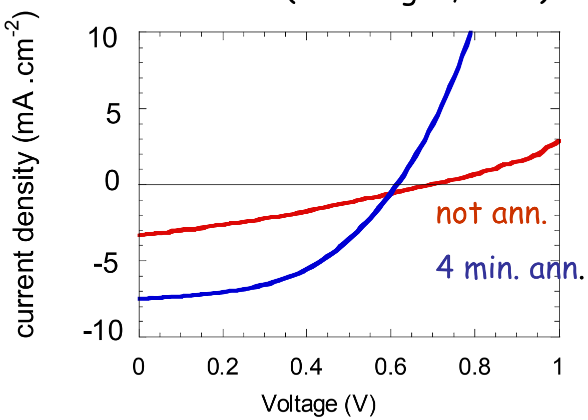
EQE: (nr. elettroni/nr fotoni inc.)



✓Enhancement of the degree of order/cristallinity of P3HT

✓Order/demixing favour p and n percolation paths formation

I-V curves (white light, 1 sun)

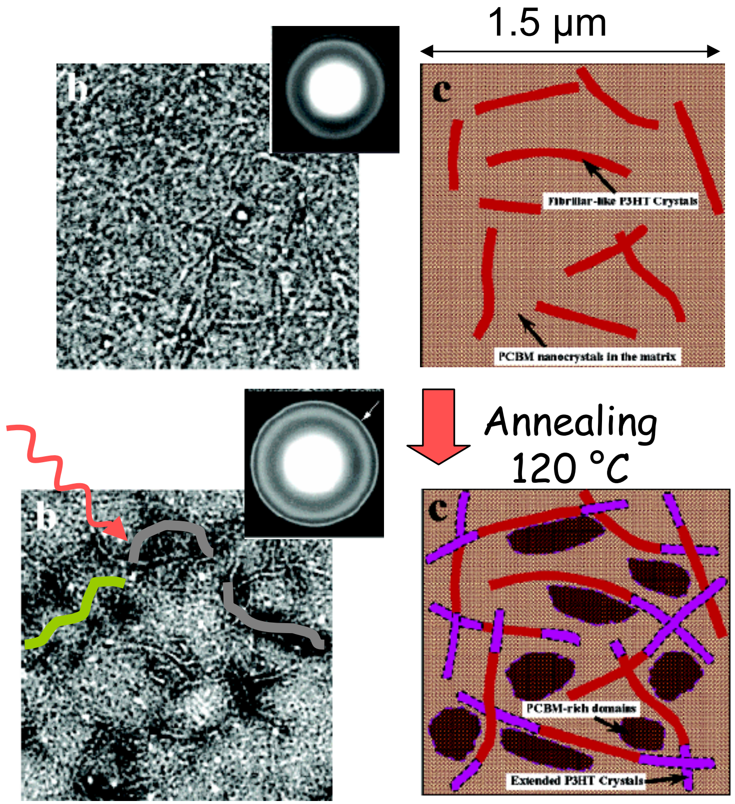


ISMAC *R.Cugola,et als, Thin Solid Films, 511-512 (2006) 489*

order ↔ phase segregation

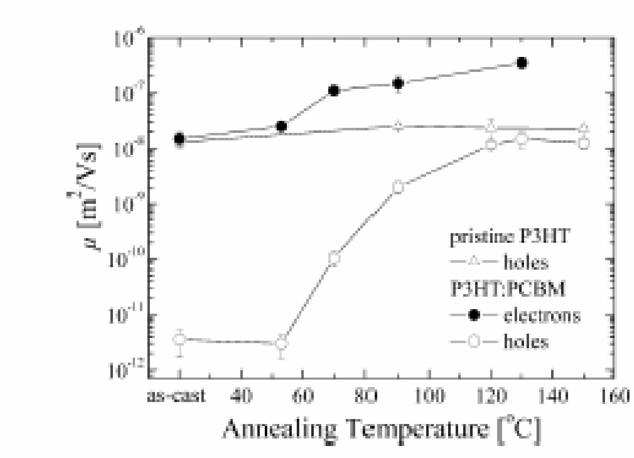
P3HT:PCBM, 1:1

Microscopia TEM



X. Yang et als. NanoLetters 5, 579 (2005)

Space Charge Limited mobilities

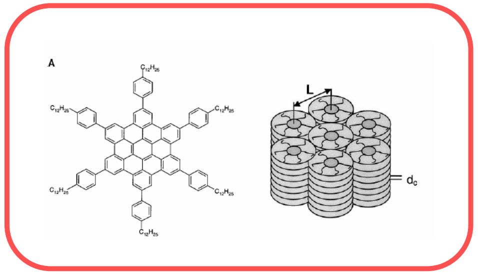


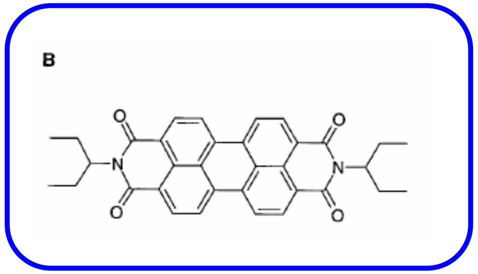
Michailetchi, Adv. Funct. Mater. **2006**, *16*, 699

upon annealing, hole mobility in the blend reaches P3HT prist. values !

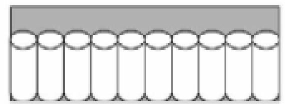
D:A self-organisation?

D : A

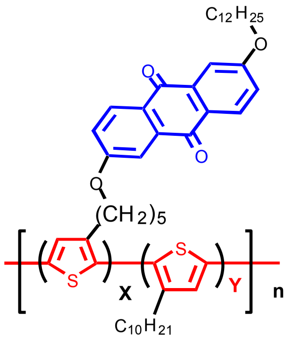




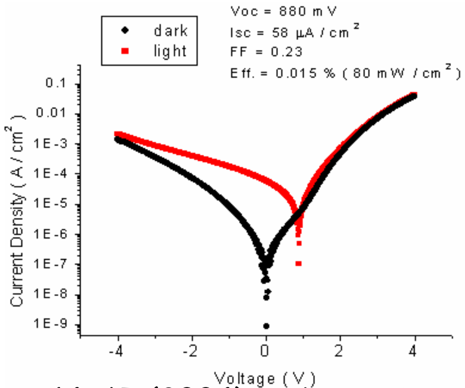
40:60

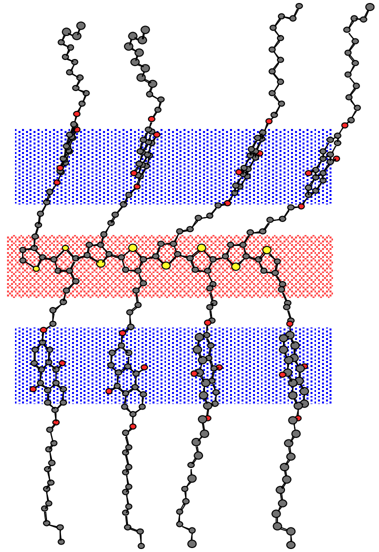


L. Schmidt-Mende et als. Science (2001) ***293****, 1119*



Double cable



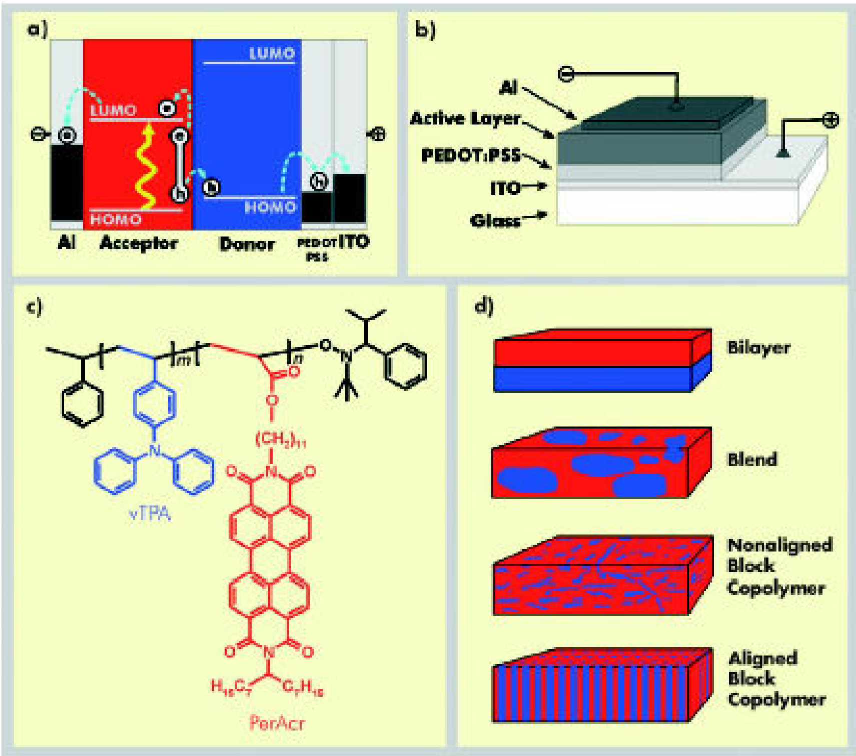


M. Catellani et als., J. Mater. Chem. 14, 67 (2004); S. Luzzati et als. Proc. SPIE Vol. 5215, p. 41, Organic Photovoltaics IV (2004)

Another example of self organisation

Angew. Chem. Int. Ed. 2006, 45, 3364–3368

Thellakat group,
Freiburg Univ.



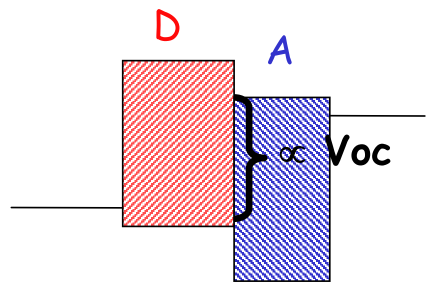
Interesting morphologies but very low efficiencies

Currently D:A blends leads to better performances

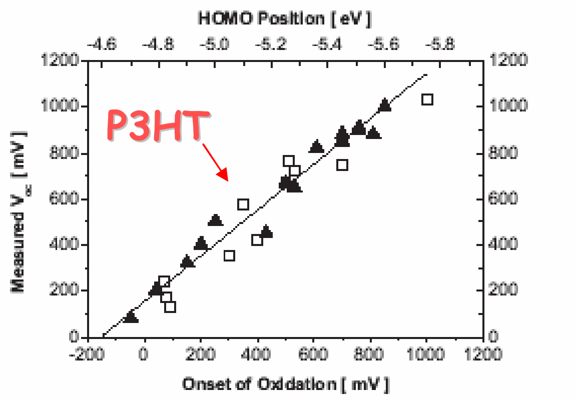
Key properties of BHJ active materials

$$\eta = \frac{P_{el.\,out}}{P_{inc.}} = FF\,\frac{I_{sc}\,V_{oc}}{P_{inc.}}$$

- ✓ morphology and charge transport
  - solar spectrum harvesting
- ✓ HOMO-LUMO levels



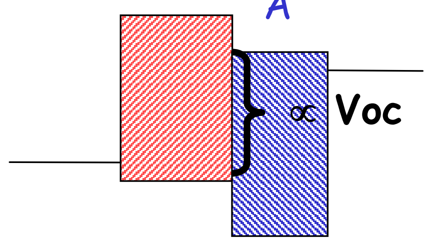
Design of new polymers
P:PCBM bulk heterojunction



Voc ∝ Lumo-Homo

New P (better than P3HT) :

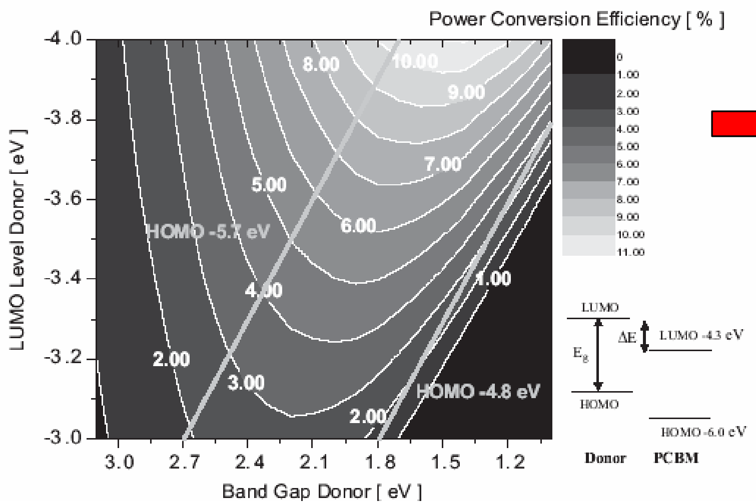
- **Lowering band gap**
- **Increasing oxidation potential**



lowering band gap often decreases ox. potential !

Ideal donor polymers for P:PCBM BHJ

conv. eff.



Donor polymer features

- ✓ HOMO ~ 5.7- 5.8 eV
- ✓ Eg ~ 1.8-2 eV
- ✓ good charge mobility
- ✓ good blend morphology

Polymer:pcbm solar cells up to 10-12% eff

*charge photogeneration and transport similar to P3HT:PCBM

M. Scharber et als, Adv. Mater 18, 789 (2006)

conclusions

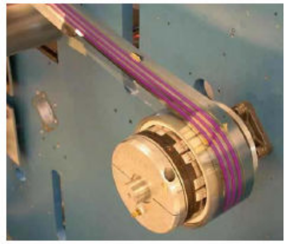
"plastic" solar cells: low cost and unconventional applications

efficiencies have drastically improved in the last three years, reaching 5 %, a threshold that opens up to the market

the design of the organic photoactive material has a key role for the efficiencies so far attained, and for future progresses

in the near future 10-12 % eff are expected for single cells and 15 % for tandem cells

Technological issues



Rooftop testing of BHJ solar cells at KONARKA

Konarka®

Flexible Organic P3HT:PCBM Bulk-Heterojunction Modules with more than 1 Year Outdoor Lifetime

Aspetti tecnologici: incapsulamento OPV flessibili

Celle solari incapsulate

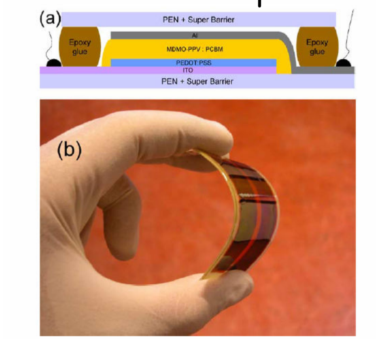


Fig. 3. (a) Cross-sectional view of the conjugated polymer:fullerene solar cells investigated here; (b) picture of a bent device.

Stabilità all'aria mdmoppv:pcbm

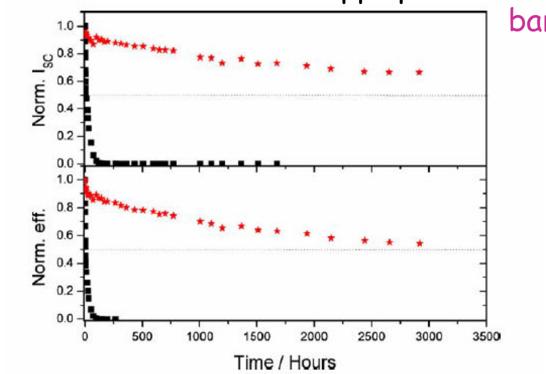


Fig. 5. Normalized I_{SC} and efficiency of solar cells encapsulated with uncoated PET (■) and with flexible gas barrier material (★) versus storage time in the dark under ambient air.

G. Dennler et al., J. Mater Res. 20, 3324, (2005);

- ■ Incapsulamento con film di PET
- * Incapsulamento con film di polietilennaftalene trattato con barriera

Requisiti di impermeabilità all'ossigeno e all'acqua per l'elettronica organica

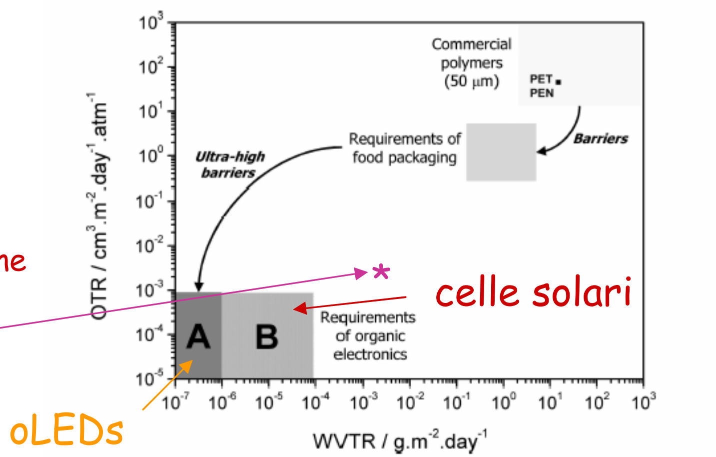
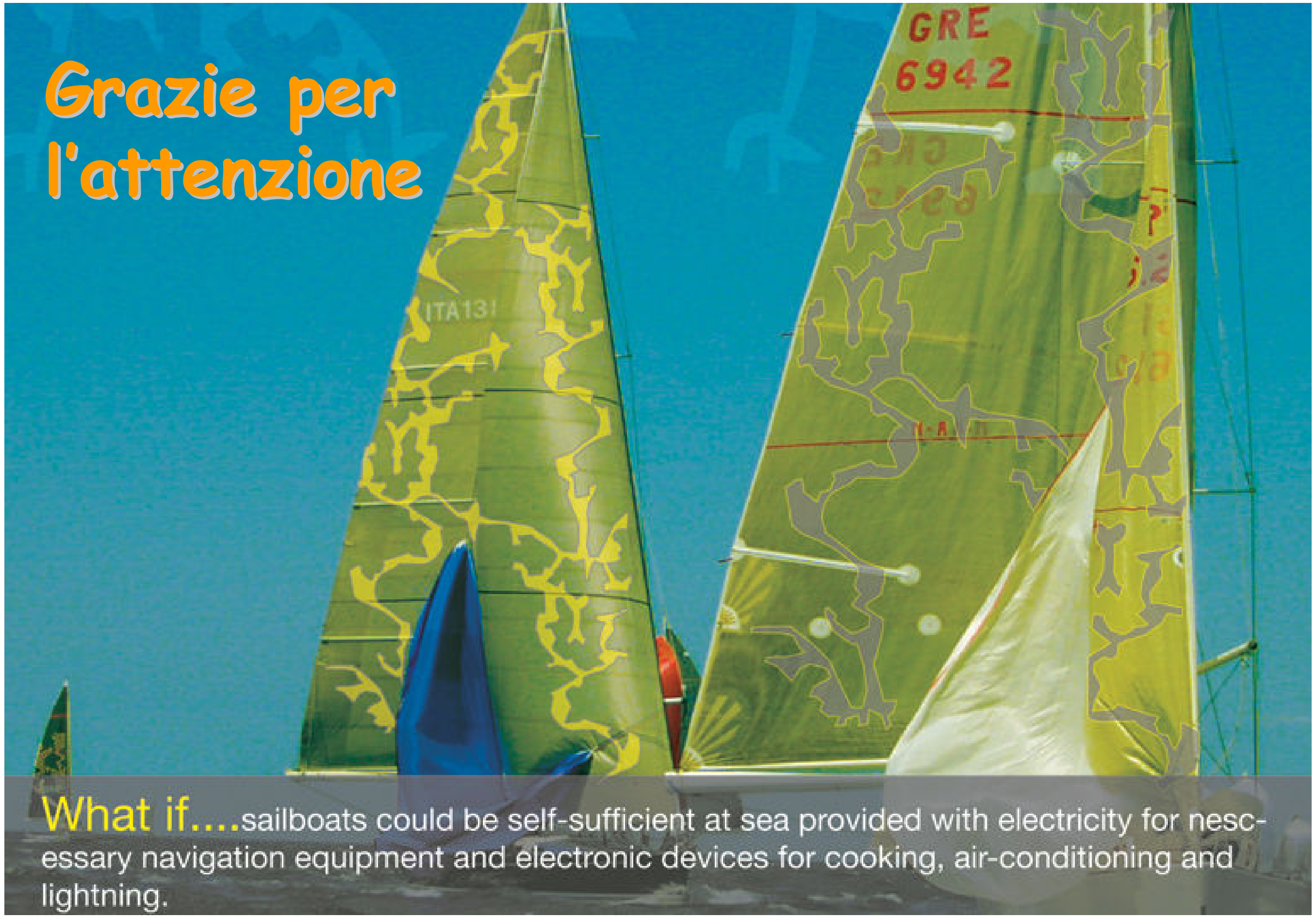


FIG. 5. Oxygen transmission rate (OTR) versus water vapor transmission rate (WVTR) for commercial polymers, encapsulations required for food packaging and for organic electronics purposes (A: organic light emitting diode grade; B: solar cell grade).

barriera: multilayer org/inorg

P. Madakasira et als, Synth. Metals 155 332 (2005)



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