Energy Conversion by Semiconductor Devices

Jun-Ho YUM
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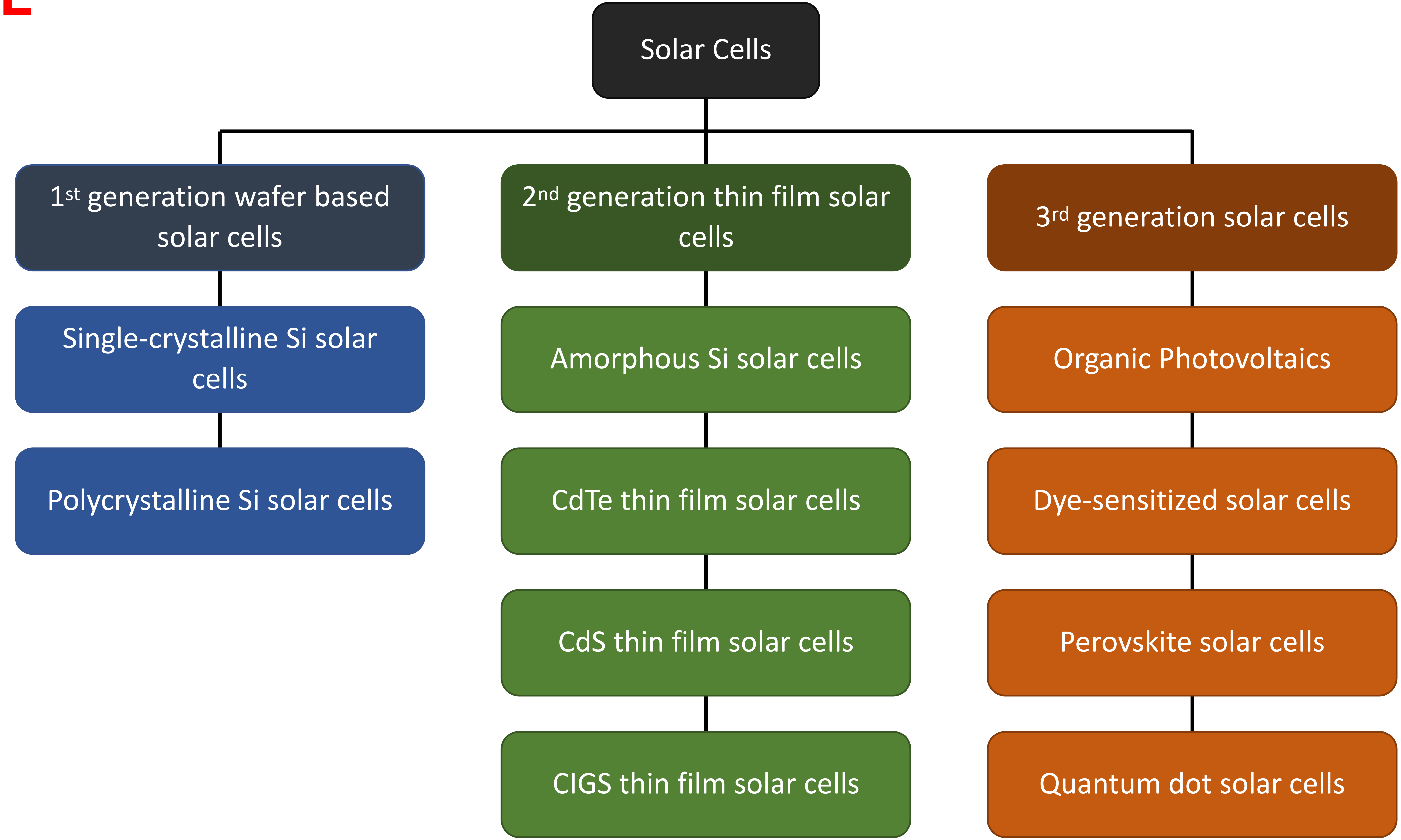
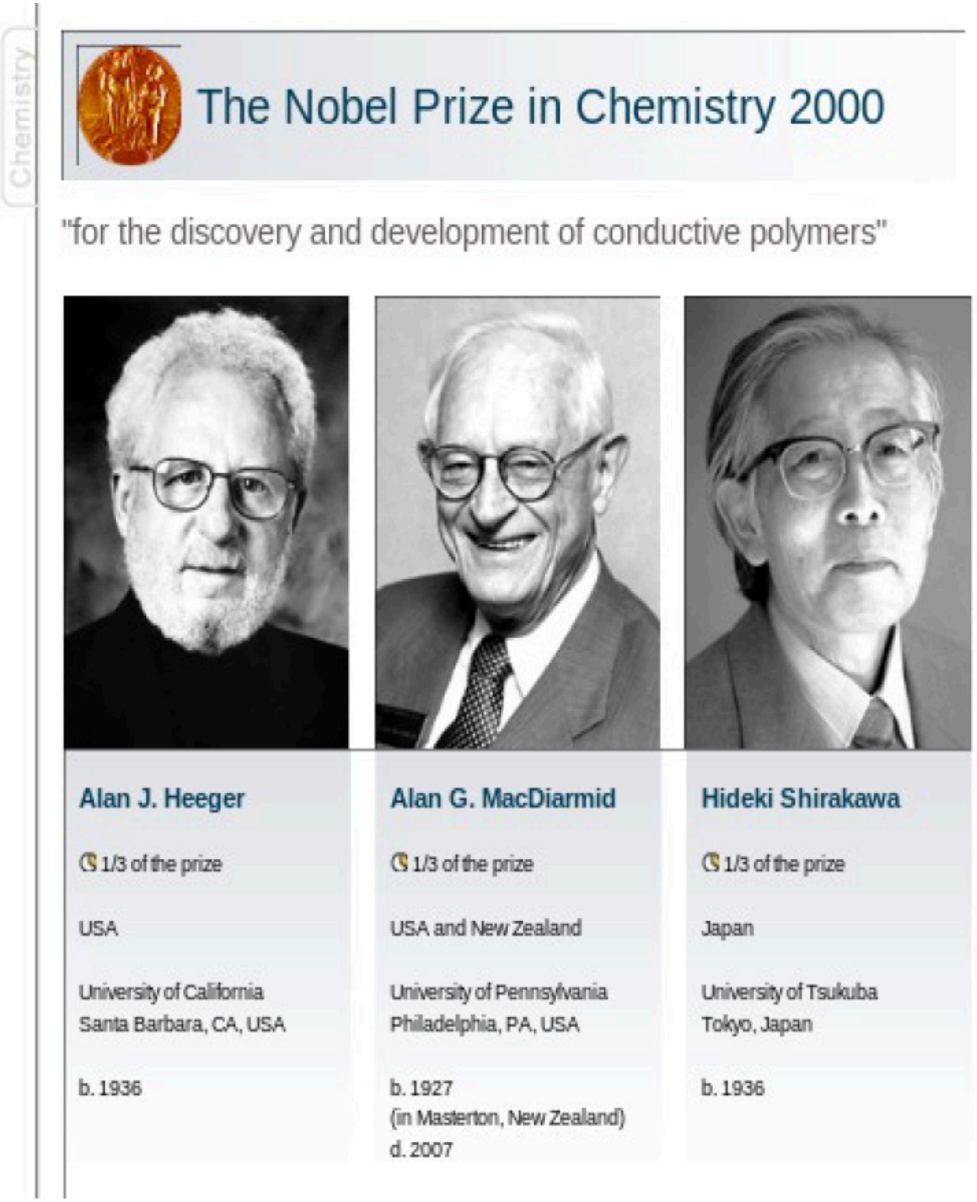
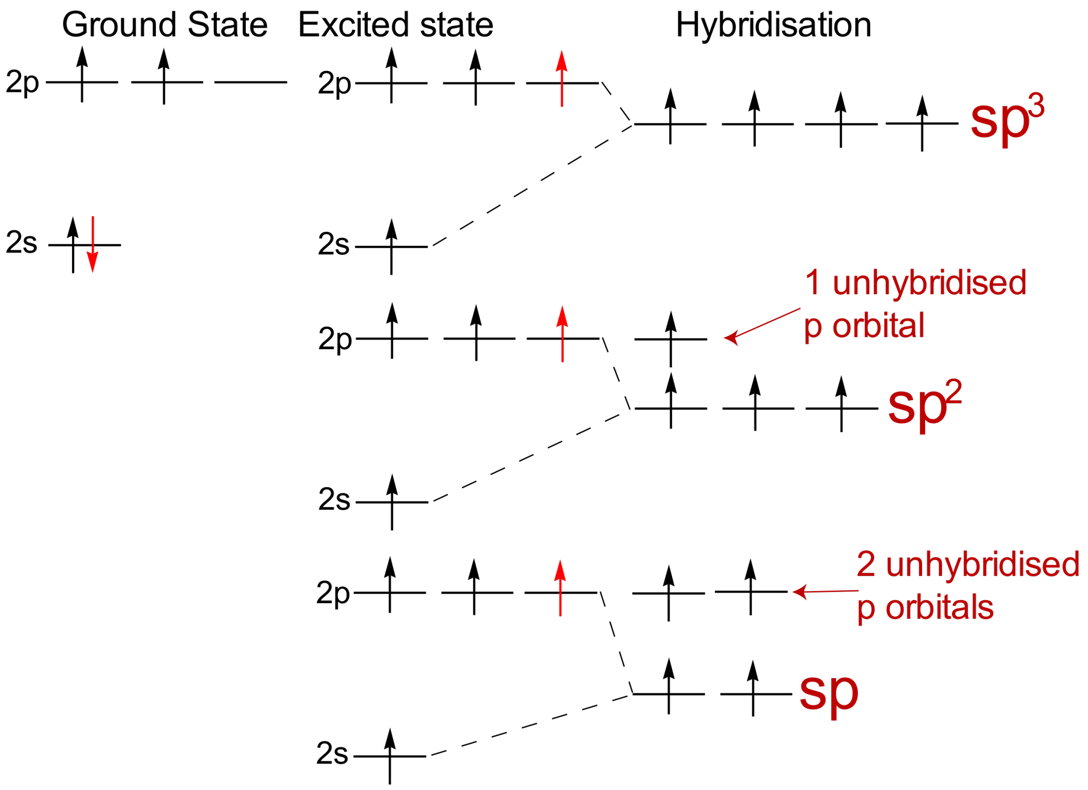

Solar Cells
1st generation wafer based solar cells
Single-crystalline Si solar cells
Polycrystalline Si solar cells
2nd generation thin film solar cells
Amorphous Si solar cells
CdTe thin film solar cells
CdS thin film solar cells
CIGS thin film solar cells
3rd generation solar cells
Organic Photovoltaics
Dye-sensitized solar cells
Perovskite solar cells
Quantum dot solar cells

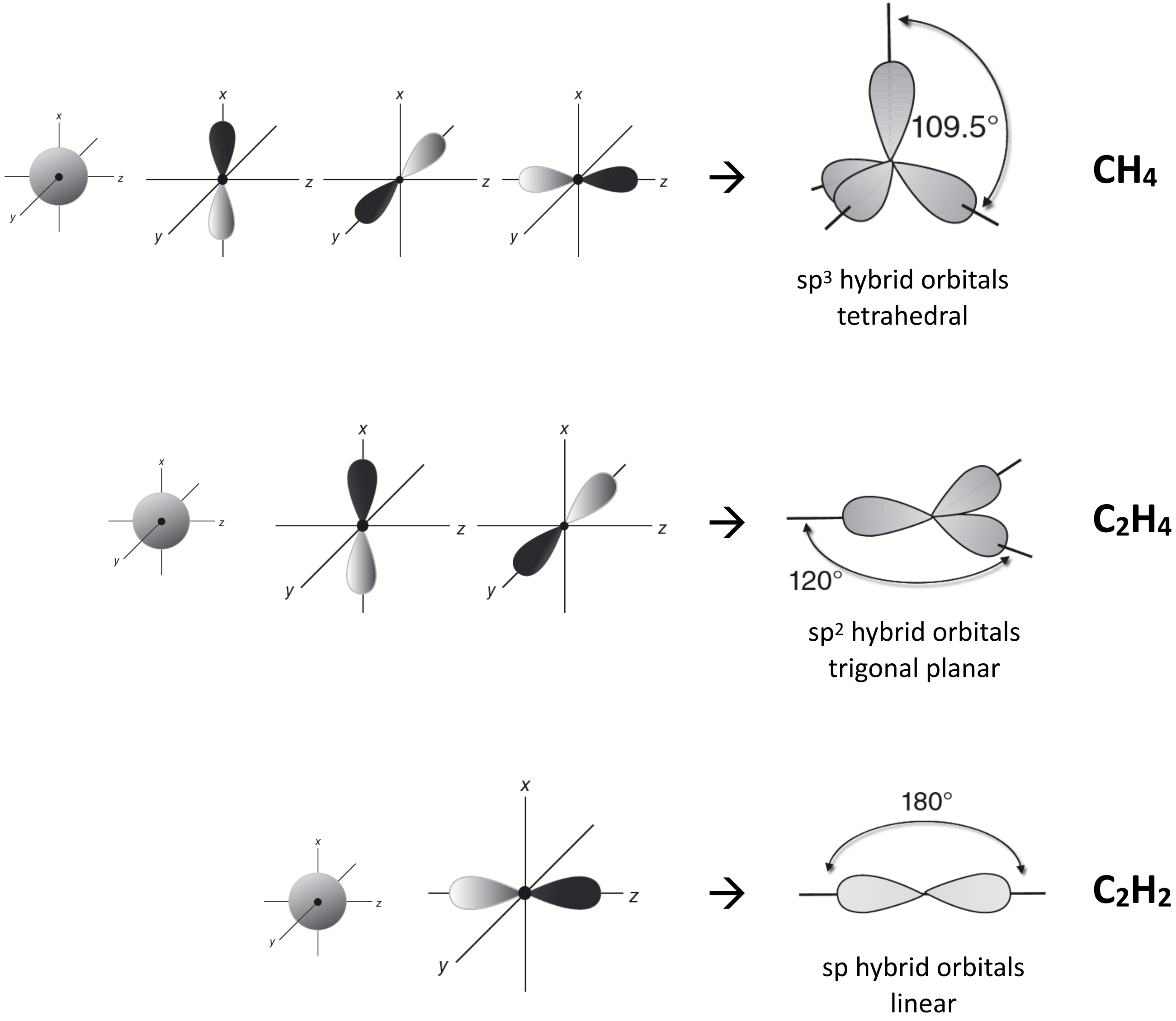
Organic Semiconductors



- **Thin films**
- **Strongly absorbing capability**
- **Tunability of optoelectronic properties**
- **Light and flexible**
- **Process from solution e.g. printing (especially for polymers) (vacuum evaporation can be used for processing small molecules)**

Organic Semiconductors

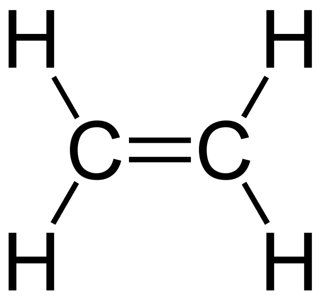


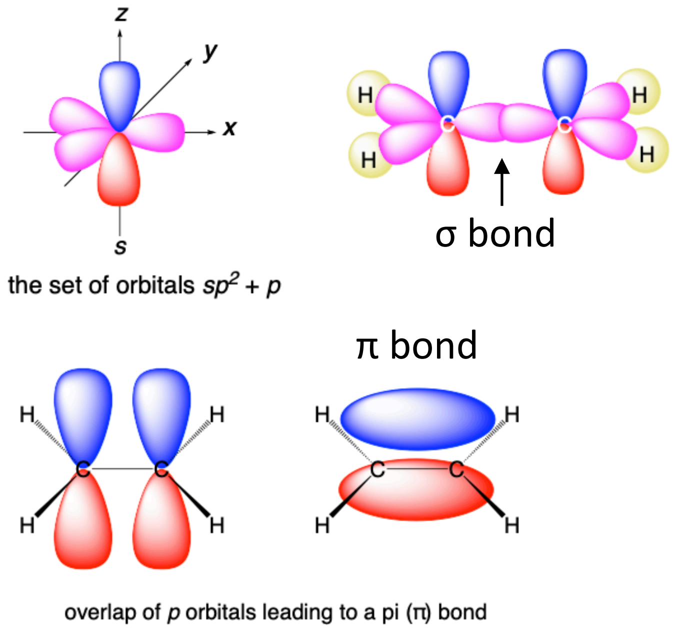


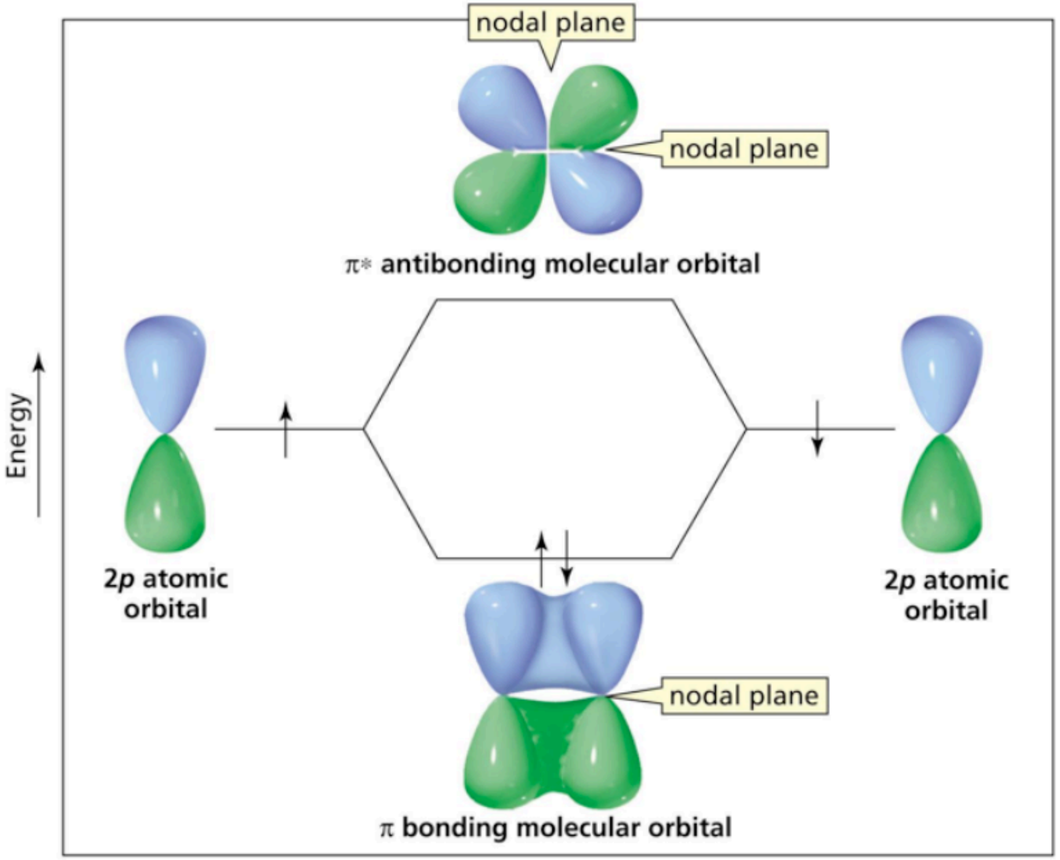
According to Valence Bond Theory (VB Theory)

Organic Semiconductors

Ethene







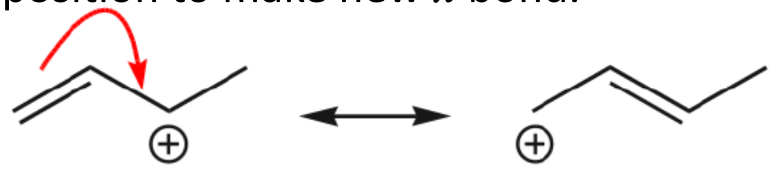
According to Molecular Orbital Theory (MO Theory)

Image taken from https://ecampusontario.pressbooks.pub/mcmasterchem1aa3/chapter/chapter-2-2-valence-bond-theory/2/

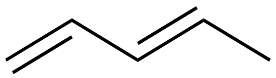
Organic Semiconductors

Overlap of π electron (conjugation) allows for the delocalization of electrons (resonance).

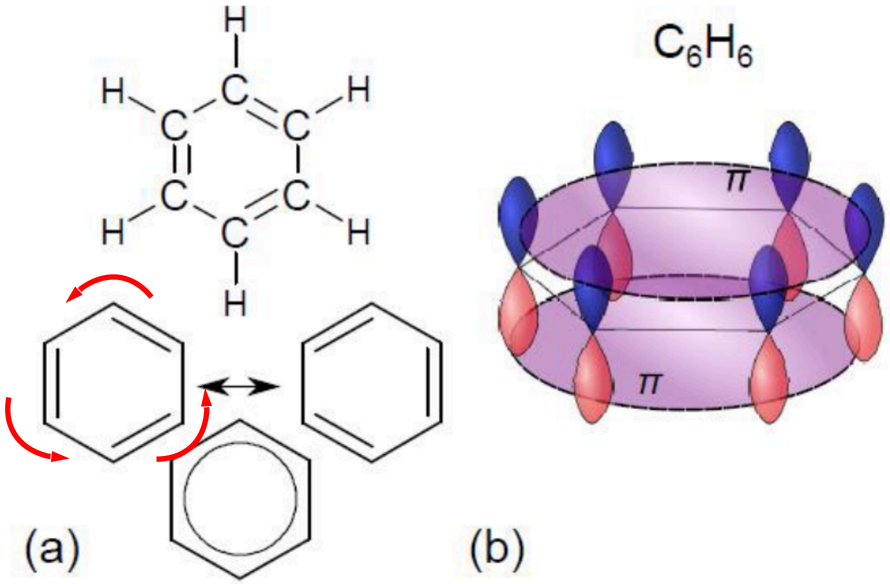
The π electrons can move to an adjacent position to make new π bond.



Conjugated



Not conjugated



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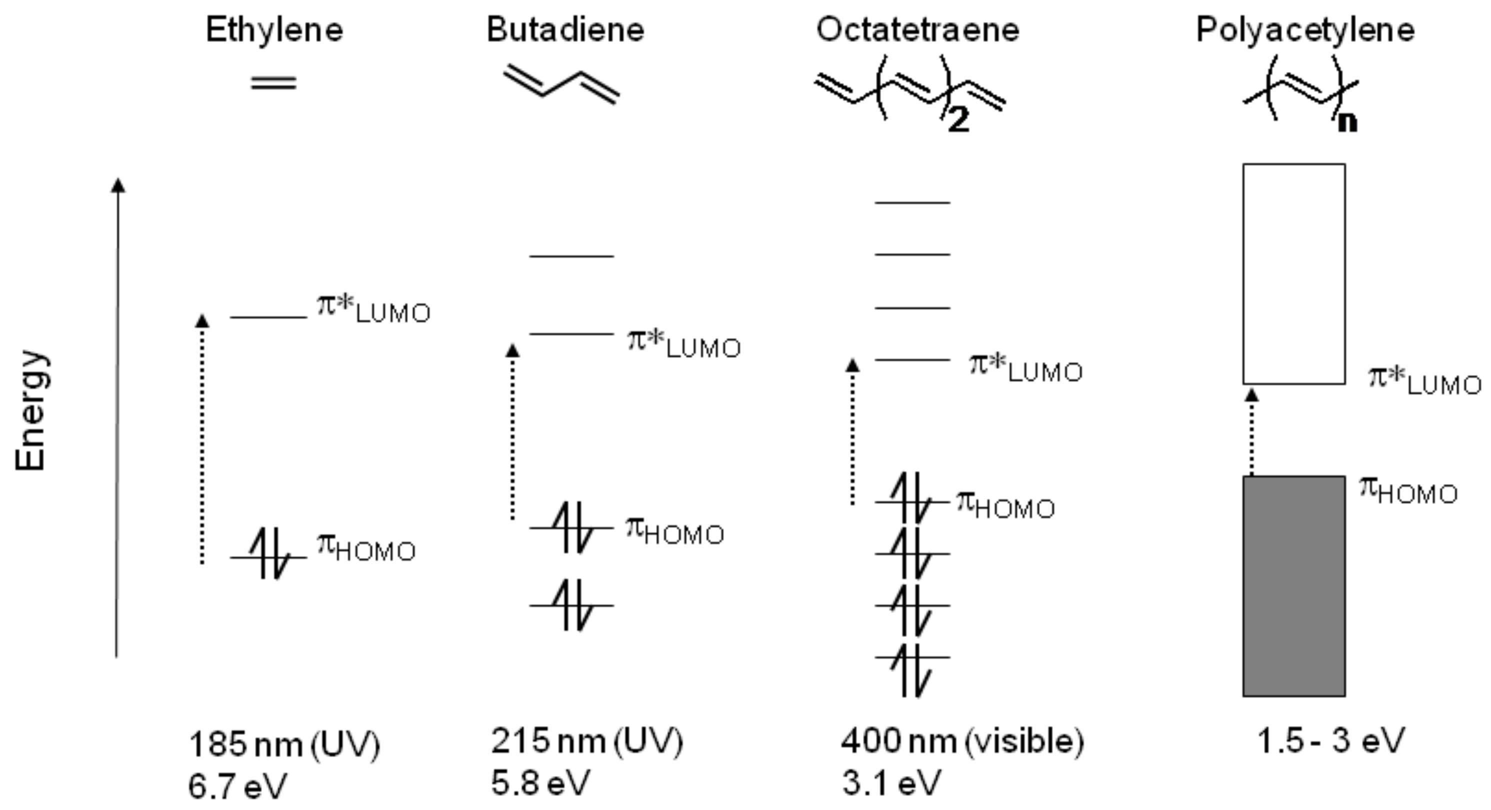
Organic Semiconductors



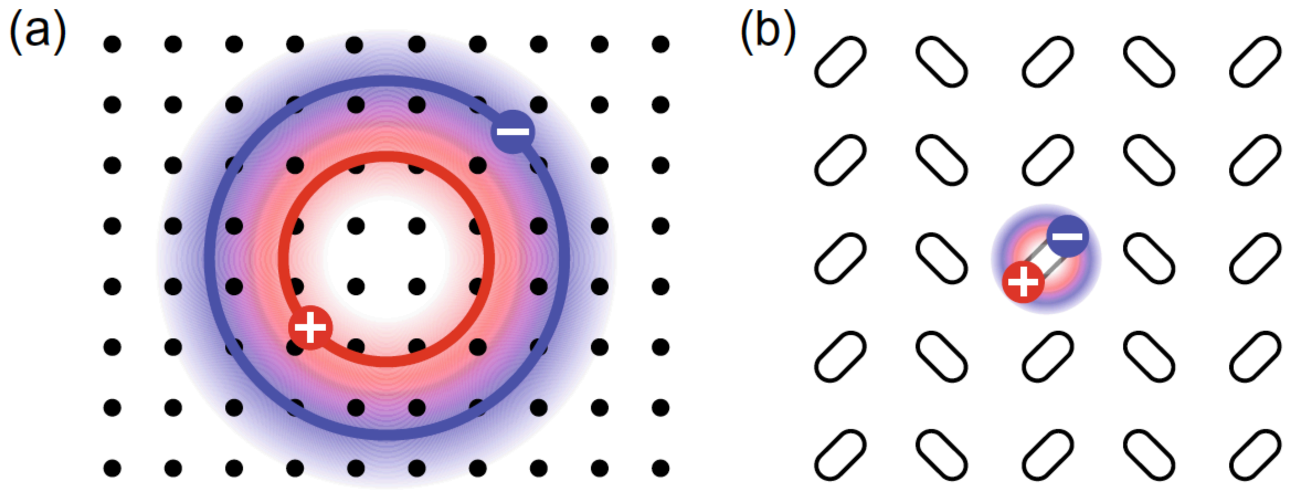
- **Frontier orbitals:**

  - Lowest Unoccupied Molecular Orbital (LUMO)

  - Highest Occupied Molecular Orbital (HOMO)

- **HOMO LUMO transitions determines the minimum photon energy to be absorbed.**

Excitonic Semiconductors



Udo W. Pohl, Epitaxy of Semiconductors, 2nd edition, Springer

(a) **Wannier exciton** with a large radius extending over many lattice constants.
(b) **Frenkel exciton** with a small radius localized at a molecule

$$E_H = \frac{m_0 q^4}{8\varepsilon_0^2 h^2} = 13.6\ \text{eV}$$

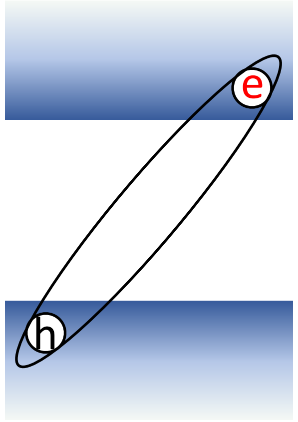
$$E_{X_{BE}} = \frac{m^* q^4}{8(\varepsilon_0 \varepsilon_r)^2 h^2} = E_H \cdot m^*/\varepsilon_r^2$$

- **Wannier exciton**
  - Inorganic semiconductors.
  - Typical energies 2 – 40 meV.
  - Exciton radii: a few nm.

- **Frenkel exciton**
  - Relatively small dielectric constants, large effective masses, resulting in strong Coulomb interaction.
  - Organic molecules.
  - Large binding energy exceeding 500 meV.
  - Localised on one molecule.

Inorganic Semiconductor vs Organic Semiconductor

ISC

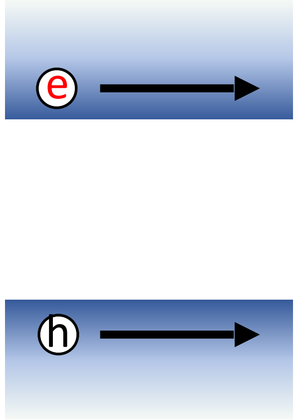


Conduction Band Minimum

(CBM)

Valence Band Maximum

(VBM)



$\mu = q\tau(T)/m^*$ (Drude model)

τ(T): the temperature dependent scattering time which decreases with increasing temperature, e.g. scattering with lattice phonons.

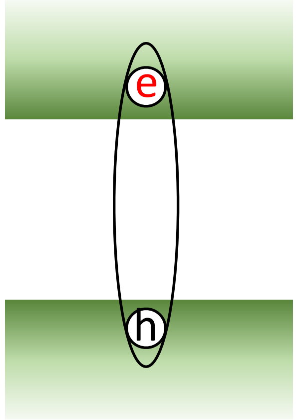
OSC

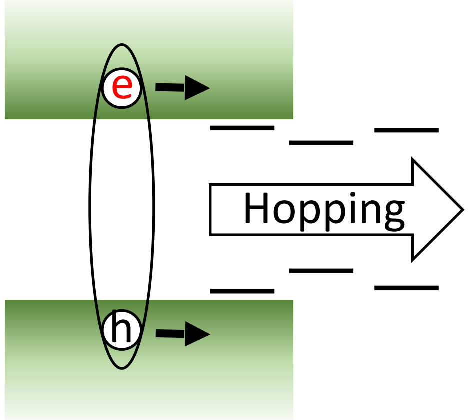
Lowest Unoccupied Molecular Orbital

(LUMO)

Highest Occupied Molecular Orbital

(HOMO)





$\mu = Dq/k_B$

$D = \alpha^2 k_{ET}$

Marcus-Hush's theory

$$k_{ET} = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi k_B T}} t^2 \exp\left(-\frac{\lambda}{4k_B T}\right)$$

$\boldsymbol{\alpha}$: intermolecular spacing

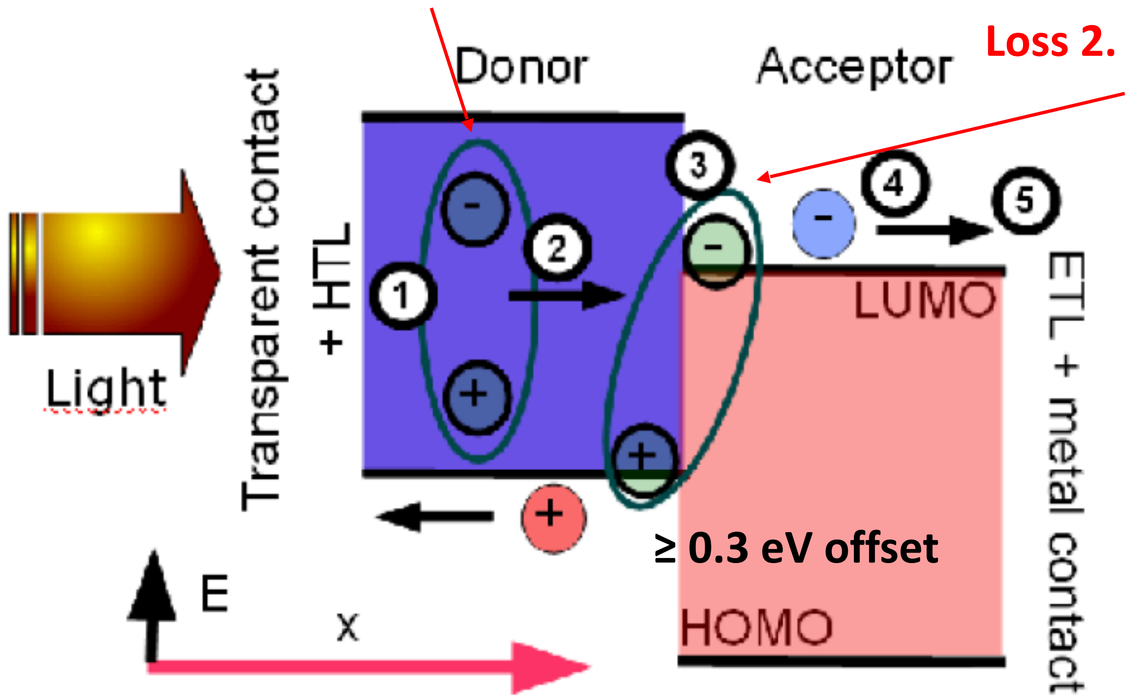
$\boldsymbol{k_{ET}}$: the charge transfer rate between neighboring molecules

$\boldsymbol{\lambda}$: the reorganization energy

Donor-Acceptor Concept

Loss 1. Monomolecular (Geminate) Recombination

Loss 2. Bimolecular (Nongeminate) Recombination



Steps of energy conversion

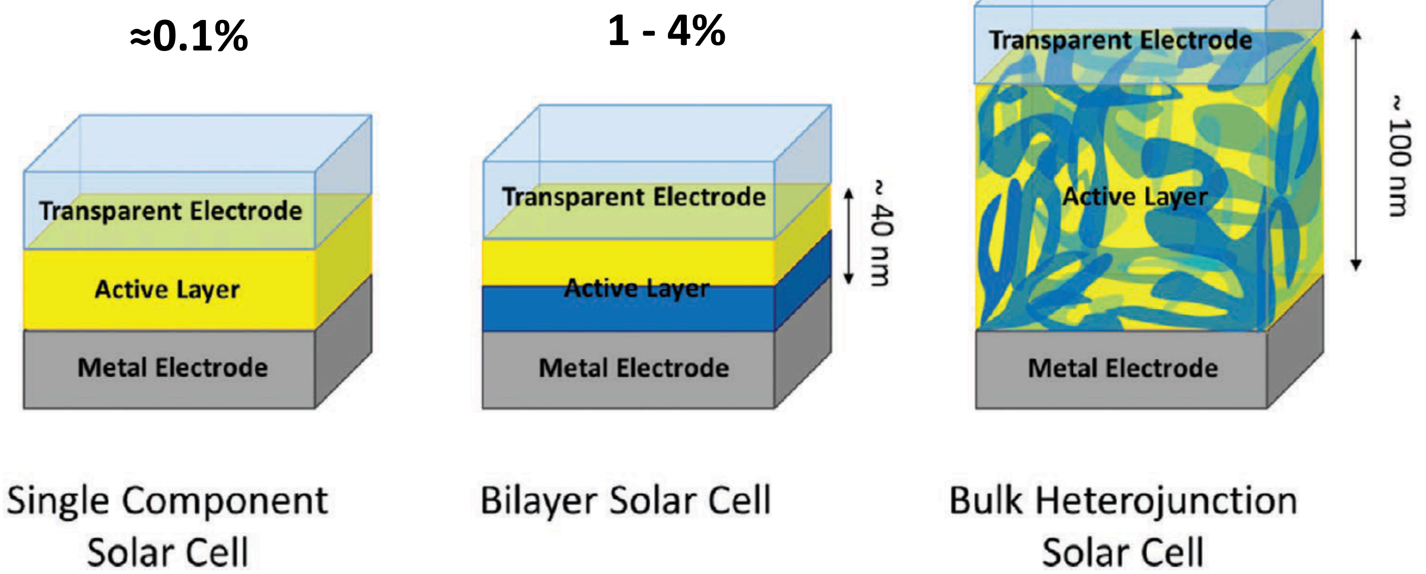
1. Exciton generation via light absorption
2. Exciton migration (diffusion)
3. Charge transfer (CT) state formation, exciton separation and dissociation from the CT state
4. Charge carrier transport
5. Charge carrier collection/injection

CT state: Electron transfer dissociates the exciton, giving an electron on the acceptor and hole on the donor. The hole and electron are still 0.5 − 1 nm apart, at which separation they should have significant Coulomb binding energy and form a charge-transfer state.

Schematic of Organic Solar Cells

- The photovoltaic effect in organic planar heterojunction in 1986 (C. W. Tang, *Appl. Phys. Lett.* 48, 183 (1986).
- Donor-Acceptor heterojunction to overcome the high exciton binding energy.
- The state-of-the-art high efficiencies are achieved by the **bulk heterojunction (BHJ)**: Randomly mixed donor and acceptor molecules provide contiguous percolation pathways of donor- and acceptor-rich domains, interpenetrating network of donor and acceptor domains on the length scale of 10 – 20 nm, thicker film without substantial increasing recombination losses.

Starting from 3 - 5%
and now over 18%



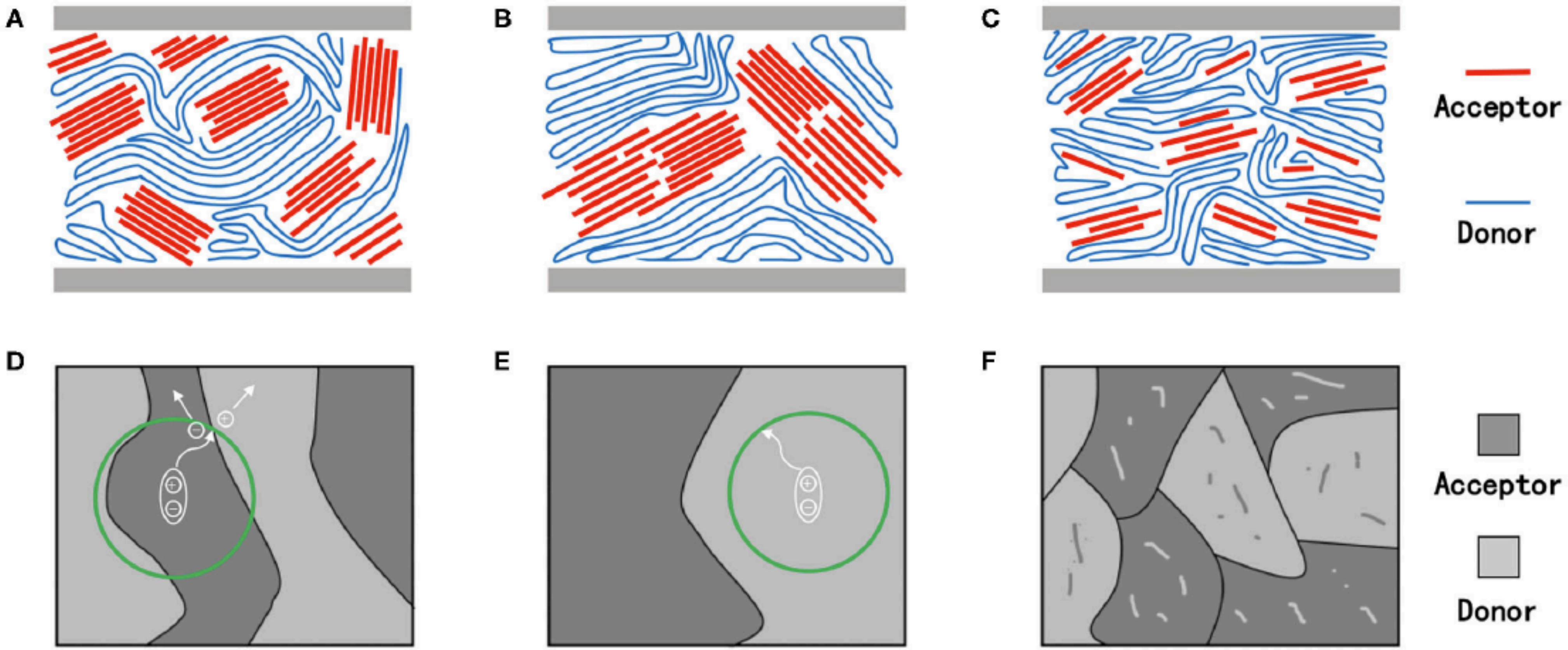
Film Morphology and Charge Transfer

- **The domain size of the active layer film should be equivalent to the exciton diffusion length.**

Good domain size!

Domains with excessive crystallinity
Large domains > diffusion length
Modest phase separation

Domains with low crystallinity
Poor film formation
Weak phase aggregation



D. Qiu et al., *Frontiers in Chemistry*, **8**, 603134 (2020)

Schematic of Organic Solar Cells

- Engineering of interfaces with an electron transport layer (ETL) and/or a hole transporting layer (HTL) helps to extract maximum charge output.

- Low work function metal tends to oxidize relatively easily than high work function metal → introduction of inverted device architecture.

Conventional OSC **Inverted OSC**

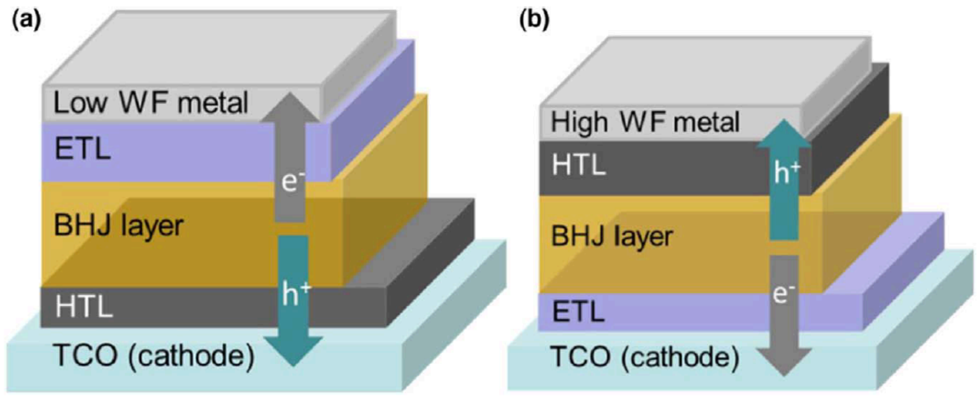
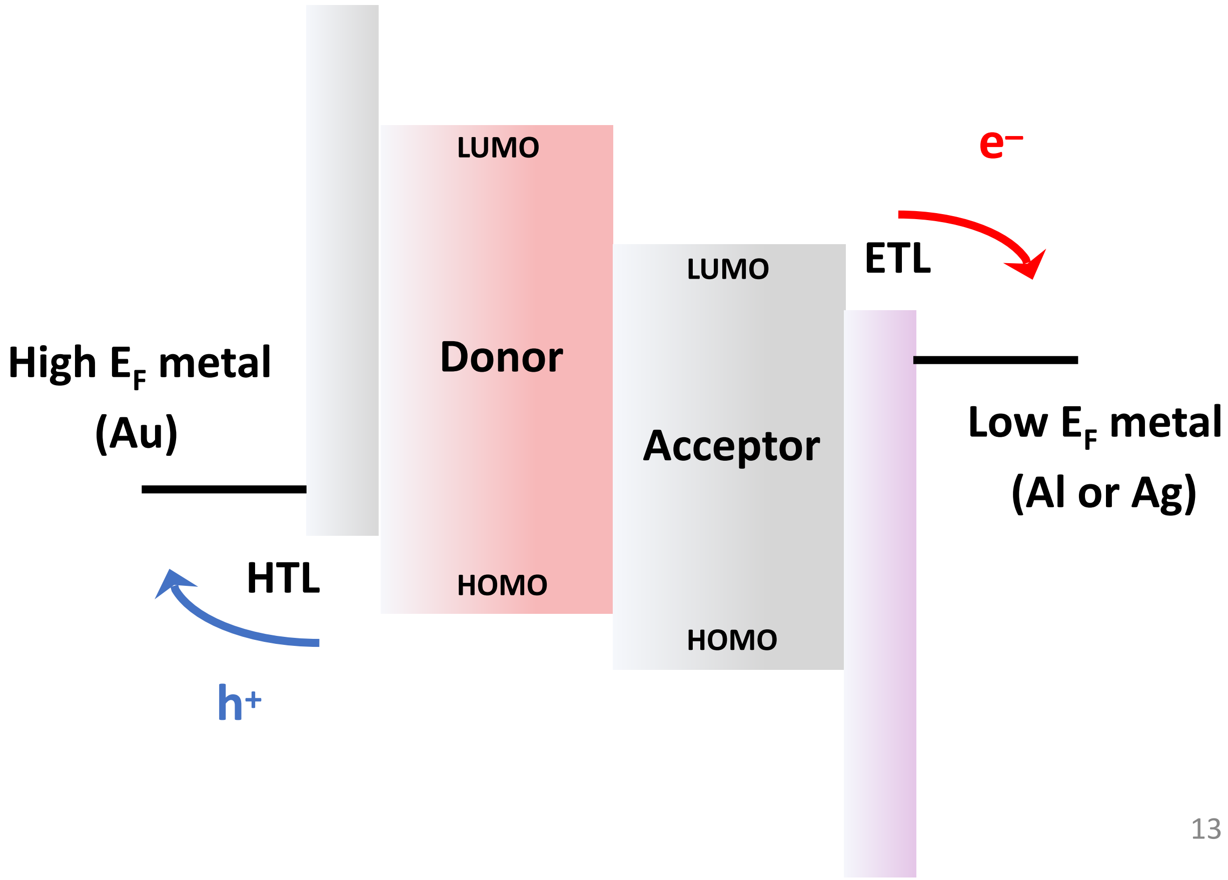


Image from S. O. Oseni et al., *Sol. Energy Mater. Sol. Cells*, 160, 241 (2017)



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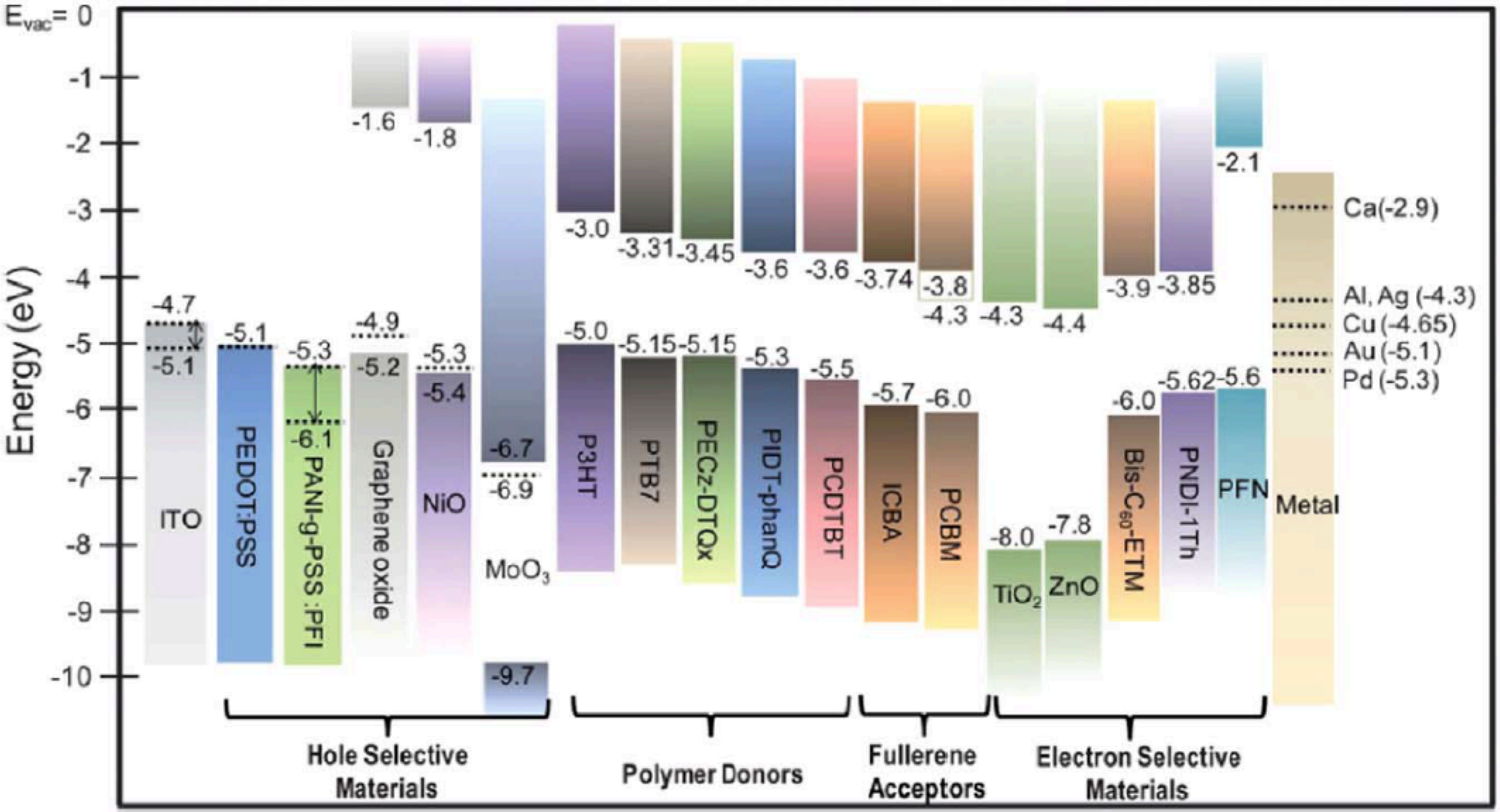
Schematic of Organic Solar Cells



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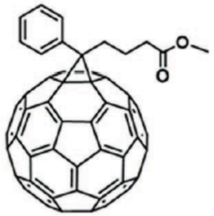
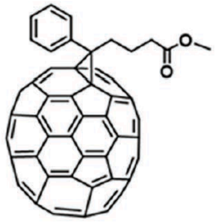
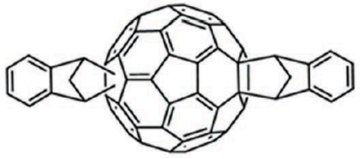
Chemical Structure of Conjugated Polymers

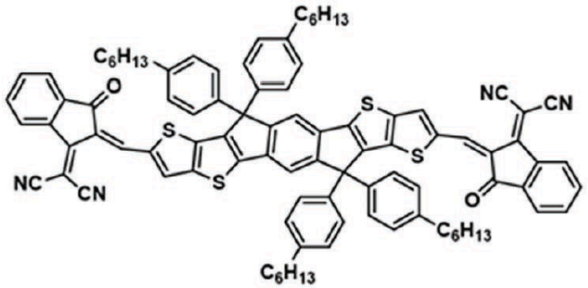
Donors

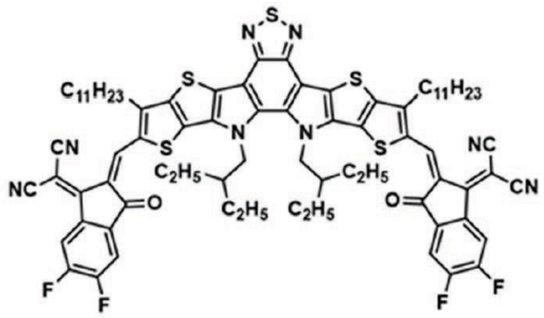
Acceptors

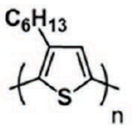

$PC_{61}BM$

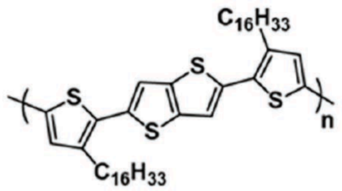

$PC_{71}BM$

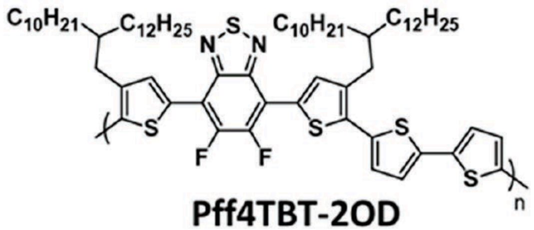

ICBA

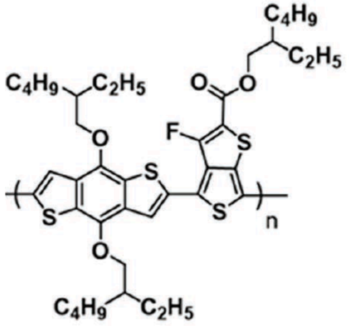

ITIC

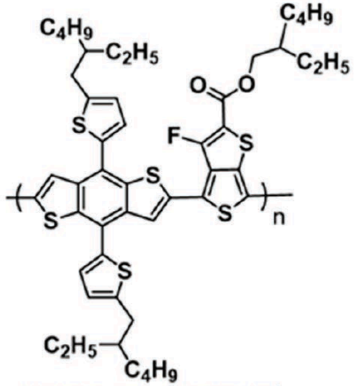

Y6

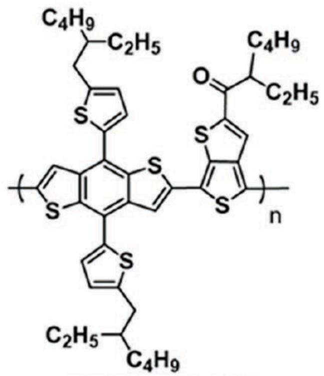

P3HT

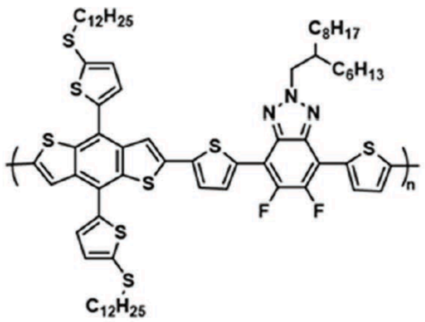

pBTTT

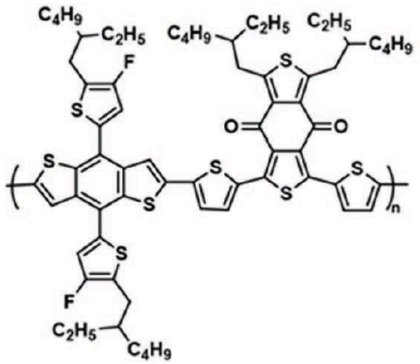

Pff4TBT-2OD

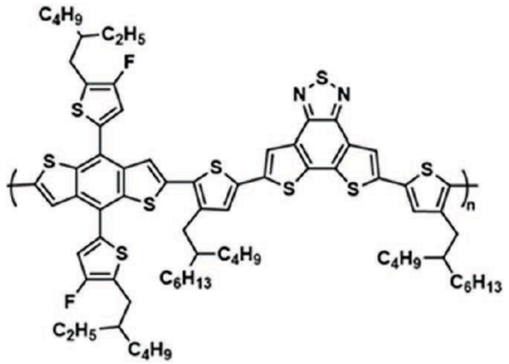

PTB7


PTB7-Th (PCE10)


PBDTTT-C-T


J61


PM6 > 15%


D18 > 18%

How to Improve Photovoltage in OPV

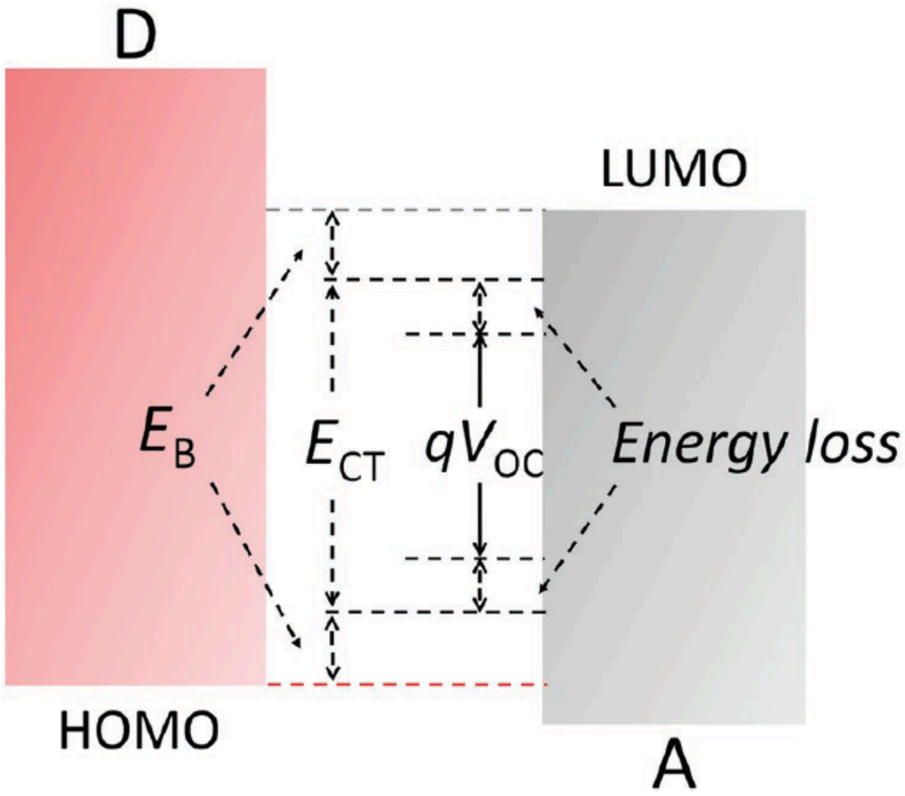
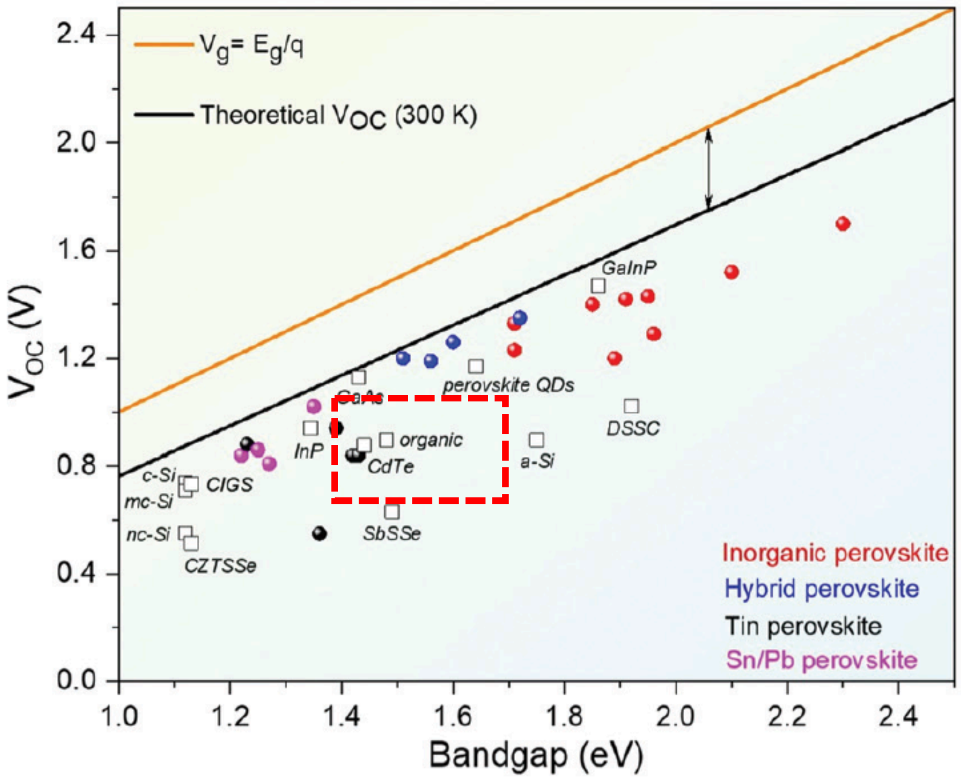


Image from Y. Liu et al., *Adv. Funct. Mater.* 2206707 (2022)

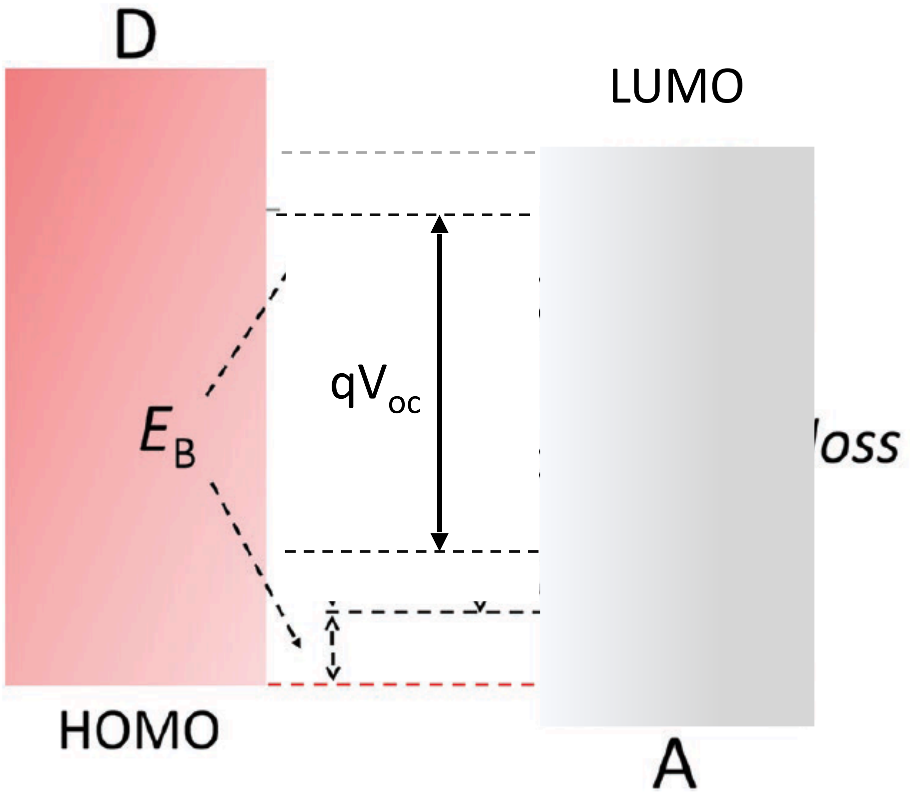
V_{oc} *vs* various solar cells



- $E_{loss} = E_g - eV_{oc} \approx 0.64\ V$
- The loss is bigger than perovskite or GaAs PV.

Image from *ACS Energy Lett.*, 5, 3029−3033 (2020)

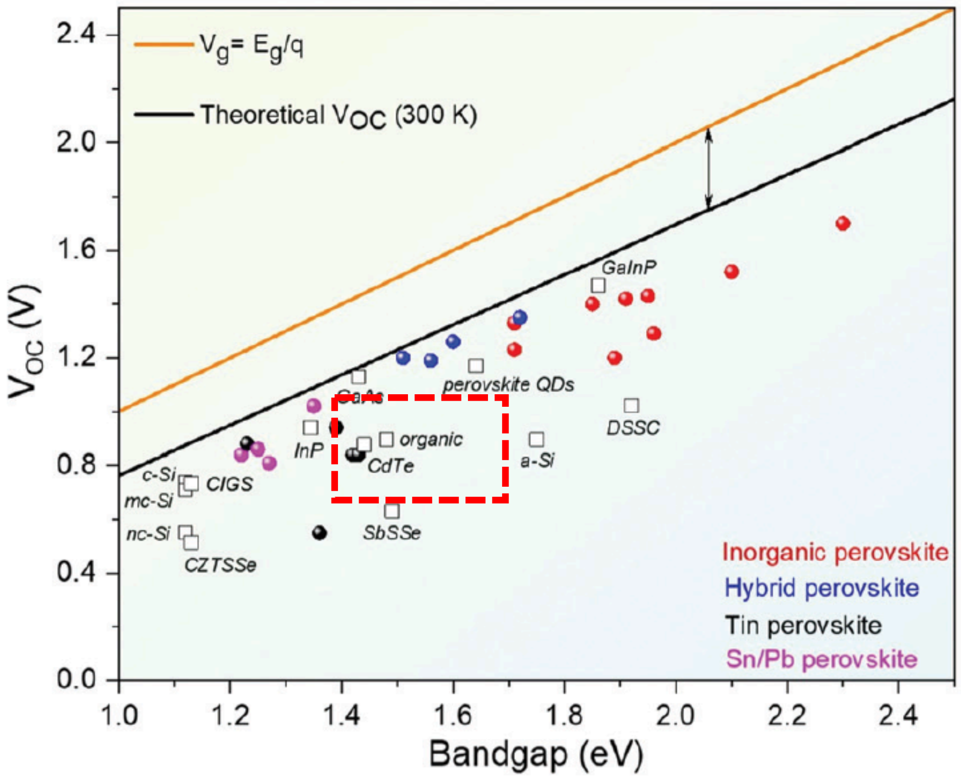
How to Improve Photovoltage in OPV



- Reduce "offset" energies.
- Mitigate "charge recombination".

Image from Y. Liu et al., *Adv. Funct. Mater.* 2206707 (2022)

V_{oc} *vs* various solar cells



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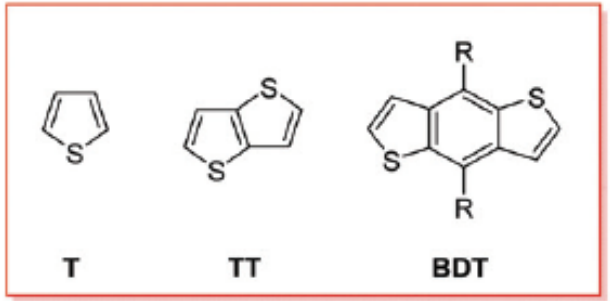
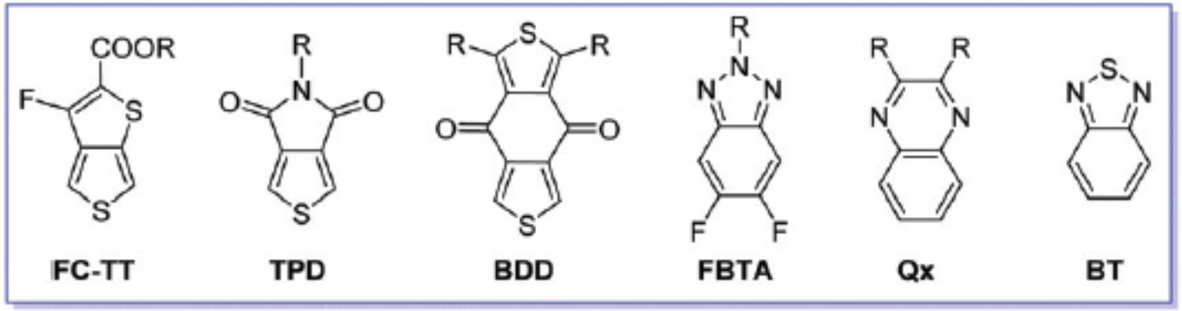
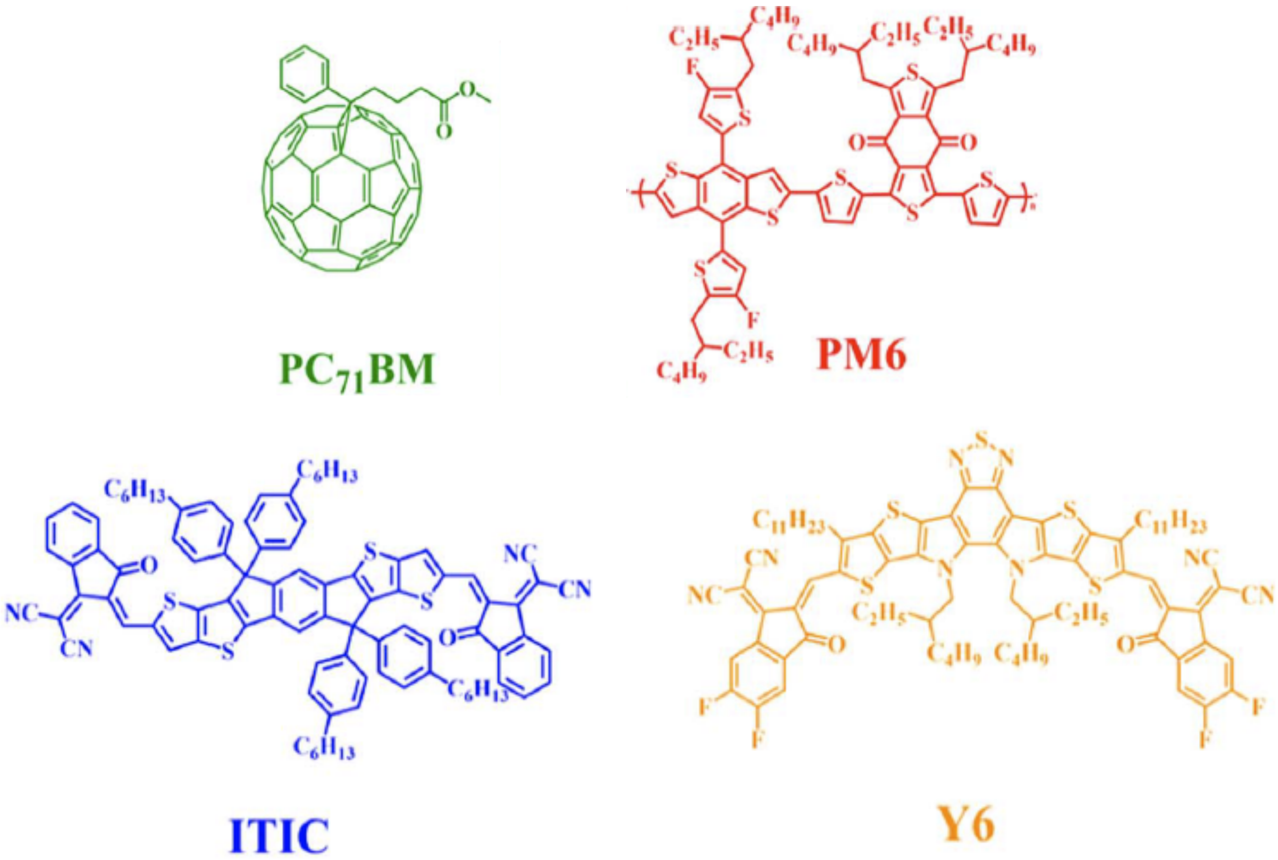
How to Improve Photocurrent in OPV



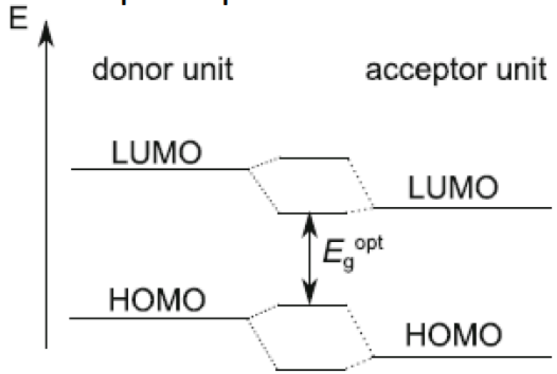
D building blocks



A building blocks



push-pull molecules



How to Improve Photocurrent in OPV

UV (3 - 5%) **Vis (42 - 45%)** **NIR**

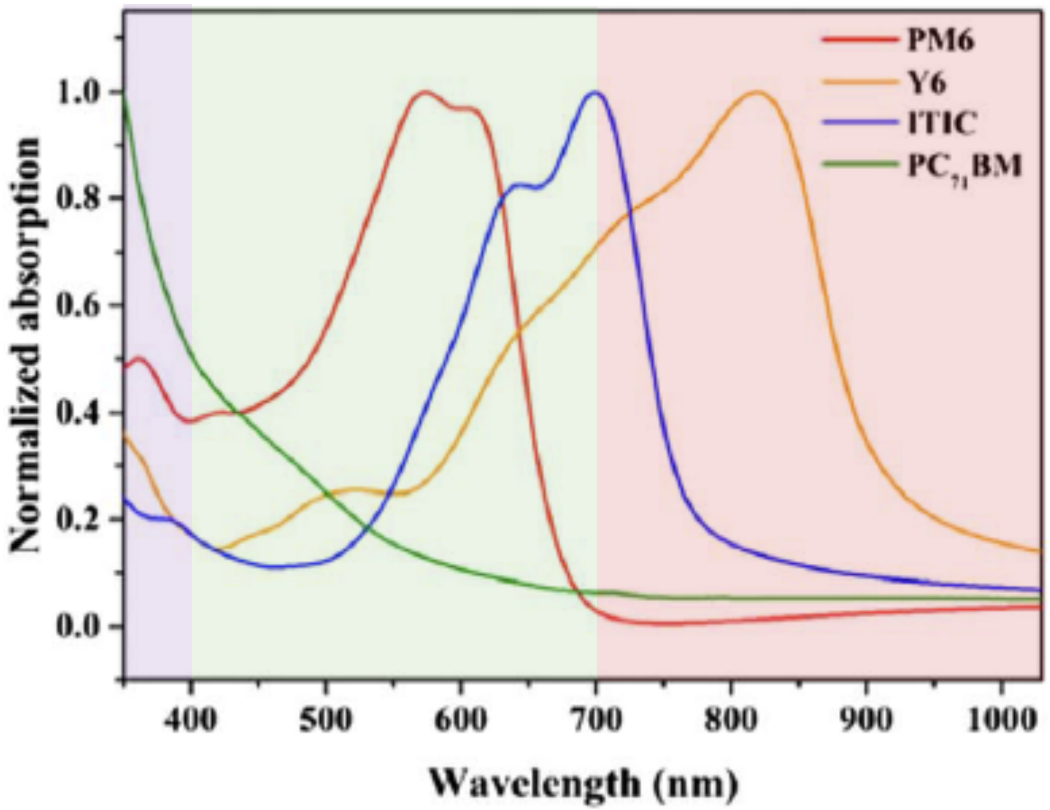
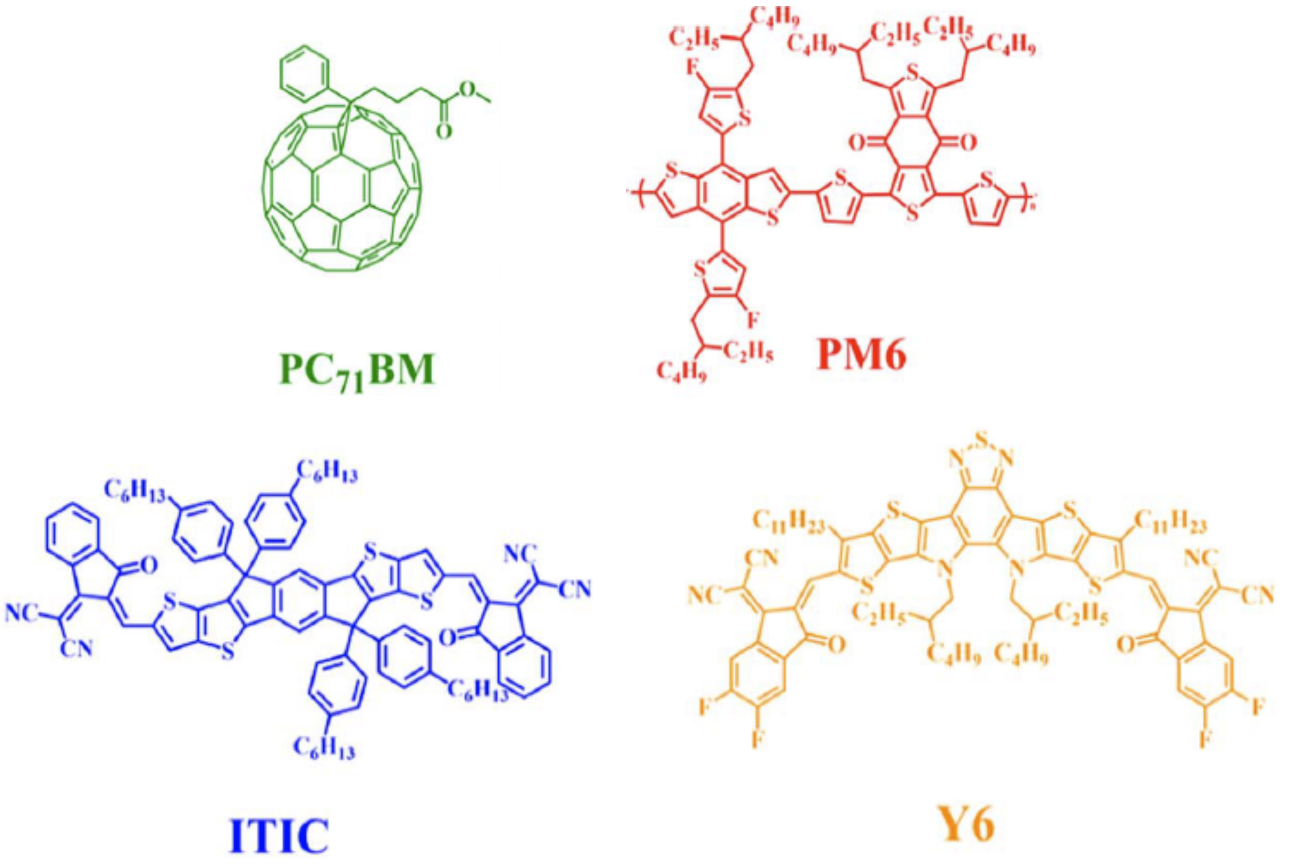
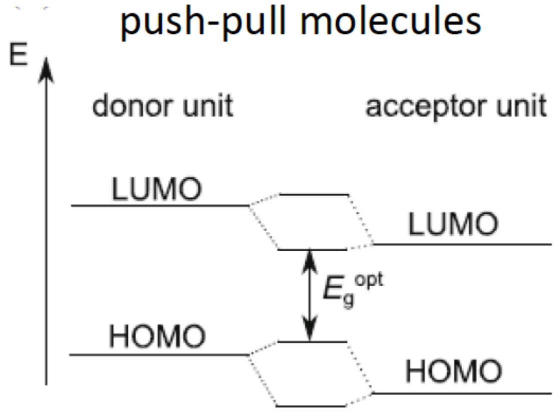


Image from Z. Jia et al., *Photonics Res.*, 9, 324 (2021)

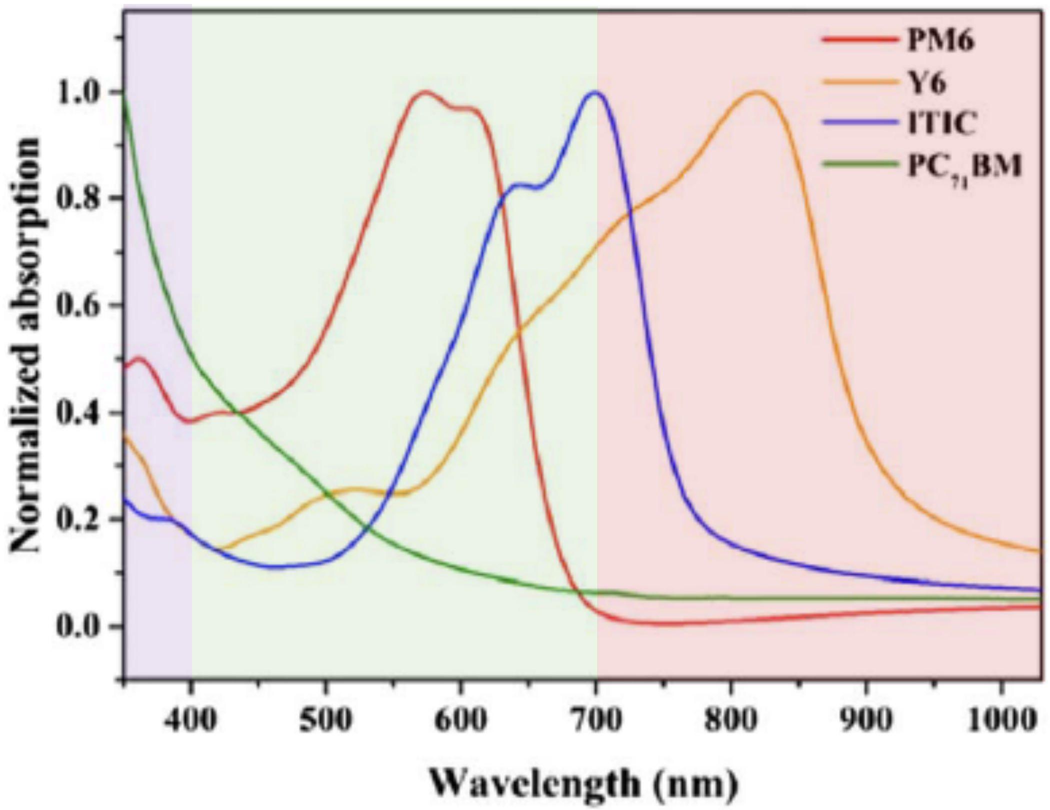


- Low band gap materials e.g. push-pull molecules.



How to Improve Photocurrent in OPV

UV (3 - 5%) Vis (42 - 45%) NIR



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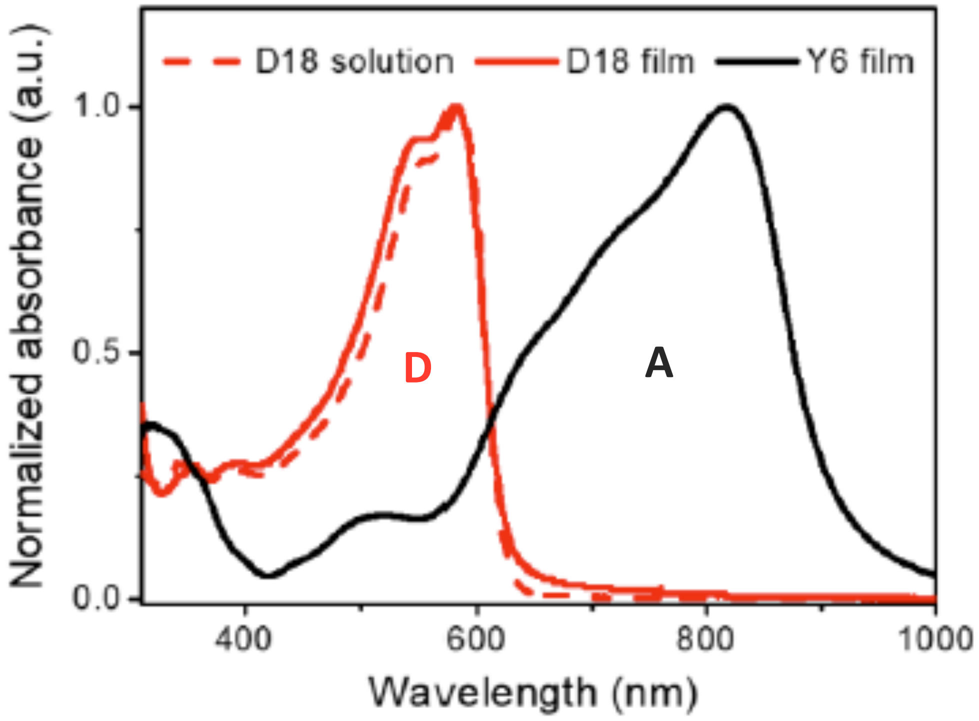


Image from Q. Liu et al., *Sci. Bulletin*, 65, 272 (2020)

- Low band gap materials e.g. push-pull molecules.
- Complementary absorption of D and A molecules.

Trade-off between Photovoltage and Photocurrent in OPV

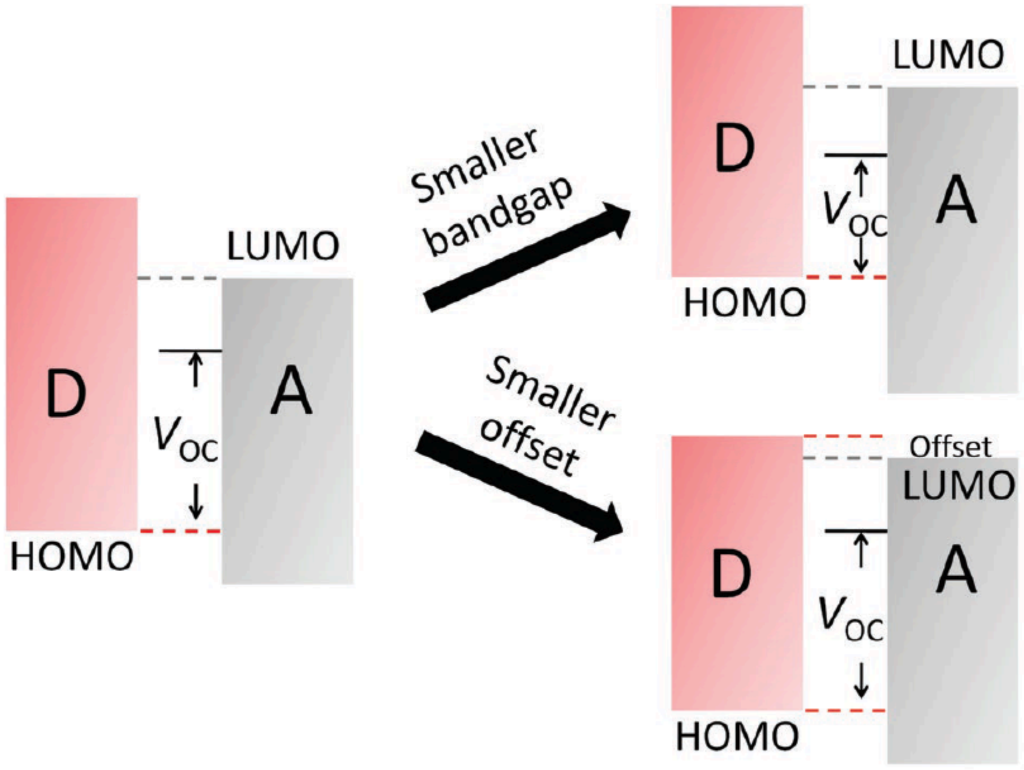
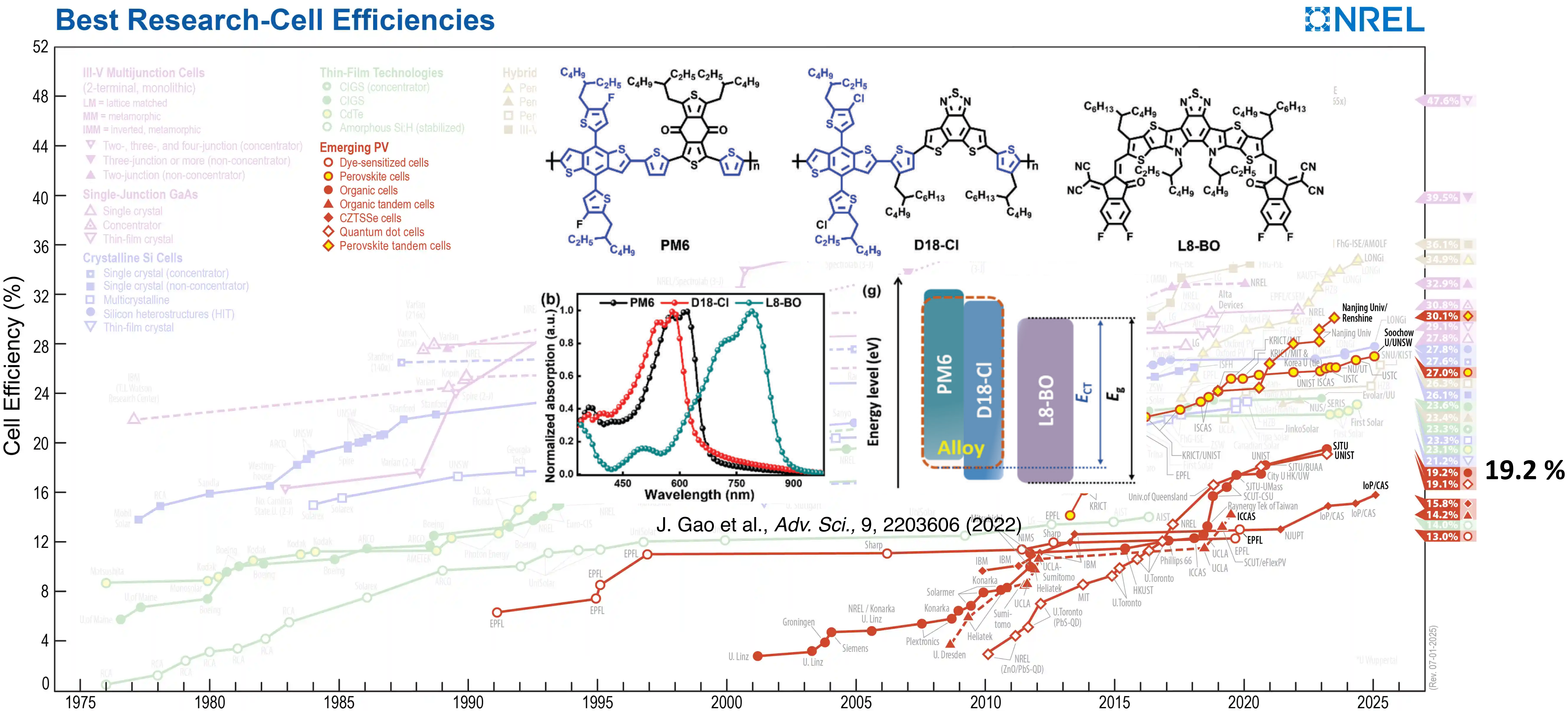


Image from Y. Liu et al., *Adv. Funct. Mater.* 2206707 (2022)

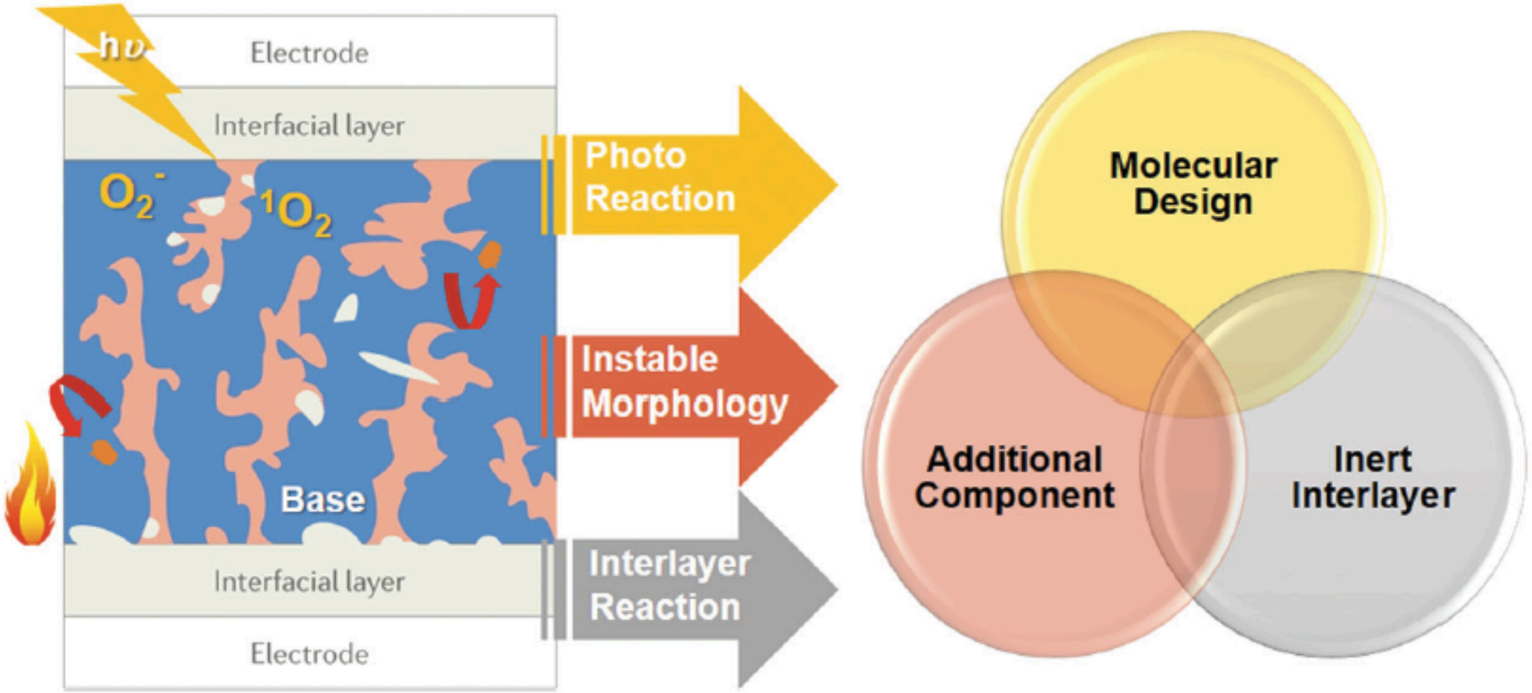
- Broadening light absorption by making a material with a smaller HOMO-LUMO gap would be a convenient option.
- Shrinking the energetic difference between the HOMO of Donor and LUMO of Acceptor.
- Reducing the maximum V_{OC} attainable in OPV.
- By contrast, deriving higher V_{OC} by enlarging the bandgap would degrade the photocurrent production.
- Empirical 0.3 eV offset is required for the CT process, which has been reported in several fullerene-based systems.

Organic Photovoltaics



J. Gao et al., *Adv. Sci.*, 9, 2203606 (2022)

Stability Issues

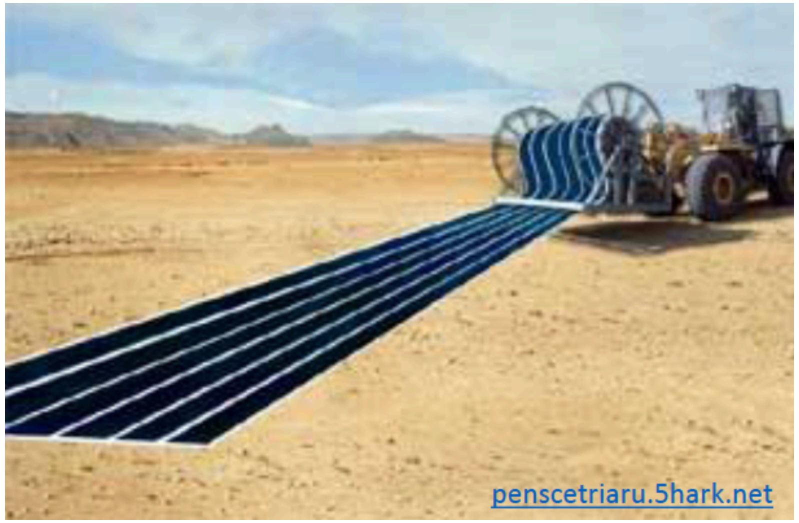


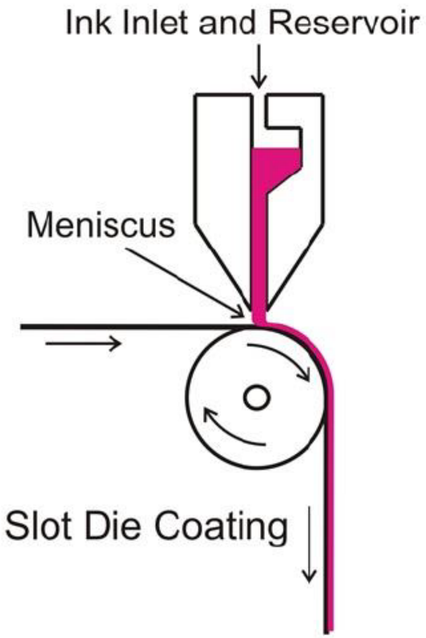
Y. Li et al., *Mater. Chem. Front., 5,* 2907–2930 (2021)

L. Duan et al., *Adv. Sci.,* **7**, 1903259 (2020)

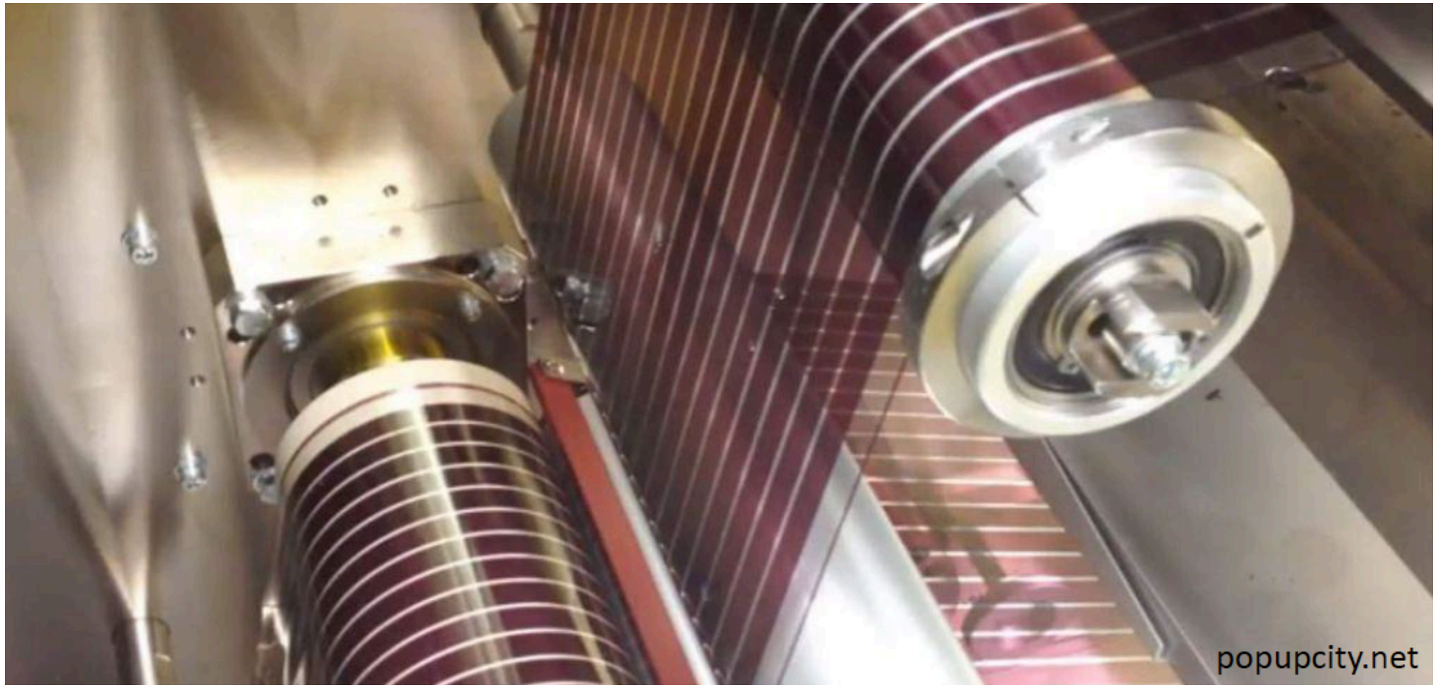
Roll-to-Roll Fabrication

- **Low-Cost: Roll-to-roll**
  - Printing
  - Slot die coating
  - Evaporation



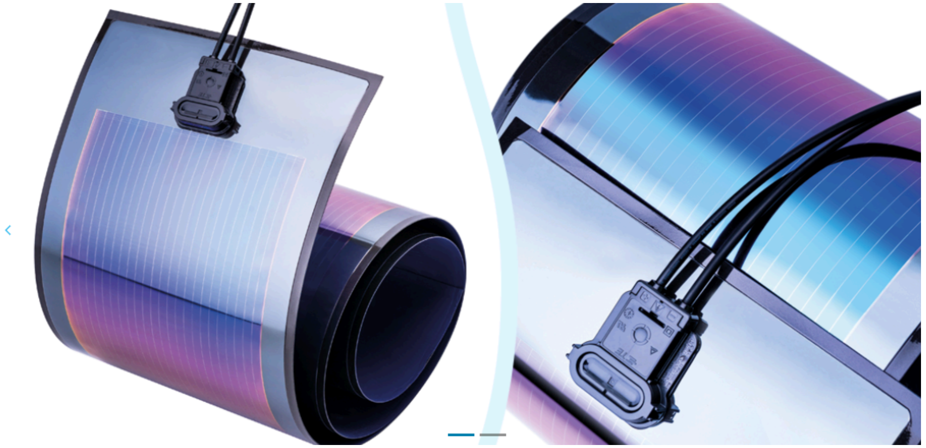


https://www.tu-ilmenau.de/



Vacuum Roll-to-Roll Production

- Building integrated, Flexible, Colorful
- In 2016, Record 13.2 % under laboratory conditions
- 50 W power (2000 mm x 436 mm x 1.8 mm, < 2kg/m^2)



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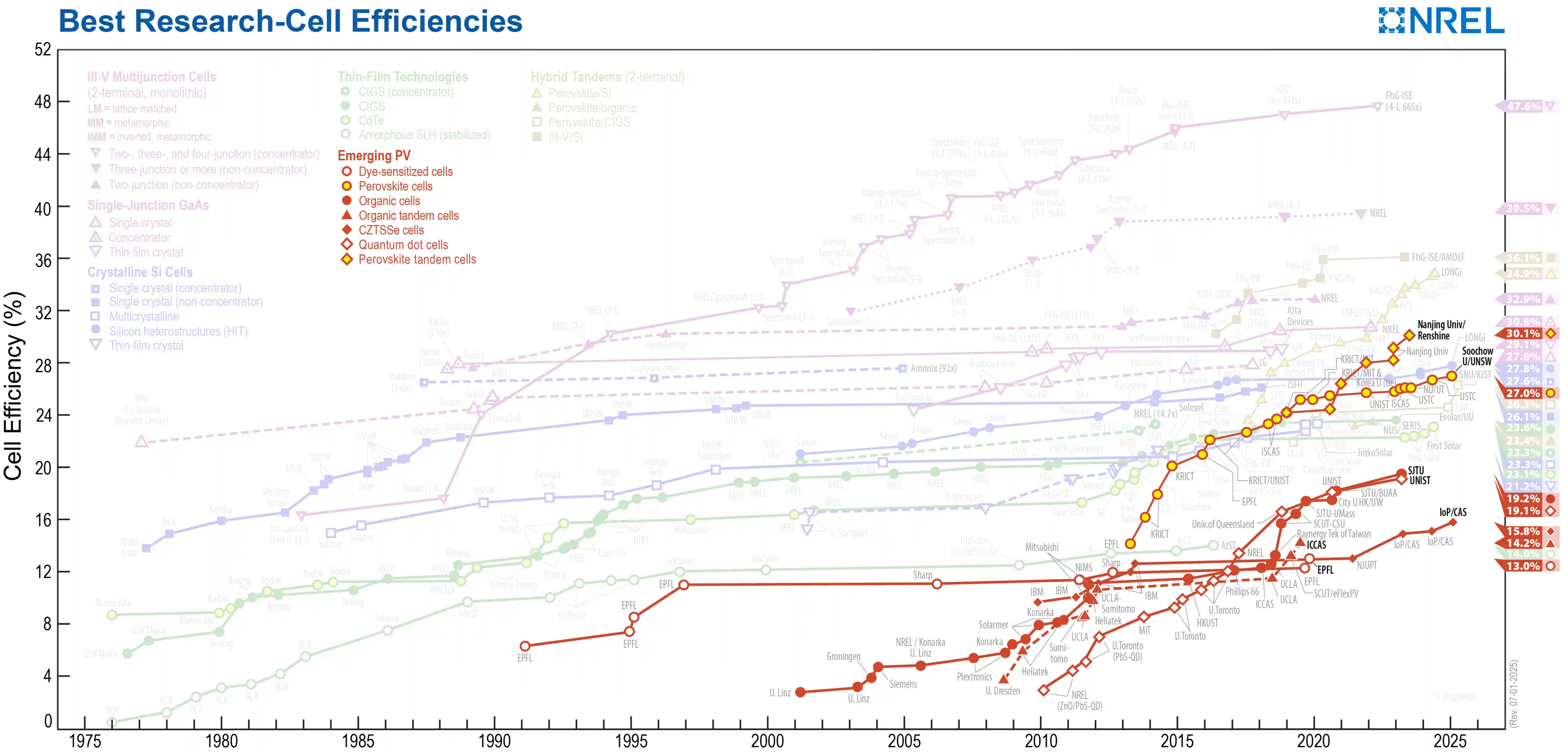
Jun-Ho YUM, junho.yum@epfl.ch

Future Applications

Dye-Sensitized Solar Cells



13.0%

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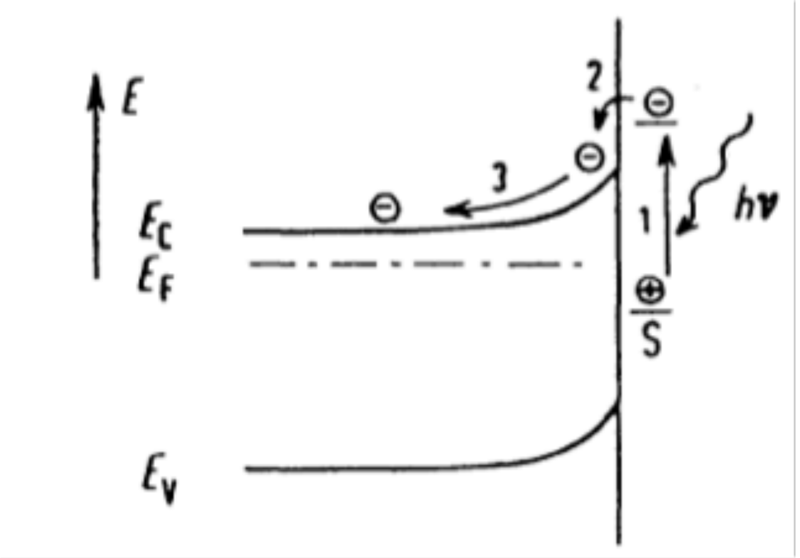
Dye-Sensitized Solar Cells



Rose bengal on ZnO. H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.* 72 (1968) 437.

Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisirung.[1]

Von Dr. James Moser.

(Aus dem physikalisch-chemischen Laboratorium der Wiener Universität).

(Vorgelegt in der Sitzung am 23. Juni 1887.)

Ich erlaube mir mitzutheilen, dass ich die von Herrn E. Becquerel entdeckten photoelektrischen Ströme erheblich dadurch verstärken konnte, dass ich die beiden chlorirten, jodirten oder bromirten Silberplatten in einer Farbstofflösung, z. B. Erythrosin, badete.

Beispielsweise war zwischen zwei chlorirten Silberplatten die elektromotorische Kraft im Sonnenlicht 0·02, zwischen zwei anderen in gleicher Weise behandelten, aber gebadeten Platten 0·04 Volt.

Bisher sind nur an jodirten Platten von Herrn Egoroff elektromotorische Kräfte beobachtet, und zwar bis $^1/_{15}$ Volt. Ich konnte bei jodirten und bromirten Platten durch Baden in Erythrosin $^1/_4$ Volt erreichen.

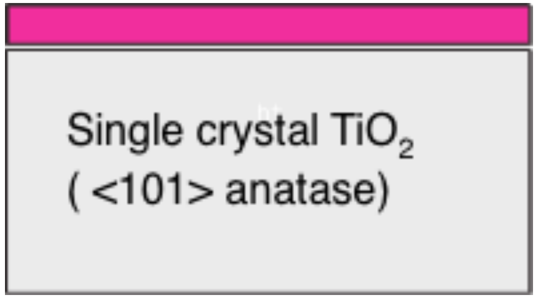
Ich halte es für meine Pflicht, schon an dieser Stelle Herrn Max Reiner, der mir bei diesen Versuchen assistirt, meinen verbindlichsten Dank auszusprechen.

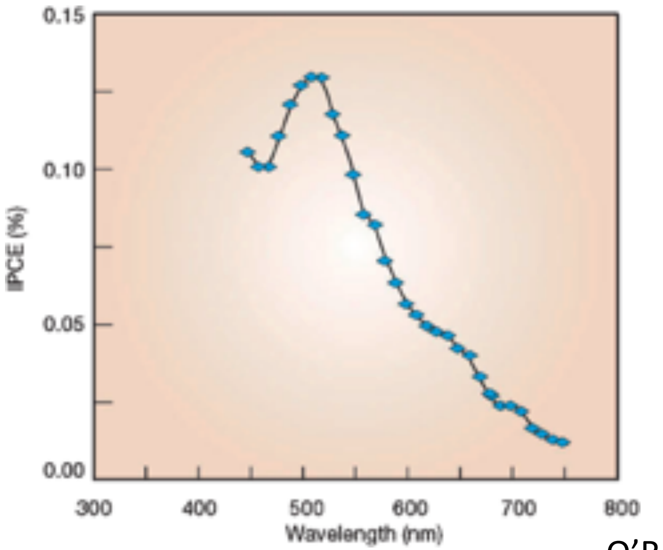
[1] Akadem. Anzeiger Nr. XVI.

Colour Photography, Erythrosine dye on Ag-halides. J. Moser, Monatsh. Chem. 8 (1887) 373

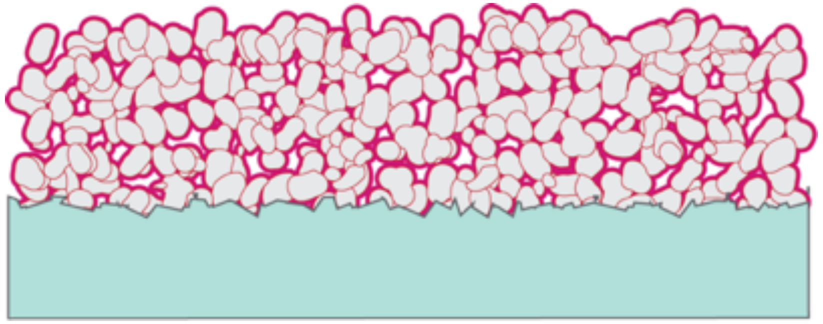
Mesoporous Structure in Dye-Sensitized Solar Cells

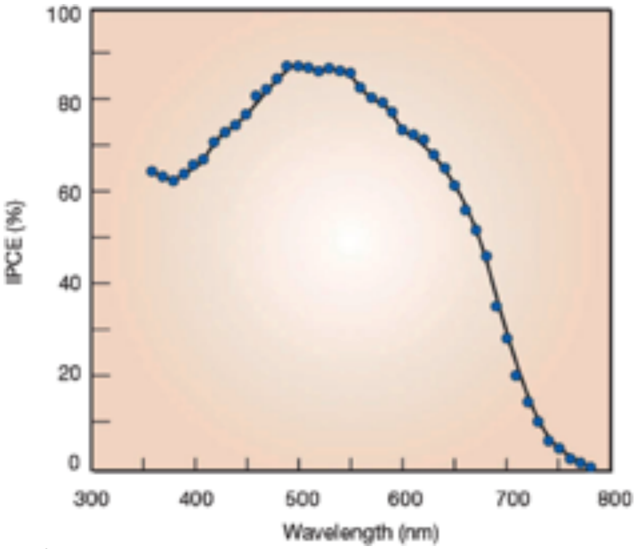
Dye monolayer on flat surface





Dye sensitized nanocrystalline TiO_2 film





O'Regan, B.; Grätzel, M. *Nature,* **353**, 737-740 (1991).

Incident photon to current conversion efficiency (IPCE) increases from 0.12 to 90 %

B.O'Regan and M.Grätzel, *Nature*, 353, 7377-7380 (1991).

Mesoporous Structure in Dye-Sensitized Solar Cells

$$\text{IPCE (EQE)} = \eta_{abs} \Phi_{cg} \eta_{coll}$$

η_{ab}: light harvesting efficiency

Φ_{cg}: quantum yield of charge carrier generation

$$\Phi_{cg} = \Phi_{\text{injection}} \, \Phi_{\text{dye regeneration}}$$

η_{coll} = efficiency of charge carrier collection

$$\eta_{ab}(LHE) = 1 - 10^{-A} = 1 - 10^{-\sigma\Gamma}$$

σ is the absorption cross section (cm^2/mol) = ε (the molar extinction coefficient $M^{-1}cm^{-1}$) x 1000 (cm^3/L),
Γ is the dye loading per projected surface area of the film,

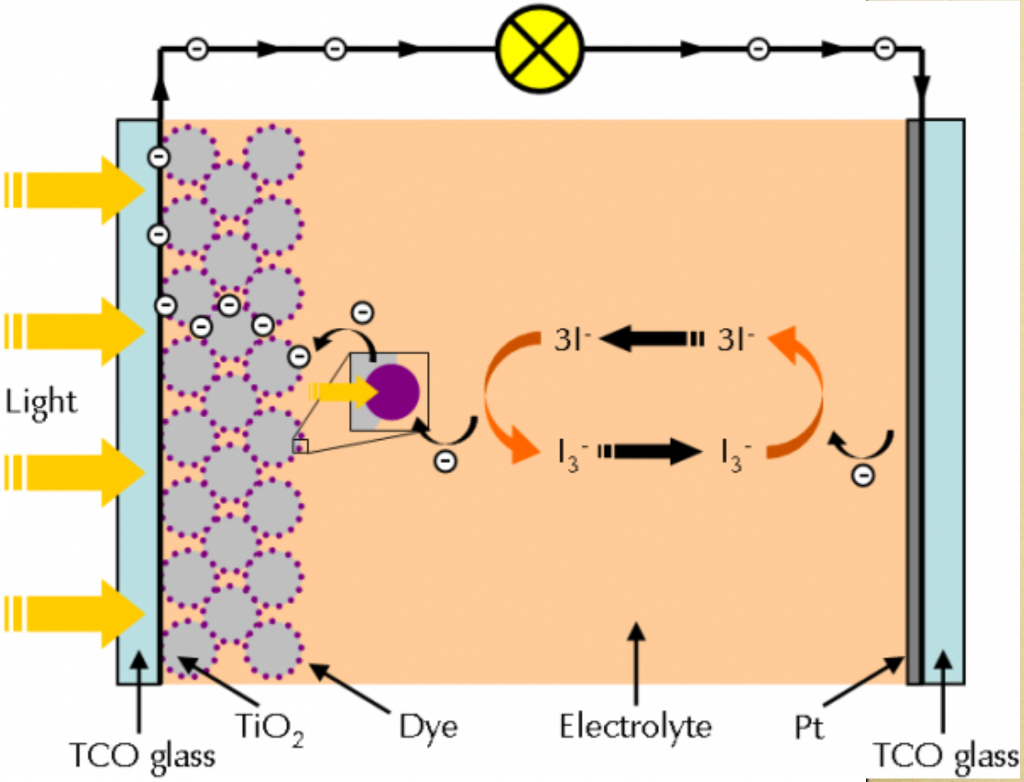
High ε and/or Γ is needed for high LHE.

Surface coverage of 10^{-10} mol/cm^2 (flat)
$\varepsilon = 10^4$
A = 0.001,
LHE = 0.23%

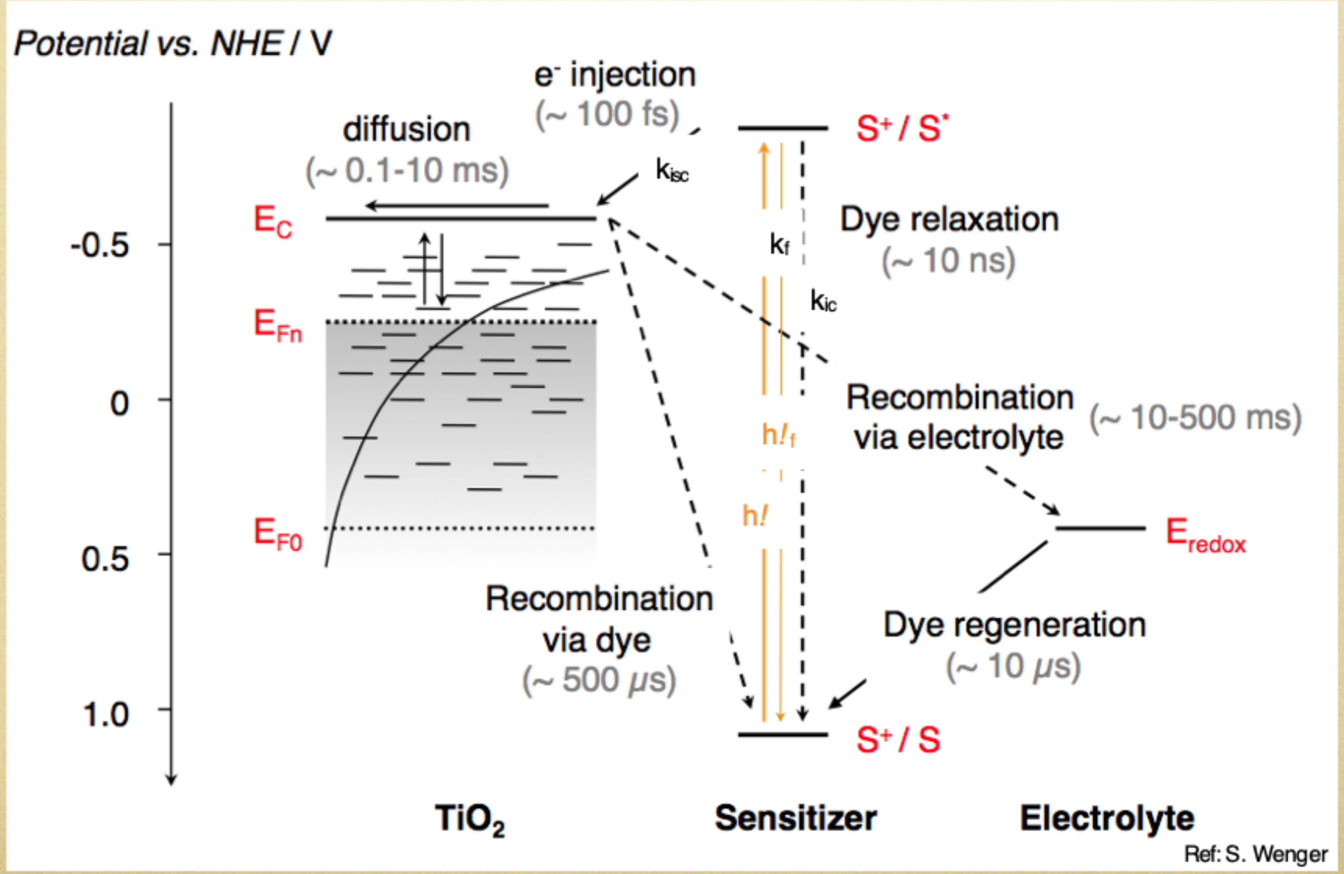
$\varepsilon = 10^5$
A = 0.01,
LHE = 2.3%

$\Gamma = 10^{-7}$ mol/cm^2 (nanocrystailline TiO_2, 20 - 50 nm)
$\varepsilon = 10^4$
A = 1,
LHE = 90%

Operational Principle of Dye-Sensitized Solar Cells

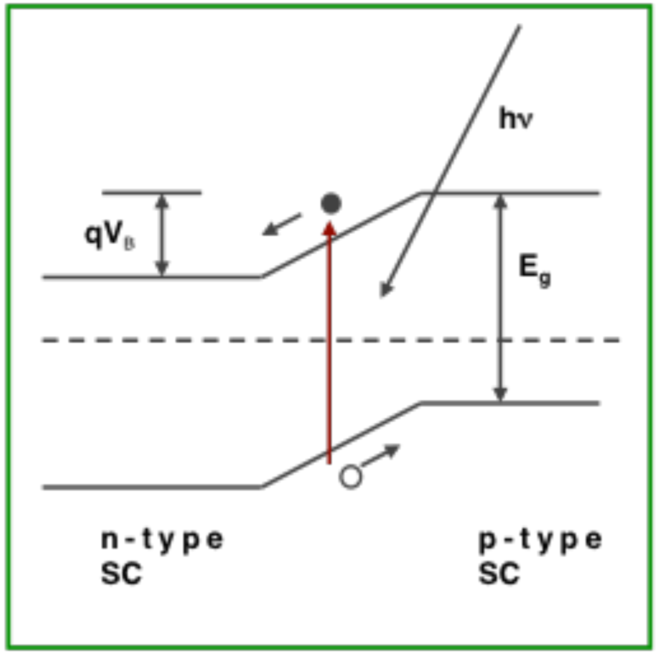


Summary of the key processes involved in the regenerative cycle taking place in a dye-sensitized solar cell under illumination.



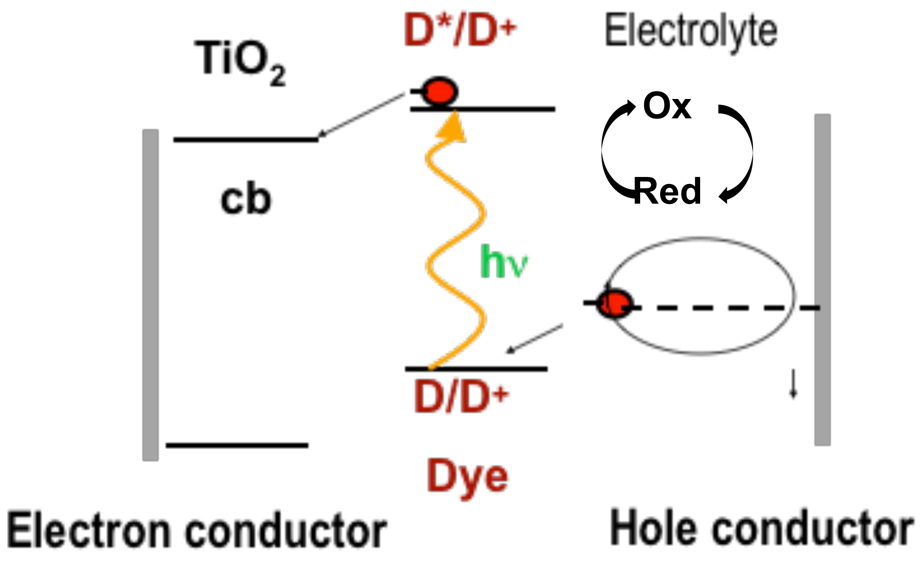
pn Junction Solar Cells vs Dye-Sensitized Solar Cells

p-n junction photovoltaic cells



Charge separation by electric field at the p-n junction

dye sensitized solar cells DSC



Charge separation by kinetic competition as in photosynthesis

Light absorption and charge transport are decoupled.
Relaxed constraints for individual components.

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Sensitizers in Dye-Sensitized Solar Cells

1. Distribution on the surface of semiconductor oxide

2. Firmly graft to the surface of semiconductor (carboxylate or phosphonate).

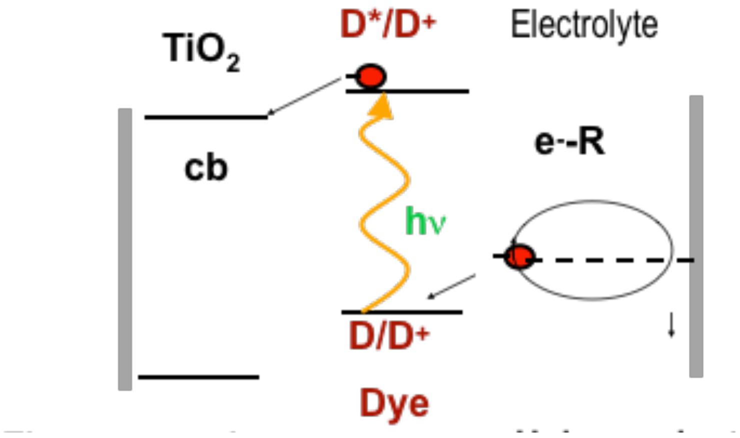
3. Absorption range (standard global AM 1.5 sunlight to electricity below a threshold wavelength, about 920 nm)

4. Quantum yield (injection of electrons into the solid) = 1

5. The energy level

   Excited state (LUMO) > Conduction band of the oxide

   Ground state (HOMO) < redox potential



6. Stability enough to sustain above 100 millions turnover cycles (= about 20 years of exposure to natural light)

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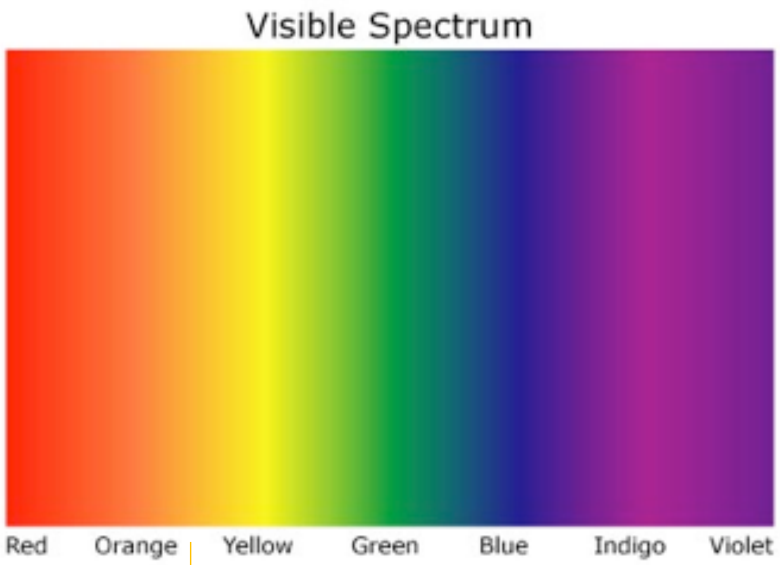
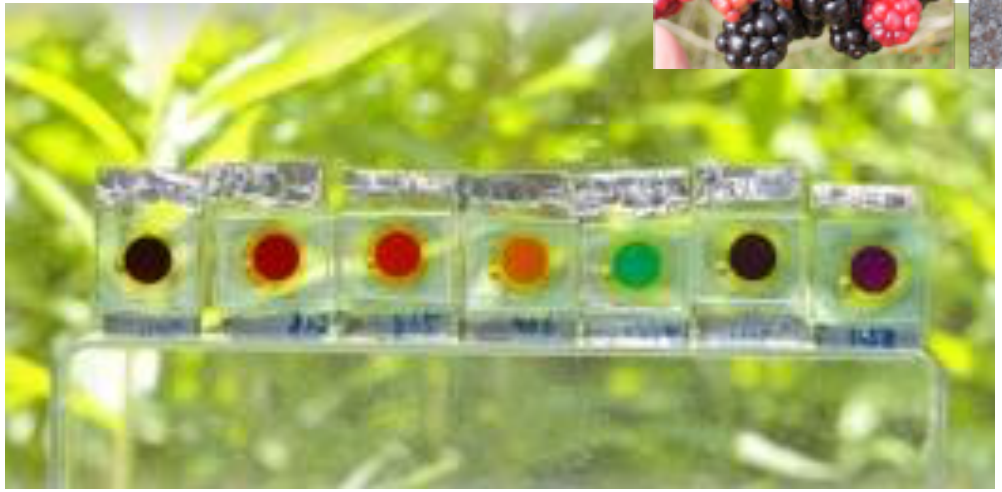
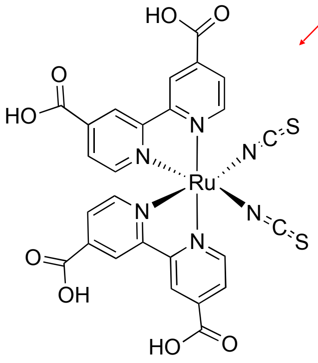
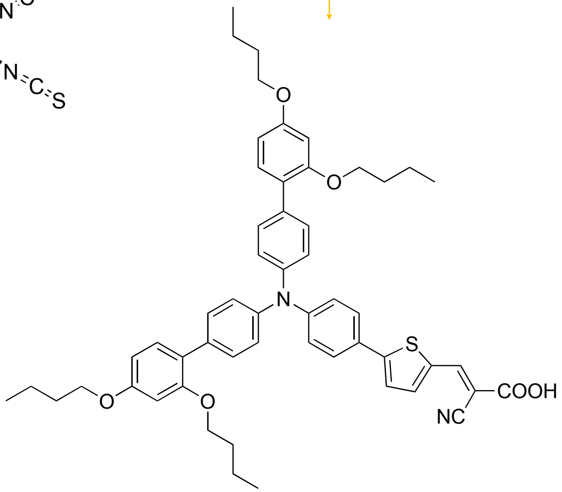
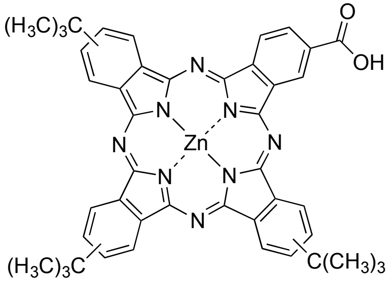
Sensitizers in Dye-Sensitized Solar Cells

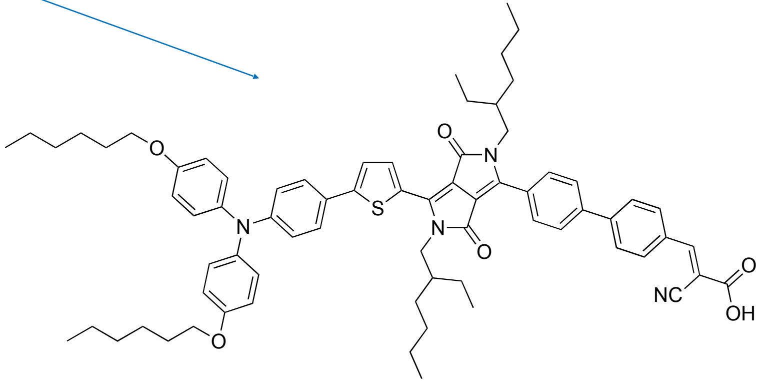


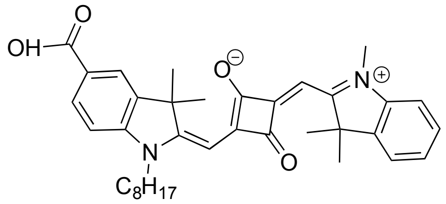












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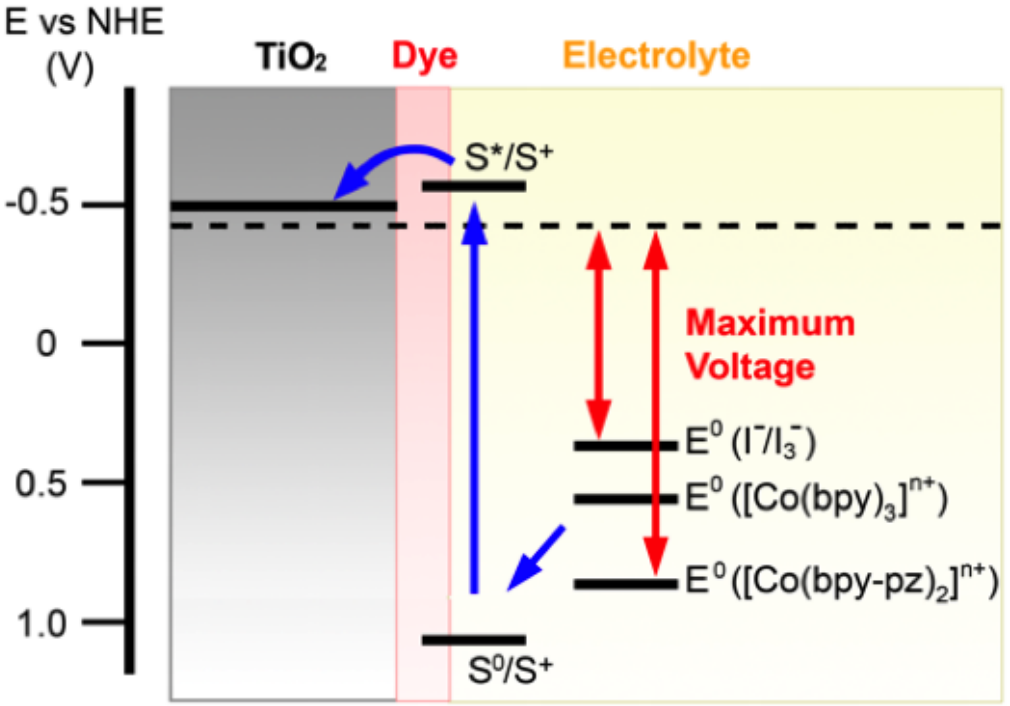
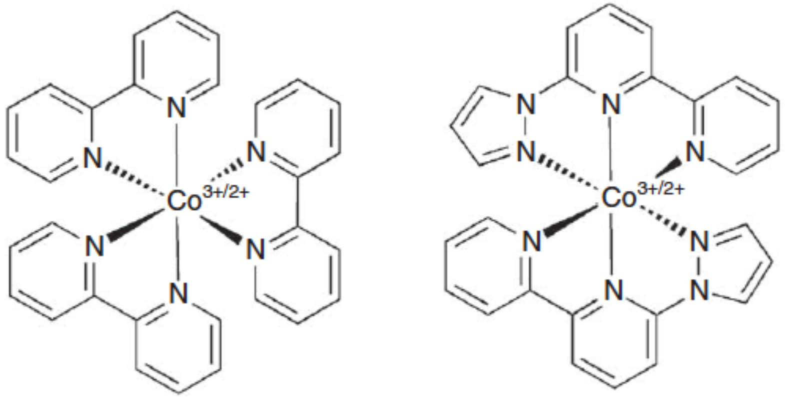
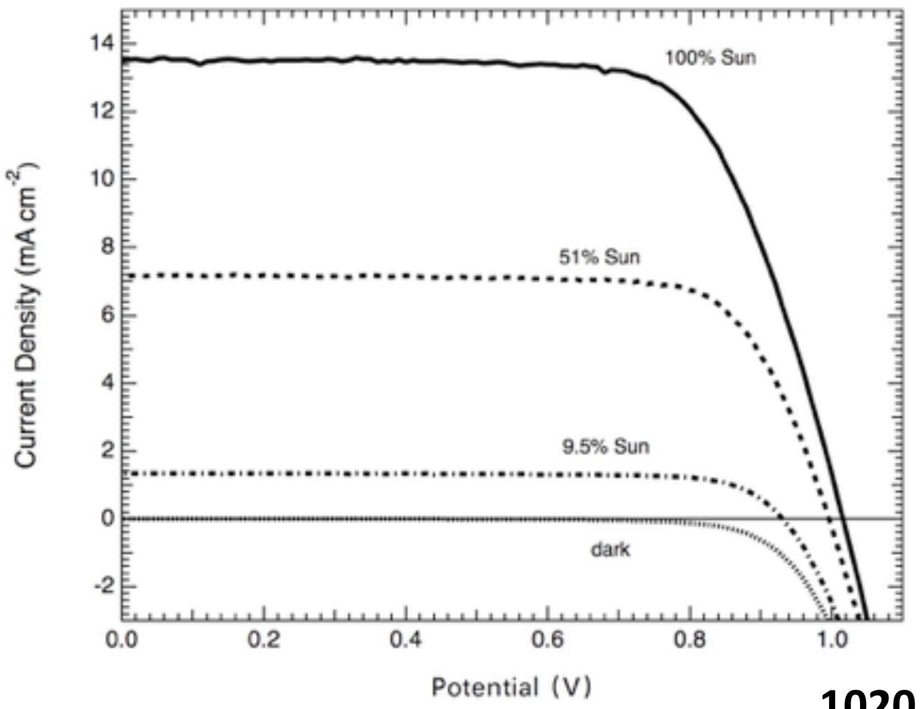
Towards High Photovoltage







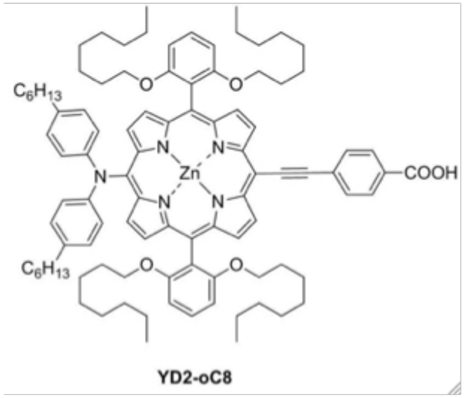
Further and meticulous optimization affords **1.1 V** of photovoltage generation.

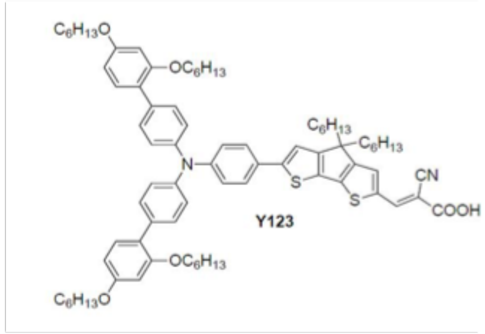
1020 mV

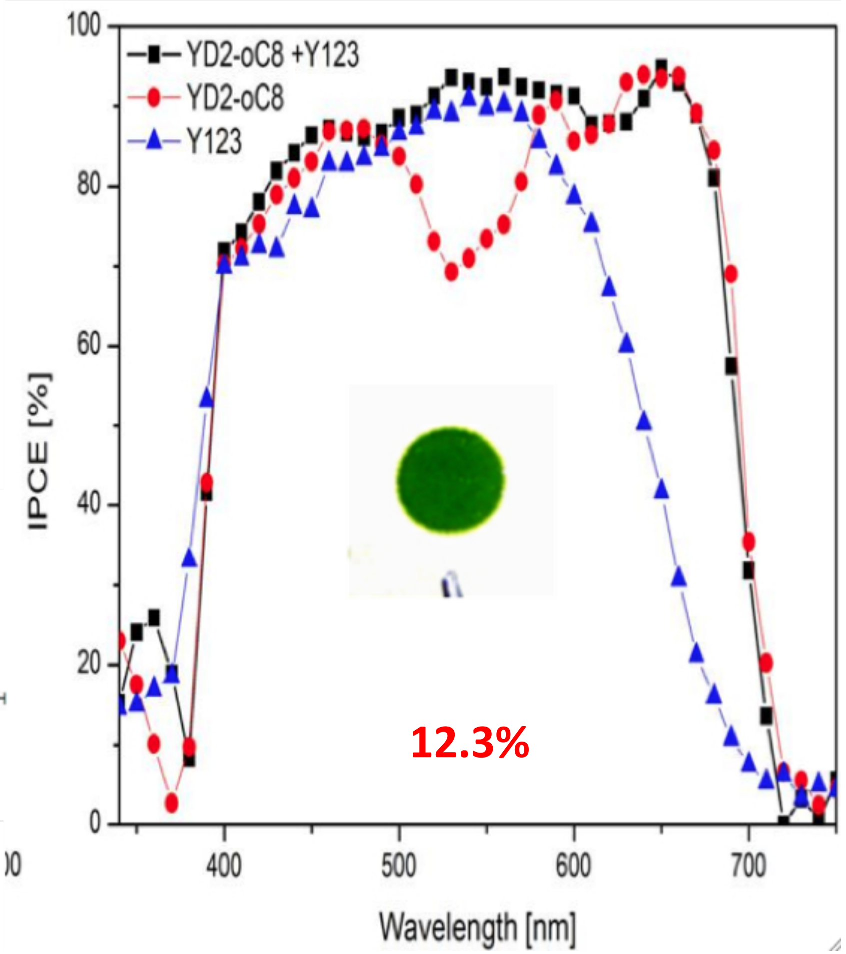
Nat. Commun. 3:631 (2012).

High Performing Dye-Sensitized Solar Cells

YD2-o-C8







Y123

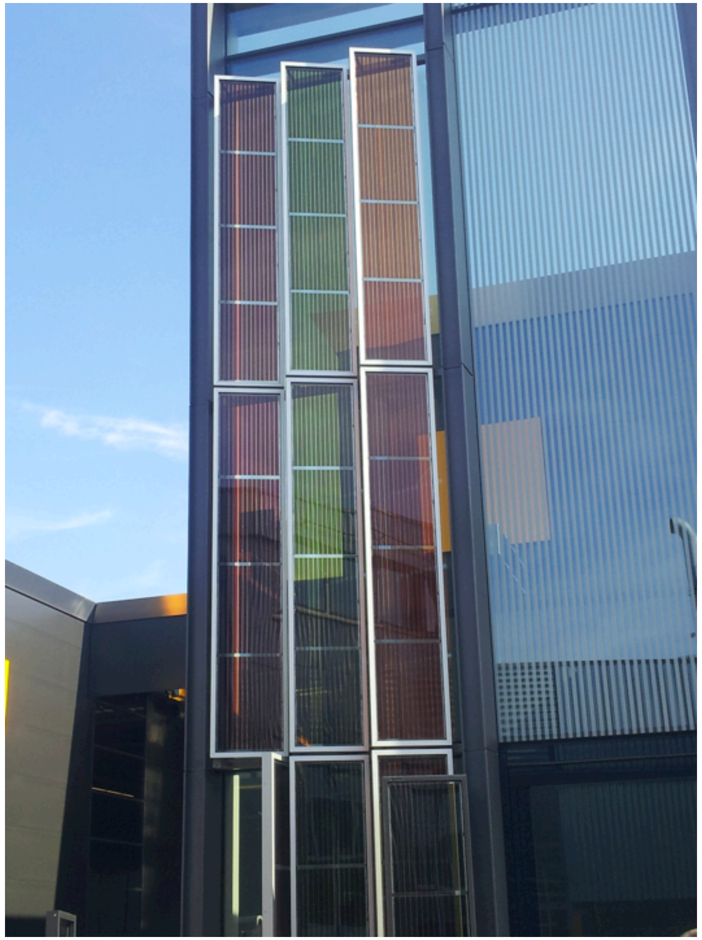
- Co-sensitized system → higher photocurrent
- Co(II/III) as redox mediator → higher photovoltage

A. Yella *et al.* *Science* **334,** 629–634 (2011).

Easy Processable Technology

Dye-Sensitized Solar Module

Dye-Sensitized Solar Cells for Building-integrated photovoltaics



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